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Concentration, enrichment and distribution of heavy metals in surface sediments of the Tangier Bay, Morocco

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SUMMARY: The distribution, enrichment, and accumulation of heavy metals in the surface sediments of the Tangier Bay, Morocco, were investigated. Surface sediment samples from eleven locations in the Bay of Tangier were collected in 2007 and characterized for grain size, organic matter and metal content (e.g. Fe, Mn, Cr, Cu, Ni, Pb, Zn and Cd). The evaluation of the heavy metal contamination status of the bay showed minor enrichment by the enrichment factors (EF) calculation, corroborated by the metal pollution index (MPI). The results of a Pearson correlation showed high positive correlations among organic carbon and most metals ($0.788<r<0.939$) and cluster analysis grouped the stations inside the harbour (stations 1, 10 and 9) and in the vicinity of the principal rivers in the bay (stations 3 and 11), which showed the highest concentrations of metal content. The main sources of contamination are domestic and industrial effluents, which arise due to the lack of sewage treatment. However, these areas could not be classified as polluted when the data were compared with sediment quality guidelines (USEPA, 1997).

Keywords: metals, contamination, sediments, Tangier Bay, enrichment factors, Tangier Harbour, Morocco.

RESUMEN: CONCENTRACIÓN, ENRIQUECIMIENTO Y DISTRIBUCIÓN DE METALES PESADOS EN SEDIMENTOS DE LA BAHÍA DE TÁNGER, MARRUECOS. – Se ha investigado la distribución y acumulación de metales pesados en sedimentos superficiales de la bahía de Tánger, Marruecos. Se tomaron 11 muestras de sedimentos superficiales ubicadas en la bahía de Tánger durante el año 2007 y se analizaron los metales (Fe, Mn, Cr, Cu, Ni, Pb, Zn y Cd), materia orgánica y distribución granulométrica. El estado de contaminación por metales de la bahía, se evaluó mediante el cálculo del factor de enriquecimiento (EF) y en general mostró bajo enriquecimiento, corroborado por el uso del índice de polución metálica (MPI). Los resultados de la correlación de Pearson presentaron una correlación significativa importante entre el carbono orgánico y la mayoría de los metales ($0.788<r<0.939$). El análisis clúster agrupó las estaciones dentro del puerto (estaciones 1, 10 y 9) y en las proximidades de los ríos que desembocan en la bahía (estaciones 3 y 11), que mostraron la mayor concentración del contenido de metales. Las principales fuentes de contaminación fueron los efluentes domésticos e industriales, como consecuencia del escaso tratamiento de estos vertidos. Sin embargo, esta zona no puede ser clasificada como contaminada al comparar los datos con las normas de calidad de sedimentos (USEPA, 1997).

Palabras clave: metales, contaminación, sedimentos, bahía de Tánger, factor de enriquecimiento, puerto de Tánger, Marruecos.

INTRODUCTION

Tangier Harbour is strategically located on the northwestern part of the Moroccan coast and faces the key trade waterway running between the Atlantic Ocean and the Mediterranean Sea, the Gibraltar Strait. Until recently it was the largest international sea port in Morocco. In 2007, a new port situated about 40 km east of the city of Tangier was opened mainly for container transport (<www.TMSA.ma>).

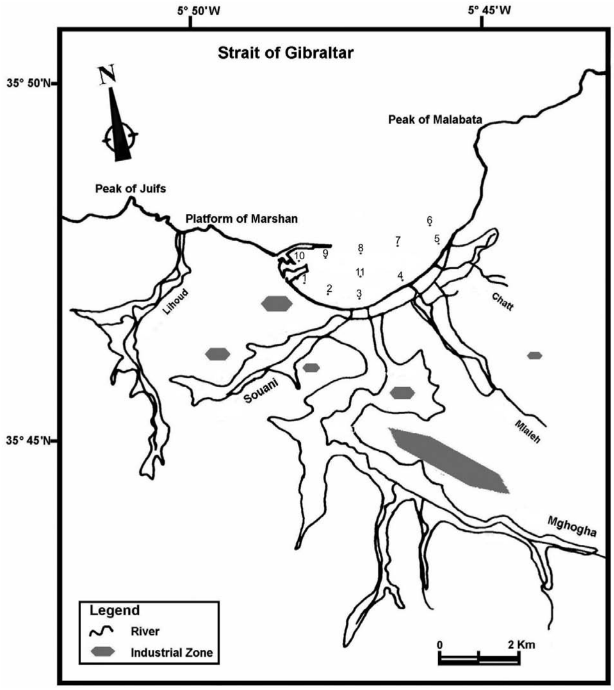

FIG. 1. – Location of sampling stations and geographical situation of the study area.

Tangier is the largest industrial city in northern Morocco, with a population of over 1 million. It receives water flows from four rivers (Fig. 1), namely the River Souani, the River Mghogha, the River Mlaleh and the River Chatt (Achab *et al*., 2007), which run through the heart of metropolitan Tangier. There was no sewage system until 2007 and all wastewater effluents were directly discharged untreated into nearby rivers (Rodríguez-Barroso *et al*., 2009). During most years, these rivers do not have a significant fresh water discharge and instead serve as the main pathway for urban runoff and sewage and industrial waste water discharge into the Bay of Tangier. In 2006, the Tangier city authorities started to construct sewage systems with an outfall in the west of the bay, and the household connection to the sewage system at the end of 2007 reached about 40% of the wastewater discharges (AMENDIS, 2005). Today, over 60% of domestic wastewater is still directly being discharged untreated into rivers. Moreover, there are several industrial parks (e.g. textile manufacturing plants, agro-food processing, and to a less extent chemicals, metals and wood processing factories) located in the nearby Mghogha complex that contribute a significant amount of untreated and / or minimally treated wastewater to the rivers and ultimately to the bay. This situation has created a great threat to public health and has impacted the biological and geochemical conditions of all four rivers, the bay and the harbour. In 2007 a sewage treatment plant was built to resolve the untreated wastewater problem. The sewage systems with an outfall in the west of the Bay were finished in late 2008.

It is well known that heavy metal concentrations in harbour or estuarine sediments are usually quite high due to anthropogenic metal loadings carried by rivers or their tributaries (Paetzel *et al*., 2003; Muniz *et al*., 2004; Guerra-García and García-Gómez, 2005). The sediments serve as a metal pool that—depending on the environmental conditions or processes—can retain metals or release metals to the overlying water via natural or anthropogenic processes. The metals released into the water column can cause adverse health effects to the ecosystems (Poulton *et al*., 1996; Fatoki and Mathabatha, 2001; McCready *et al*., 2006). Moreover, marine organisms or biota can take up metals, in turn enhancing the potential of some metals entering the food chain.

Very few studies have been made on harbour or estuarine sediments in northern Morocco. Some authors have focused on sediments from rivers flowing into the Tangier Bay, mainly from the Rivers Souani and Mghogha (e.g. El Hatimi, 2002; El Aouarram *et al*., 2008; Rodríguez-Barroso *et al*., 2009). Furthermore, El Arrim (2001) and Achab *et al*. (2005, 2007) studied sediments in the Tangier Bay. However, all of these studies were previous to the building of the treatment plant and the outfall.

A study of concentration, enrichment and distribution of heavy metals in Tangier Bay sediments is important in order to assess the state of contamination of the area and to estimate the possible influence of anthropogenic activities on harbour waters (Hung and Hsu, 2004; Morillo *et al*., 2004; Chen *et al*., 2007). In the present study, the physical and chemical properties of sediments in the Harbour and Tangier Bay were characterized, including mud and sand composition, organic content (OC) and the distribution of Fe, Mn, Cr, Cu, Ni, Pb, Zn and Cd. The extent of metal contamination was assessed using the enrichment factor (EF) and the metal pollution index (MPI) (Reddy *et al*., 2004; Selvaraj *et al*., 2004; Usero *et al*., 2000). A statistical correlation analysis between relevant sediment characteristics and sediment metal concentrations was performed to determine the possible factors controlling trace metal concentration in the Tangier Bay sediments.

MATERIALS AND METHODS

Sample collection

Surface sediment samples were collected from eleven stations in the Tangier Bay (Fig. 1, GPS geographic coordinates position in Table 1), including four sampling points in the vicinity of the mouths of the four rivers that flow into the bay (station 3 near to the Rivers Souani and Mghogha; station 4 near to the River Mlaleh; station 5 near to the River Chatt) and three sampling points next to the harbour (stations 1, 9 and 10). The other four samples were collected in the middle of the bay (stations 6, 7, 8 and 11) in a profile along the river influence. The sampling depths of stations 1 to 5 and 11 were below 7.5 m and the depths of stations

TABLE 1. – Location of the sampling stations and characteristics in the sediment of all stations studied in Tangier Bay.

Station	Location N	W	Grain size % Mud (<0.063 mm)	% sand (0.063 – 2 mm)	OC %
1	35º47.097'	05º47.861'	58.35	41.65	0.87
2	35º46.929'	05º47.519'	88.53	11.47	0.58
3	35º46.766'	05º47.028'	26.27	73.73	1.37
4	35º47.056'	05º46.180'	40.49	59.51	0.58
5	35º48.094'	05º45.073'	3.13	96.87	0.13
6	35º48.146'	05º45.679'	13.76	86.24	0.69
7	35º47.358'	05º46.571'	3.80	96.20	0.32
8	35º47.401'	05º47.017'	8.42	91.58	0.20
9	35º47.301'	05º47.329'	43.32	56.68	1.13
10	35º47.357'	05º47.979'	80.24	19.76	1.56
11	35º47.097'	05º47.861'	57.82	42.18	0.81

6 to 10 were 18, 11.5, 14.5, 13 and 11 m, respectively. These stations were chosen because they are located in the outlet of the four rivers that are the major contributories to the input of sewage into the bay.

The sampling campaign was carried out in October 2007, and about 2 kg of sediment samples were obtained using a van Veen dredge grab sampler. Samples were transferred to acid-washed plastic bags and placed in a cooler at 4ºC, and then transported to the laboratory for analysis.

Sample processing

Sediment samples were first dried in an oven at 60ºC for at least 24 h. The dried sediments were ground to powder using an agate mortar and pestle. The particles with a size of less than 63 μm were collected and used for the trace metal analysis according to the procedures published by Bellucci *et al*. (2002). A sediment sample of about 0.25 g dry weight was digested with a mixture of concentrated acids before analysis (H_2O_2: HCl: HNO_3 = 2:3:9 v/v) (duplicate digestions were made for each sample); a Milestone Ethos 1600 model microwave oven was used.

Sample analysis

Particle size was determined by wet sieving after elimination of the organic fraction with H_2O_2, to separate sand from the fine fractions. Wet sediment samples were placed in an oven at 105ºC and heated to a constant weight. Organic carbon (% OC) was determined by mineralization of the organic matter to CO_2: 0.2–0.5 g of sediment was oxidized with potassium dichromate (Gaudette *et al*., 1974).

Heavy metals (e.g. Fe, Mn, Cr, Cu, Ni, Pb, Zn and Cd) in digested sediment samples were determined by flame atomic absorption spectrometry (FAAS-Perkin Elmer type 100). For Fe, Mn, Ni, Cu, Cr, Cd, and Zn, the flame atomic absorption spectroscopy technique was employed; for Cd, the graphite furnace technique was used; detection limits are shown in Table 2. Calibration standards were regularly performed to evaluate the accuracy of the analytical method. Two certified reference standard sediments, MESS-3 and PACS-2, from the National Research Council of Canada were used to test the analytical and instrument accuracy of the method. The results indicate good agreement between certified and analytical values (recovery was over 94% for MESS-3 and over 90% for PACS-2, except for Cr and Mn in both cases). The statistical techniques of the Pearson matrix to test the relationship between sediment characteristics and trace metal concentrations and cluster analysis were performed using the Statistical Program for Social Sciences (version 14.0 for Windows).

TABLE 2. – Comparison of the analytical results of the reference material (MESS-3 and PACS-2, *National Research Council, Canada*) with the certified data. Detection limits.

Element	MESS-3 Certified value	MESS-3 Measured value	PACS-2 Certified value	PACS-2 Measured value	Detection limits
Fe (%)	4.34	3.98	4.09	3.58	1.00
Mn (mg kg^{-1})	324	293	440	316	0.100
Cr (mg kg^{-1})	105	78.1	90.7	55.4	0.500
Cu (mg kg^{-1})	33.9	29.1	310	289.1	0.600
Ni (mg kg^{-1})	46.9	46.5	39.5	39.7	0.700
Pb (mg kg^{-1})	21.1	19.6	183	171	0.004
Zn (mg kg^{-1})	159	152	364	384	0.500
Cd (mg kg^{-1})	0.240	0.277	2.110	2.154	0.005

RESULTS

Sediment characteristics

Table 1 presents the values of sediment characteristics in the sediments of all stations analyzed in the Tangier Bay. Texturally, mud (<0.063 mm) prevailed in the sediments from stations 2 and 10, varying between 80.2% and 88.5%. Sand (>0.063 mm) showed maximum values at stations 3, 5, 6, 7 and 8 ranging between 73.7 and 96.8%, while stations 1, and 11 were characterized as slightly sandy mud and stations 4 and 9 were muddy sand.

Organic carbon

The organic carbon in sediments of the Tangier Bay ranged from 0.13% (station 5) to 1.56%, (Station 10), with an overall value of 0.75% (Table 1). Samples in the vicinity of the port (stations 1, 9 and 10) showed the highest values, in addition to station 3 around the mouths of the main rivers (Souani and Mghogha). Sample 11, in the middle of the bay and lined with station 3, also showed a relatively high OC (0.81%), probably due to the influence of both the river mouths and the port.

Metal contamination assessment

The primary goal of this study was to assess the contamination of heavy metals in sediments of the

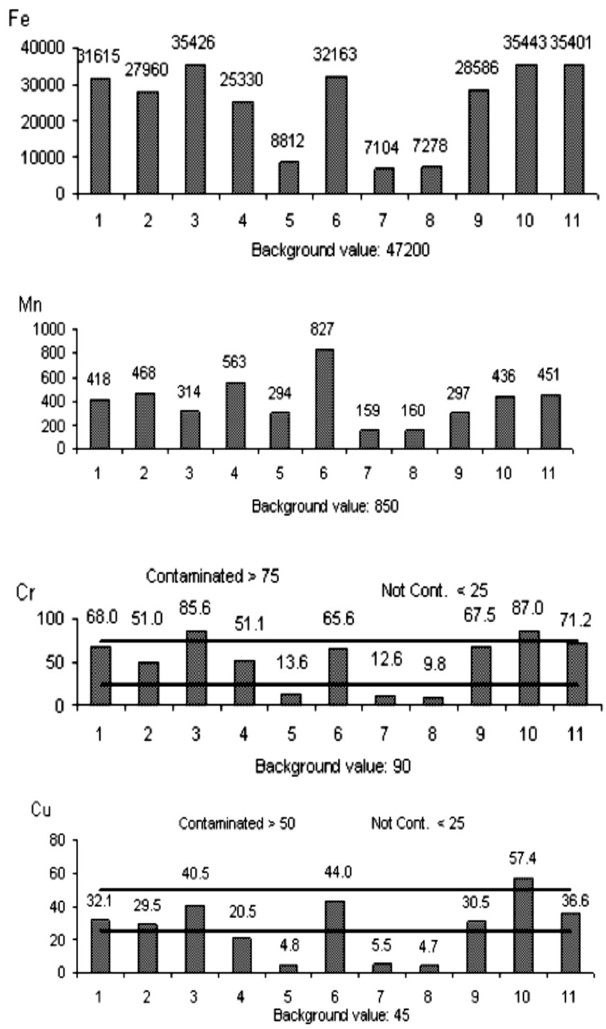

FIG. 2. – Spatial distribution of Fe, Mn, Cr and Cu concentrations (mg kg-1, dry mass). Background values (Turekian and Wedepohl, 1961); Lines indicate the limit values for contaminated (upper)/not contaminated (low) (USEPA, 1997).

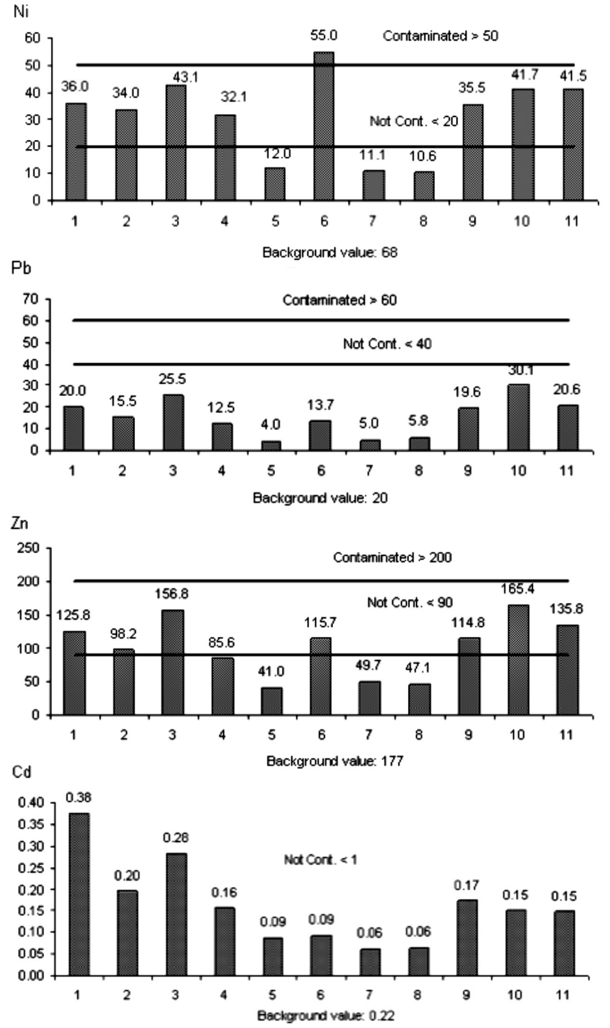

FIG. 3. – Spatial distribution of Ni, Pb, Zn and Cd concentrations (mg kg-1, dry mass). Background values (Turekian and Wedepohl, 1961); Lines indicate the limit values for contaminated (upper)/not contaminated (low) (USEPA, 1997).

Tangier Bay. The sediment quality guideline (SQG) was established to identify the level of contamination by heavy metals in marine sediments (USEPA, 1997), because there is currently no Moroccan SQG. To assess the metal contamination in surface sediments the concentrations of the most relevant toxic metals (Cr, Cu, Ni, Pb, Zn and Cd) measured in the sediments were compared with the SQG established by USEPA.

As seen in Figures 2 and 3, heavy metals measured in the surface sediments in the Tangier Bay were almost all below the contamination levels, with the exception of Cr (St 3 and 10), Cu (St 10), and Ni (St 6), which exceeded these levels. However, the Pb and Cd contents for the stations were below the non-pollution level, indicating a low significance of both metals.

A cluster analysis was carried out to identify any analogous behaviour patterns between the sites (Fig. 4). Two principal clusters emerged: (1) stations 5, 7 and 8 with very little relevance around the Chatt mouth and in the central part of the bay; and (2) other samples grouped in turn into two sets. The first set (stations 3, 11 and 10) included sites in the vicinity of the river mouths and inside the harbour, reflecting the importance of discharge of untreated industrial and municipal waste from the mouths of the Rivers Souani and Mghogha, which both drain very close (<0.5 km), focusing their discharges in the same area. The second set (stations 1, 6, 2, 9 and 4) showed concentrations in the range of values between the two defined limits according to USEPA (1997).

Pearson correlation analysis was applied to test the relationship among contaminants and sediment characteristics (Table 3). The results showed that these metals were strongly interrelated ($P<0.01$), with correction coefficients ranging from 0.609 to 0.964 at the 99% confidence level. A significant correlation was also found between organic carbon vs. Fe and both vs. all metals (ranging from 0.788 to 0.955, $P<0.01$),

TABLE 3. – Pearson matrix for sediment characteristics and metal concentrations.

Station	Fe (%)	Mn (mg kg^{-1})	Cr (mg kg^{-1})	Cu (mg kg^{-1})	Ni (mg kg^{-1})	Pb (mg kg^{-1})	Zn (mg kg^{-1})	Cd (mg kg^{-1})	Mud	Sand
Mn	-									
Cr	0.955 *	-								
Cu	0.945 *	-	0.891 *							
Ni	0.927 *	-	0.845 *	0.964 *						
Pb	0.918 *	-	0.936 *	0.836 *	0.764 *					
Zn	0.955 *	-	0.955 *	0.936 *	0.873 *	0.964 *				
Cd	-	-	0.609 *	-	-	0.655 *	-			
Mud	-	0.627 *	-	-	-	-	-	-		
Sand	-	-0.627 *	-	-	-	-	-	-	-	
OC	0.879 *	-	0.934 *	0.861 *	0.788 *	0.939 *	0.934 *	0.647	-	-

- not significant at $P>0.05$; others are significant; * Significant at $P<0.01$

indicating anthropogenic origin, except for Mn, which showed a significant positive correlation with fines and a negative one with sand.

Enrichment factor (EF)

The enrichment factor (EF) was used as an index to examine the extent of metal contamination in the sediments of the Tangier Bay. Mathematically, EF is a concentration ratio of measured metal to iron in the sample of interest divided by the background metal/iron background concentration ratio. EF is expressed as:

$$EF = \frac{(Me / Fe)_{sample}}{(Me / Fe)_{background}}$$

where $(Me/Fe)_{sample}$ is the metal to Fe ratio in the samples of interest, and $(Me/fe)_{background}$ is the natural background value of the metal to Fe ratio. Because we do not have Fe and heavy metal background values for our study area, the average crust metal values from Turekian and Wedepolh (1961) were adopted (shown in Figs. 2 and 3).

The advantage of using enrichment factor (EF) analysis is that it is possible to establish a contamination guideline. This technique has been well applied in several studies to assess metal contamination in marine sediments (Khaled *et al.*, 2006; Acevedo-Figueroa, *et al.*, 2006; Ghrefat and Yusuf, 2006). EF values were interpreted as suggested by Birch (2003), where EF<1 indicates no enrichment; <1-3 is minor; 3-5 is moderate; 5-10 is moderately severe; 10-25 is severe; 25-50 is very severe; and >50 is extremely severe. EF values for all the metals in sediments of Tangier Bay showed minor or no enrichment (EF<1) (Table 5). The highest values correspond to stations 1 and 5 (for Cd) and station 10 (for Pb) and all were <3 (minor enrichment). EF values in this study were insignificant in comparison with other similar work (Kaoshiung harbour in Taiwan), which detected high EF values (between 2.8 for Cr and 23.5 for Cd) in sediments in the vicinity of the mouth of a river which received a huge amount of metal discharge from nearby industrial plants and sewage discharges (Chen *et al.*, 2007).

Metal pollution index

Another index that can reflect the status of environmental contamination is the metal pollution index (MPI), calculated according to Usero *et al.* (2000) with the formula:

$$MPI = (Cf_1 \text{ x } Cf_2 \text{ x } \dots \text{ x } Cf_n)^{1/n},$$

where Cf_n is the concentration of the metal n in the sample.

The MPI values of the 8 heavy metals in sediments of the study area are summarized in Table 5. The highest average MPI in Tangier Bay was at the station next to the harbour (station 1), and was very similar to that recorded by Rodríguez-Barroso *et al.* (2009) near the industrial complex in the River Mghogha, one of the natural outlets into the Tangier Bay (MPI = 73.0). This index can provide a classification of the study areas according to the level of contamination. The order of stations from highest to lowest MPI values was St 1>St 3>St 6>St 10>St 2>St 11>St 9; all were located in the west part of the bay, near the port and at the mouth of the most industrialized rivers. These results were very similar to those reported by Rodríguez-Barroso *et al.*, (2009) for the same metals in the Rivers Souani and Mghogha, which discharges into the Tangier Bay (average MPI, 42 and 62, respectively). They were also very similar to those reported for the same metals by Khaled *et al.* (2006) in Gulf of Suez sediments, next to effluents from mining, hydrocarbon refineries and other industries (minimum and average values, 35 and 72, respectively).

DISCUSSION

Sediment composition

The organic carbon in sediments in Tangier Bay was relatively low but was above the values reported by Wang *et al.* (2007) in Jiaozhou Bay (China), with an average of 0.37%. The highest OC values were found next to the port (average 1.34%). Sediment samples contained a high percentage of the fine-grained fraction (<0.063 mm), although the values were quite low in comparison with those recorded in previous studies of sediments from rivers in northern Morocco that flow into this bay (ranges 0.28–9.46%), which are influenced by a large industrial complex (Rodríguez-Barroso *et al*. 2009). It must be taken into account that, in agreement with Achab *et al*. (2007), the marine dynamics in the Tangier Bay causes a dilution and diminution in the concentration of organic matter in the sediments. However, this value is lower than those reported in Kaohsiung (Taiwan), which were between 3.2% and 9.7% organic matter (Chen *et al*. 2007).

Station 3, next to the mouth of the principal tributaries of the bay (Souani and Mghogha), showed a high amount of OC (1.37%) due to sewage effluent discharged by the rivers (around 390000 equivalent inhabitants, AMENDIS, 2005). However, this value is lower than that reported by Rodríguez-Barroso *et al*. (2006) in surficial sediments from shipbuilding factories in Cadiz Bay (1.84–3.24%).

The properties of sediments, including grain size and concentrations of organic carbon, are two critical factors influencing the metal distribution in sediments (Huang and Lin, 2003; Liaghati *et al.,* 2003). As fine sediments and a high organic matter content are carriers of metals, samples around the port with a high fraction of fine sediment (2 and 10) or with muddy sand (stations 1 and 9) showed the highest metal concentrations, as did stations 3, 6 and 11, which are close to the river mouth or to the influence of the rivers (Mghogha and Chatt).

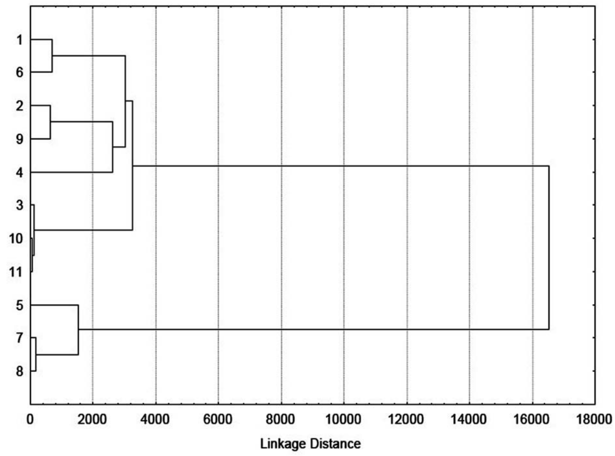

Fig. 4. – Dendrogram for hierarchical cluster analysis of 11 stations based on eight heavy-metal concentrations in Tangier Bay sediments.

Metal contents

The mouths of the Rivers Souani and Mghogha and their area of influence are also characterized by high metal contents at station 3 with a sand composition and station 11 with a sandy mud composition. Both showed relatively high organic carbon contents and high levesl of Cr, Cu, Ni, Pb and Zn. In fact, the Cr and Zn contents in these samples were similar to those reported by Rodríguez-Barroso *et al.* (2008) in industries associated with shipbuilding in the Cadiz Bay (average 67.1 mg kg^{-1} Cr and 138.5 mg kg^{-1} Zn). However, the areas considered as receiving the highest heavy metal impact cannot be classified as contaminated by USEPA (1997) or by the calculation of enrichment factors, which showed minor and no metal enrichment.

Those results were expected according to MPI values, which revealed some areas of metal enrichment such as the harbours and areas next to the mouths of the main tributaries. However, according to the low EF values detected, the MPI values are relatively low and cannot be considered as alarming data. In these areas the metal concentrations are higher than those recorded by Rodríguez-Barroso *et al*. (2010) in sediments from southern Spain, with average MPI values of 15.3 (Cádiz Bay) and 19.3 (a marsh area). Cluster analysis (Fig. 4) also revealed a group consisting of stations 3 and 11 (in the vicinity of the discharge of the Rivers Souani and Mghogha) and station 10 (inside the port)The correlation analysis of metal concentration data show high positive correlations with organic carbon and with iron concentrations (Fe vs Cr, Cu, Ni, Pb and Zn). This fact could indicate a common origin of metals, which are probably transported by the organic matter from the sewage effluents of urban influence, as reported by Rodríguez-Barroso *et al*. (2009) in sediments of the River Mghogha, probably due to a common contamination source coming from an industrial park.

Table 4. – Average metal concentrations found in sediments from different zones in north of Morocco and several harbours in the world.

Locations	Pb	Cd	Cr	Cu	Zn	Ni	Classified	Reference
Tangier Bay	4.0-30.1	0.06-0.38	9.8-85.6	4.7-57.4	41-165	10.6-55.0	Uncont.	Present study
Tangier Bay	8-82	nr	33-110	9-58	14-348	14-52	Uncont.	Achab, *et al*., 2007
Nador Lagoon, north Morocco	0-33	0.1-0.5	17-40	1-38	35-60	nr	Uncont.	Bellucci, *et al*., 2003
River Martil, north Morocco	10.1-36.6	0.06-0.18	21.9-45.2	10.4-732	33.0-105	nr	Uncont.	Bellucci, *et al*., 2003
River Mghogha, north Morocco	0-997	0.99-129.3	0.20-46.3	0.0-1.089	171-12.222	nr	Cont.	El Aouarram, *et al*., 2008
River Mghogha, north Morocco	3.8-56.1	0.1-0.4	7.0-149.4	5.1-67.1	37.2-757.8	10.7-64.9	nr	Rodríguez-Barroso *et al*., 2009
River Suani, north Morocco	4.9-58.8	0.1-0.5	8.8-113.6	6.5-65.3	41.5-216.5	11.0-36.8	nr	Rodríguez-Barroso *et al*., 2009
Kaohsiung Harbour, Taiwan	9.5-470	0.1-6.8	0.2-900	5-946	52-1369	nr	Cont.	Chen *et al*., 2007
Ceuta Harbour, Spain	10-516	nr	13-381	5-865	29-695	8-671	Cont.	Guerra-García & García-Gómez, 2005
Cádiz Harbour	5.1-86.9	0.9-1.3	0.1-14.9	7.0-202.8	21.2-378.3	0.06-21.2	nr	Casado-Martínez *et al*., 2006
Cartagena Harbour	486.7-1.397	6.8-98.5	29.5-66.6	171.1-665.9	900.8-8.661	15.3-29.0	Cont.	Casado-Martínez *et al*., 2006

nr not reported; Cont.: Contaminated; Uncont.: Uncontaminated

TABLE 5. – Enrichment factor of heavy metals in Tangier Bay sediments. Metal Pollution Index (MPI).

Stations	Mn	Cr	Cu	Ni	Pb	Zn	Cd	MPI
1	0.73	1.13	0.53	0.79	1.50	1.06	2.55	75
2	0.93	0.96	0.55	0.84	1.31	0.94	1.51	38
3	0.49	1.27	0.60	0.84	1.70	1.18	1.72	48
4	1.24	1.06	0.42	0.88	1.16	0.90	1.33	29
5	1.85	0.81	0.29	0.95	1.06	1.24	2.11	12
6	1.43	1.07	0.72	1.19	1.01	0.96	0.61	46
7	1.24	0.93	0.40	1.08	1.66	1.86	1.82	11
8	1.22	0.70	0.34	1.01	1.87	1.73	1.88	10
9	0.58	1.24	0.56	0.86	1.62	1.07	1.29	34
10	0.68	1.29	0.85	0.82	2.01	1.24	0.92	43
11	0.71	1.05	0.54	0.81	1.37	1.02	0.90	36

Comparison with other zones

Table 4 shows the average metal concentrations reported in sediments from different parts of northern Morocco and other harbours and bays in the world (Achab *et al*., 2007; Bellucci *et al*., 2003; Chen *et al*., 2007; Guerra-García and García-Gómez, 2005; Casado-Martínez *et al*., 2006). Sediments coming from northern Morocco (a salt marsh core from Nador) showed low metal concentrations and the authors suggested that they are probably very close to the natural background (Bellucci *et al*., 2003). These values are also very close to those found in this study. However, in other zones studied by the same authors (sediments from the River Martil), higher concentrations of heavy metals were found, probably due to a significant role of the urban and industrial settlements of Tétouan. The same characteristic was shown by the River Mghogha, which crosses the city of Tangier and is affected by the urban and industrial liquid and solid discharges from the industrial area of Tangier (around 70000 t/year of solid inputs), according to El Aouarram, *et al*. (2008). Levels of Pb, Cd, Cu and Zn in Tangier Bay were lower than those recorded by these authors in the River Mghogha, with the exception of Cr, which showed higher levels in the bay. Another study in the Rivers Mghogha and Souani in the city of Tangier (Rodríguez-Barroso *et al*., 2009) revealed higher levels of Pb, Cr and Zn than those recorded in this study, but levels of Cd and Cu were comparable or slightly lower and only levels of Ni in Tangier Bay were higher than those recorded in the River Souani. In another study in the Tangier Bay, Achab *et al*. (2007) recorded high values in the harbour and values very similar to those found in this study in the bay, and suggested that the concentrations were related to the routine activities of the port (rejection of hydrocarbons, chemicals products and other activities), as well as to the domestic and industrial effluents of anthropogenic origin. Higher values were obtained in the Kaohsiung harbours in Taiwan, with similar characteristics to those of the Tangier Bay, where over 70% of domestic wastewaters were still directly being discharged untreated into the rivers and several industrial parks considered as contaminated zones were located around the city of Kaohsiung (Chen *et al*., 2007). Others works related to contamination of sediments in Spanish harbours have reported higher values of Cu, Pb, Cd and Zn than in the Tangier Bay in Ceuta (Guerra-Garcia and García-Gómez, 2005), Cartagena and Cádiz (Casado-Martínez *et al*., 2006). The Cr and Ni levels in the Tangier Bay were generally lower than those reported in the Cartagena and Cádiz harbours. Compared with these works, in the present study heavy metals did not show high values, probably due to the high hydrodynamic energy in the Tangier Bay, where the surges of NW direction reach the bay perpendicularly to the coast; the diffraction of these surges creates a side current responsible for the transport of the sediments towards the west of the bay (Achab *et al*., 2007). In general, the degree of marine contamination in Tangier remains relatively low in comparison with the sites described.

It is also important to emphasize the limited influence of the mouths of the Rivers Mlaleh and Chatt. This is obviously because these rivers are small and represent a minor percentage of the discharges collected. In fact, stations 4 and 5 showed no enrichment (EF<1) and MPI values were very low, although sample 4 seems to show a higher MPI value than sample 5. This was corroborated by cluster analysis, which grouped station 4 with samples that were fairly polluted by metals. The effect range-median (ERM) sediment quality guidelines in the United States, which represents the chemical level above which effects frequently occur to aquatic organisms (NOAA (NS&T: National State and Trend Programme)) were also taken into account. Only station 6 (mouth of the River Chatt) had an Ni chemical level above which effects frequently occur to aquatic organisms (ERM 51.6 mg kg^{-1}).

It is important to take into account that the outfall was built at the west side of the harbour. The predominant currents in the east could move and deposit pollutants inside the bay, and ultimately in sediments. The present study could be considered as a preliminary study of the possible influence of discharges by the outfall into the bay.

Therefore, proper treatment of industrial waste effluents and municipal wastewater is a better strategy for controlling metal sediments in the Tangier Bay. Results obtained from this study would be helpful in developing more effective watershed and bay management strategies for controlling metal discharges into the bay and developing a managerial protocol for the remediation of contaminated sediments. Finally, this work could be used to verify the possible impact that the outfall might have in the future.

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