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An assessment of heavy metal contamination in surface sediment using statistical analysis

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Abstract The distribution and accumulation of heavy metals in the sediments, especially those nearest of wastewater discharges of south of Spain, were investigated. Sediment samples from 14 locations were collected and characterised for metal content (e.g. Ni, Cu, Zn, Cr, Pb, Mn, Cd and Hg), organic carbon, total nitrogen, total phosphorous, *n*-hexane-extractable material, carbonates and grain size. Concentration data were processed using correlation analysis and factor analysis. The correlation analysis of concentrations data showed important positive correlations among organic carbon, total phosphorus, Cu, Zn, Cd and Hg, otherwise weak correlations among Mn, Cr, Ni and $CO_3{}^{2-}$, indicating that these metals have complicated geochemical behaviours. The use of statistical factor analysis also confirmed these results. Sediments pollution assessment was carried out using geoaccumulation and metal pollution indexes (MPI_8). The results revealed that sediments of Cádiz bay and Sancti Petri channel were uncontaminated with the studied metals.

Keywords Chemical parameters · Urban pollution · Sediment · Pollution · Quality · Standards

Introduction

Estuaries and coastal areas are extremely important as source of nutrients, sediments and pollutants for the marine environment. Pollution of the natural environment by heavy metals is a worldwide problem because these metals are indestructible and most of them have toxic effects on living organisms when they exceed a certain concentration (Nuremberg 1984; Forstner 1990; MacFarlane and Burchett 2000). Heavy metals are of high ecological significance since they are not removed from water as a result of self-purification but accumulate in reservoirs and enter the food chain (Loska and Wiechula 2003). The elevation of metal levels in a reservoir is shown mainly by an increase in their concentrations in the bottom sediment. Their occurrence in the environment results primarily from anthropogenic activities.

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Sediments are normally mixtures of several components including different mineral species as well as organic debris. Sediments represent one of the ultimate sinks for heavy metals discharged into the environment (Gibbs 1972; Luoma and Bryan 1981; Bettinetti et al. 2003; Hollert et al. 2003). In recent years, considerable attention has been given to assessing the state of the coast receiving discharges of wastewater. Wastewater treatment is a solution to the pollution problems that would be brought about by their direct discharge onto shores and into rivers (Ghrefat and Yusuf 2006; Chen et al. 2007; Rodríguez-Barroso et al. 2009a, b).

The Bay of Cádiz is located southwest of the Spain coast and is divided into two zones: outside and inside bay. The inside bay is connected with the open waters of the Atlantic Ocean by natural channels that cross great marshes, known as the Sancti Petri channel. Bay of Cádiz has a population of over 700,000, and there was no sewage system until 2002 and all wastewater effluents were directly discharged to the nearest of the cities with hardly any treatment (Rodríguez-Barroso et al. 2008). Since 2002, Cádiz City Administration started to construct a treatment plant (375,000 equivalent inhabitants), and today, all domestic wastewater is discharged to Atlantic Ocean with treatment. This has created a great impact on the biological and geochemical conditions of both bay and the shoreline.

A study of the distribution, enrichment and accumulation of heavy metals in the Cádiz Bay sediments is important to the assessment of the possible influence of anthropogenic activities on bay waters (Hung and Hsu 2004; Morillo et al. 2002; Chen et al. 2007). In the present study, we characterised the physical–chemical properties of the bay and shoreline sediments, namely clay, silt, sand, carbonates, organic carbon (OC) total nitrogen (TN), total phosphorus (TP) and *n*-hexane-extractable material (HEM) and examined the distribution of heavy metals such as Ni, Cu, Zn, Cr, Pb, Mn, Cd and Hg in the sediments at 14 stations (Fig. 1) during 2000. The extent of metal contamination was assessed using metal pollution index and the geoaccumulation index (I_{geo}; Aloupi and Angelidis 2001; Usero et al. 2000; Reddy et al. 2004; Selvaraj et al. 2004). A statistic correlation analysis between pertinent sediment characteristics and metal concentration was performed to determine the possible factors controlling the trace metal concentration in Cádiz Bay and Sancti Petri channel sediments. The overall objectives of this study were to determine distribution, degree of contamination and sources in surficial sediments along the inside Cádiz Bay and Sancti Petri channel due to untreated urban and industrial sewage discharges.

Materials and methods

Study areas

Two zones in the south of Spain were studied: Cádiz Bay and the Sancti Petri channel. Both of them are characterised by receiving effluents from the adjacent populations. Some of the cities in these zones have not treated their effluents until recent years; therefore, the sediments close to the discharge channels have been subjected to substantial contamination of urban and/or industrial origin. The Bay of Cádiz covers an area approximately 30,000 ha, located at the southwestern tip of Europe. The main industries located in this zone are related to marine construction (ships and offshore platforms) and aerospace manufacturing; rapid economic development has contributed to increasingly serious pollution of ecosystems in this zone. In holiday periods, this part of the coast hosts a large number of tourists; the size of the population can easily double or triple, which inevitably increases the load of contaminants discharged in wastewaters. The Sancti Petri channel is an arm of sea, 18 km long, which links the southern part of Cádiz Bay with the open waters of the Atlantic Ocean; it constitutes the main artery of a complex system of channels and lagoons known as the Sancti Petri marshes. The direct discharges received by this channel are mainly of urban origin and, to some extent, from a naval construction facility. Numerous studies dealing with the contamination in this zone (Del Valls et al. 1998; Blasco et al. 2000; Carrasco et al. 2003; Rodríguez-Barroso et al. 2006, 2008) have shown high levels of pollution that are very dangerous for aquatic fauna and their direct predators, marine birds and

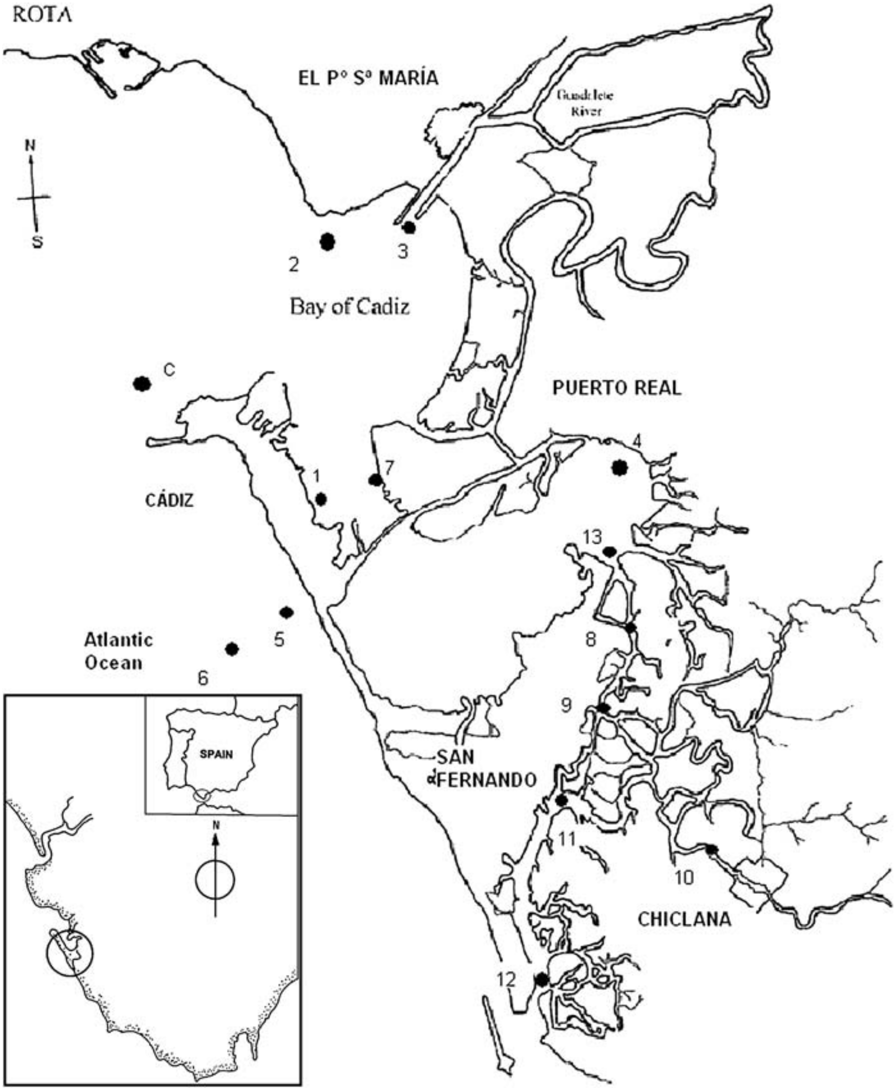

Fig. 1 Map of the southwestern part of Spain showing the sampling sites in Bay of Cádiz and Sancti Petri Channel

humans. Among the contaminating agents identified, organic matter (detergents, petroleum, oil, grease, etc.) and heavy metals are particularly notable for their harmful effects.

Sample collection

Sampling points in the two studied zones were selected to cover the area expected to be polluted due to wastewater discharges (Fig. 1). Surface sediments were collected once during the year 2000 at a total of 14 points, using a 0.025-m^2 Van-Veen grab sampler. At each sampling location, three sediment samples (0- to 10-cm depth) were collected, mixed together and kept fresh until their pretreatment in laboratory. Seven samples were taken from Cádiz Bay. Six stations (1 to 6) were located close to the to the domestic origin wastewaters discharge. Samples 5 and 6 (located outside the Bay) received the most important discharges of the city occurring through a submarine emissary, and another was located near an industrial area related to shipbuilding (7). In the zone of the Sancti Petri channel, samples were taken at six stations in areas associated with discharges of anthropogenic origin (8 to 12), and another station was located near an industrial site related to shipbuilding (13). At the last station (C), unpolluted sediment was sampled as a control.

Sample analysis

Seven physical–chemical variables were determined: grain size, carbonates, organic carbon, total nitrogen, total phosphorus, heavy metals and HEM. Samples were dried at 60°C and disaggregated. Organic carbon (% OC) was determined by mineralisation of the organic matter by means of a sediment oxidation with potassium dichromate (Gaudette et al. 1974). Total nitrogen was determined according to the standard methods (APHA et al. 1992) after an acid digestion using a digestion unit (Bloc-Digest 6P 4000629). TP was analyzed according to USEPA method 365.2. The calciometry method (Loring and Rantala 1992) was used to determine the content of carbonate (CO_3^{2-}) in the sediments. In this method, the amount of CO_2 released from the reaction is dependent on the amount of $CaCO_3$ in the sample. Metals were extracted at room temperature with H_2O_2, HCl and HNO_3 in sequence, according to Bellucci et al. (2002), using a Milestone Ethos 1600 model microwave oven and then determined by atomic absorption spectrometry (Perkin Elmer type 100). In the case of Ni, Cu, Cr, Cd and Zn, the furnace atomic absorption spectrometry (FAAS) technique was employed; for Cd, the graphite furnace technique (GFAAS) was used. Calibration standards were regularly performed to evaluate the accuracy of the analytical method. A certified reference standard sediment, MESS-3, from the National Research Council of Canada was used to test the analytical and instrument accuracy of the method. Differences between certified and measured results were less than 10% for the metals studied in this paper; this showed agreement to more than 90% with the certified values. Results are expressed as milligram per kilogram of dry sediment. HEM was analysed in accordance with method 9071, USEPA for sludge, sediment and solid samples, based on an extraction by Soxhlet employing *n*-hexane as solvent. Granulometric analysis was determined using a mechanical sieve for the sand fraction and laser measurement of the fraction <63-μm particle size. Results are reported as weight percent sand, silt and clay and were dried at 105°C to constant weight.

Statistical analysis

Multivariate techniques were applied to assess the regional distribution pattern of the assemblages of the elements in the study area. Group averaging cluster analysis was applied using the city block (Manhattan) distance coefficient. Stepwise factor analysis was performed to verify if the station clusters groups can be discriminated. In addition, linear correlation coefficients were calculated to understand the inter-element relationships. Statistical analysis was performed using Statistical Program for Social Sciences (SPSS program version 14.0 for Windows).

Results and discussion

Sediment characteristic

It has been reported that the distribution of grain size and organic matter content were two critical factors influencing the metal distribution in sediments (Aloupi and Angelidis 2001; Liaghati et al. 2003). Anthropogenic pollutants such as TN and TP may also be correlated with metal distribution in sediments. Table 1 presents the values of sediment characteristics for the 14 stations. Results show that there exists a great granulometric variability between the two studied zones, with essentially clay (<2 μm) sediments on the one hand (sites 1, 3, 4, 7, 9, 10, 11 and 13) and typically sandy (>63 μm) sediments with a fairly significant gravel and sand content on the other (sites C, 2, 5, 6 and 12).

Mean values of the chemical variables analysed for the samples are shown in Table 1. The most relevant concentrations of OC (9.30% and 3.24%) were those measured in samples taken from Sancti Petri channel (station 11) and Cádiz Bay (station 1), respectively. OC concentrations are generally dependent on sediment grain size and composition and the correlation is better with clays than with the sum of fines, which corroborates the high levels of OC detected at sampling points 11 (92% clays) and 1, (43% silt + 40% clay) The lowest levels were presented by points 2, 5, 12 and

Table 1 Mean values of major of sediment characteristic in the sediments of all stations studied in south of Spain

Station	Clay (%, <2 μm)	Silt (%, >2–63 μm)	Sand (%, >63 μm)	CO_3^{2-} (%)	OC (%)	TN (mg/kg)	TP (mg/kg)	HEM (mg/kg)
C	20.55	10.91	68.54	19.4	0.37	280	13.9	320
Cádiz Bay								
1	40.36	42.71	16.93	21.0	3.24	2,610	31.5	1,010
2	32.97	0.15	66.88	17.0	0.50	120	13.9	1,020
3	87.12	0.03	12.85	34.6	1.79	1,480	31.5	1,250
4	61.47	35.63	2.9	25.2	2.06	1,820	37.3	33,780
5	4.15	1.3	94.55	26.7	0.57	70	9.5	1,300
6	1.06	0.8	98.14	16.4	1.10	70	13.4	2,130
7[a]	56.31	36.77	6.92	23.9	1.84	1,590	28.4	7,030
Sancti Petri Channel								
8	30.76	24.14	45.1	14.5	1.91	2,190	20.6	3,140
9	52.7	0.38	46.92	16.9	1.14	560	30.1	2,480
10	74.93	0.58	24.49	13.8	2.13	1,520	39.7	3,840
11	92.4	4.98	2.62	7.8	9.30	1,650	48.5	2,190
12	16.88	0.13	82.99	28.6	0.50	210	18.4	650
13[a]	52.87	46.07	1.06	17.7	2.57	2,180	39.3	17,440

C control sample
[a] Stations from areas affected by industrial waste

the control where sandy textures are predominant (>67%).

Sediments from areas close to industries related to shipbuilding (stations 7 and 13) presented high levels of HEM, as was expected. According to Bergueiro and Domínguez (1992), the accidents that occur in the transport of oil and discharges, both industrial and urban, contribute significantly to the supply of HEM. Another station (station 4) showed the highest level (33.78 g/kg), pick up next to a pier and with a fine granulometry (clay + silt ~97%).

The co-precipitation with carbonate minerals is of importance for a number of metals, such as cadmium and zinc (Fostner and Wittmann 1983; Alloway 1990). The carbonate content (CO_3^{2-}) of Cádiz sediments ranges between 10.0% and 34.6%, with an average of 23.0%, whilst in Sancti Petri ranges between 7.8% and 28.6%, with an average of 16.5%.

Metal distribution

The results of the total metal contents found in the studied areas are shown in Table 2. The method detection limit is also presented and the results of the analysis of the reference material (MESS-3) and the level catalogued by the USEPA and Ontario Ministry of Environment, Canada as "polluted level" for each metal (USEPA 1997). A comparison of the metal concentrations with the threshold values proposed by USEPA reveals that most of the samples from these zones may be classed as "contaminated" with mercury (approximately the 62% of samples in Cádiz Bay and 100% in Sancti Petri pipe). This result may be an explanation of the role of organic matter in the sorption of Hg on marine sediments due to the presence of charged surfaces. In this context, Langston (1986) found that Hg was affected by the organic content of sediments. Crecelius et al. (1975) observed that 82% of Hg in marine sediments was associated with the organic matter. They speculated that protein with an –SH group and humic acid fraction of organic matter in the marine sediments is a favourable binding site for Hg. Marcovecchio et al. (1986) found a positive correlation between concentrations of Hg and humic substances in the sediments near a sewage outfall. Interaction between organic carbon and Hg was also reported by Ramamoorthy and Rust (1976) in the river sediments and Bartlett and

Table 2 Heavy metals (mg/kg, dry weight; mean ± SD) in sediments from study area, method detection limit (m.d.l., dry weight), quality levels (threshold values proposed by USEPA and Ontario Ministry of Environment, Canada) and results of the analysis of the MESS-3 reference material

Station	Ni	Cu	Zn	Cr	Pb	Mn	Cd	Hg	MPI$_8$
C	21.5 ± 2.5	9 ± 0.08	35.9 ± 0.8	24.4 ± 2.1	11.6 ± 1	448 ± 11	0.06 ± 0.01	0.89 ± 0.04	9.1
Cádiz Bay									
1	25.3 ± 0.4	61.8 ± 0.8	161 ± 3	60.6 ± 0.1	43.5 ± 5.6	328 ± 6	0.4 ± 0.1	2.35 ± 0.09	25.9
2	[a]	5.58 ± 0.76	26.3 ± 0.4	–[a]	–[a]	266 ± 5	0.07 ± 0.01	0.65 ± 0.04	5.2
3	25.4 ± 1.1	34.4 ± 1.4	97.1 ± 6.9	43.9 ± 2.7	45.7 ± 10.1	396 ± 8	0.31 ± 0.01	1.46 ± 0.06	20.4
4	31.1 ± 0.3	44.5 ± 1.1	133 ± 1	66.5 ± 0.6	32.9 ± 0.6	495 ± 21	0.31 ± 0.03	1.76 ± 0.01	24.0
5	–[a]	5.46 ± 0.68	27.6 ± 0.8	[a]	10.7 ± 0.1	211 ± 5	0.03 ± 0.01	1.09 ± 0.04	5.4
6	–[a]	5.73 ± 0.78	21.7 ± 1.9	[a]	[a]	110 ± 7	0.02 ± 0.01	0.6 ± 0.02	3.9
7[c]	31 ± 1.4	43.5 ± 1	124 ± 1	62.9 ± 2	30.3 ± 2.1	506 ± 19	0.24 ± 0.01	1.61 ± 0.05	22.4
Sancti Petri channel									
8	20.7 ± 1.5	83.3 ± 7.4	129 ± 10	42.9 ± 0.6	77 ± 34	197 ± 10	0.27 ± 0.05	3.94 ± 0.04	25.0
9	17.1 ± 1.1	20.7 ± 0.6	62.5 ± 3.2	37.1 ± 2.2	14.5 ± 01	257 ± 3	0.13 ± 0.04	2.84 ± 0.04	13.5
10	25.5 ± 2.5	36.9 ± 2.3	114 ± 2	49.6 ± 2.8	31.9 ± 1.8	304 ± 4	0.28 ± 0.01	1.93 ± 0.01	20.2
11	28.2 ± 1.1	58.6 ± 0.6	134 ± 1	72.9 ± 0.1	40.6 ± 0.1	212 ± 1	0.28 ± 0.01	4.08 ± 0.07	25.1
12	5.5 ± 0.1	7.7 ± 0.6	23.2 ± 1.2	[a]	[a]	147 ± 8	0.06 ± 0.01	1.68 ± 0.06	5.7
13[c]	35 ± 0.1	66.1 ± 0.8	153 ± 2	71.3 ± 4.5	35.4 ± 0.1	348 ± 4	0.41 ± 0.01	1.84 ± 0.08	26.4
m.d.l.	4.0	2.0	2.0	16.0	5.0	14.00	0.004	0.04	
Not polluted[b]	< 20	< 25	< 90	< 25	< 40	–	< 1	< 0.3	
Polluted[b]	> 50	> 50	> 200	> 75	> 60		> 6	> 1	
MESS-3 certified	46.9 ± 2.2	33.9 ± 1.6	159 ± 8	105 ± 4	21.1 ± 0.7	324 ± 12	0.24 ± 0.01	0.091 ± 0.009	
MESS-3 Analysed	43.8 ± 1.4	34.3 ± 0.1	159 ± 6	99.3 ± 1.7	20.7 ± 0.8	328 ± 5	0.28 ± 0.01	0.090 ± 0.001	
% recovery	93.3	101.2	100	94.6	98.1	101.2	116.7	98.9	

C control sample

[a] Below method detection limit

[b] USEPA (1997)

[c] Stations from areas affected by industrial waste

Craig (1981) in the estuarine sediments. On the other hand, it has been demonstrated that there exists a great content of metals in wastewater treatment plant sludge (a typical level of Hg in these sludge may be between 5 and 10 ppm; Anderson 1979), and another author had found 100 ppm (Lester et al. 1983).

In reference to the Cd levels, the zone may be classed as "not polluted" according to the reference regulations. Pb levels obtained show that in accordance with USEPA recommendations, only station 8 may be considered "polluted"; this site is located in an area of reception of domestic wastewater discharges coming from San Fernando town, around 60,000 inhabitants. In reference to the Zn, Cr and Ni levels, eight samples may be considered as "moderately polluted" and the remaining sites may be classed as "not polluted"; these sediments correspond to areas of strong anthropogenic influence (1, 3, 4, 8, 10 and 11) and to areas markedly affected by shipbuilding activities (7 and 13). With respect to Cu, there were four samples "polluted" (1, 8, 11 and 13), the last one coming from a shipbuilding industry.

Relation of sediment characteristics to trace metal concentrations

Pearson's correlation coefficients among the granulometry, OC, TN, TP, contents of metal, CO_3^{2-} and HEM in the studied sediments are presented in Table 3. The results show that with the exception of the content of Ni and Cr, which are not correlated by any fraction, all the metals are controlled negatively by the percentage of sand; this corroborates the affirmation of Haque and Subramanian (1982), according to which, the capacity of adsorption of metals is in increasing order, sand $<$ silt $<$ clay, due to the increase in the superficial area and to the content of minerals and organic matter. Nevertheless, though the majority of the metals tend to accumulate in the thin fraction of the sediment, this not always is like that, depending on the type of metal, about which it treats itself. The metals Cu, Zn and Cd are correlated positively with silt and clay; Mn with the silt and the clay fraction is correlated also with Pb and Hg, confirming the conclusion of Chakrapani and Subramanian (1993), according to which the metals Cu, Zn and Mn increase their concentration with the thinnest fractions. These authors established also that Cr decreases its content in thin sediments; in fact, in this study, its coefficient of correlation with the percentage of clay is negative ($r = -0.08$).

The content of OC, TN and TP present a good correlation with the clay, as was expected, for which the metals (Cu, Zn, Cd and Hg) in this fraction of sediment also present correlation coefficients larger than 0.53 at the confidence level of 99% (or $r > 0.53$ at $p < 0.01$) with the organic component: Cu vs. OC, TN, TP ($r = 0.57$, 0.93, 0.67), Zn vs. OC, TN, TP ($r = 0.59$, 0.94, 0.82), Cd vs. OC, TN, TP ($r = 0.52$, 0.93, 0.82) and Hg vs. OC, TN, TP ($r = 0.69$, 0.54, 0.64). Also, Pb vs. TN and TP showed high correlations ($r = 0.83$, 0.55). Positive correlation reveals that organic matter plays a great role in binding the metals in ligands. It is necessary to emphasise that the nitrogen coefficients are major than the phosphorus and organic carbon ones, and therefore, this is the following correlation order: nitrogen> phosphorus> organic carbon. Nevertheless, carbonates did not show correlations with any other component, and HEM only with silt fraction ($r = 0.58$) and with any other metal.

The result of the cluster analysis (Fig. 2) demonstrates two station groups. The first major grouping is formed by the most stations from Sancti Petri channel (8, 9, 10, 11 and 12), Cádiz Bay (1, 2, 3 and 5) and the control sample (C). The most relevant in this study is the second group, formed by three stations with a very similar content of clay + silt (>93%) located in the inner bay (St 4, 7 and 13). These stations are characterised by their shallow waters, low rate of water renewal and the preponderance of sedimentation phenomena, associated with very fine sediment. These zones have greater anthropogenic influence and, consequently, are closer to sources of contamination.

The factor analysis was applied to obtain more reliable information about the relationships among the variables (Bartolomeo et al. 2004; Glasby et al. 2004; Ghrefat and Yusuf 2006). Table 4 summarises varimax component of two factors in sediments of the southwestern part of Spain. Two significant components, whose

Table 3 Correlation coefficient matrix showing inter-element and element–granulometric relationships in sediments

	Sand	Silt	Clay	OC	TN	TP	Ni	Cu	Zn	Cr	Pb	Mn	Cd	Hg	CO_3^{2-}	HEM
Sand	1.000															
Silt	**−0.622**	1.000														
Clay	**−0.883**	0.181	1.000													
OC	**−0.591**	0.168	**0.641**	1.000												
TN	**−0.787**	**0.737**	**0.545**	0.492	1.000											
TP	**−0.902**	0.380	**0.904**	**0.750**	**0.682**	1.000										
Ni	0.164	−0.033	−0.186	−0.050	0.192	−0.136	1.000									
Cu	**−0.754**	**0.696**	**0.530**	**0.569**	**0.933**	**0.667**	0.004	1.000								
Zn	**−0.912**	**0.758**	**0.691**	**0.594**	**0.944**	**0.822**	−0.070	**0.926**	1.000							
Cr	0.035	0.062	−0.081	0.087	0.313	0.002	**0.985**	0.127	0.069	1.000						
Pb	**−0.671**	0.503	**0.541**	0.455	**0.827**	**0.550**	−0.126	**0.918**	**0.817**	−0.037	1.000					
Mn	**−0.670**	**0.565**	0.502	0.002	0.363	0.390	−0.191	0.257	0.490	−0.161	0.266	1.000				
Cd	**−0.916**	**0.709**	**0.725**	**0.520**	**0.928**	**0.825**	−0.075	**0.874**	**0.969**	0.052	**0.786**	0.498	1.000			
Hg	**−0.552**	0.242	**0.548**	**0.688**	**0.544**	**0.640**	−0.287	**0.742**	**0.639**	−0.179	**0.737**	−0.011	**0.547**	1.000		
CO_3^{2-}	−0.106	0.101	0.072	−0.372	−0.114	−0.089	−0.462	−0.180	−0.038	−0.494	0.007	0.433	0.074	−0.213	1.000	
HEM	−0.479	**0.581**	0.253	0.059	0.391	0.398	0.067	0.324	0.445	0.140	0.176	0.497	0.435	0.021	0.125	1.000

Values in bold are significant at $p < 0.01$

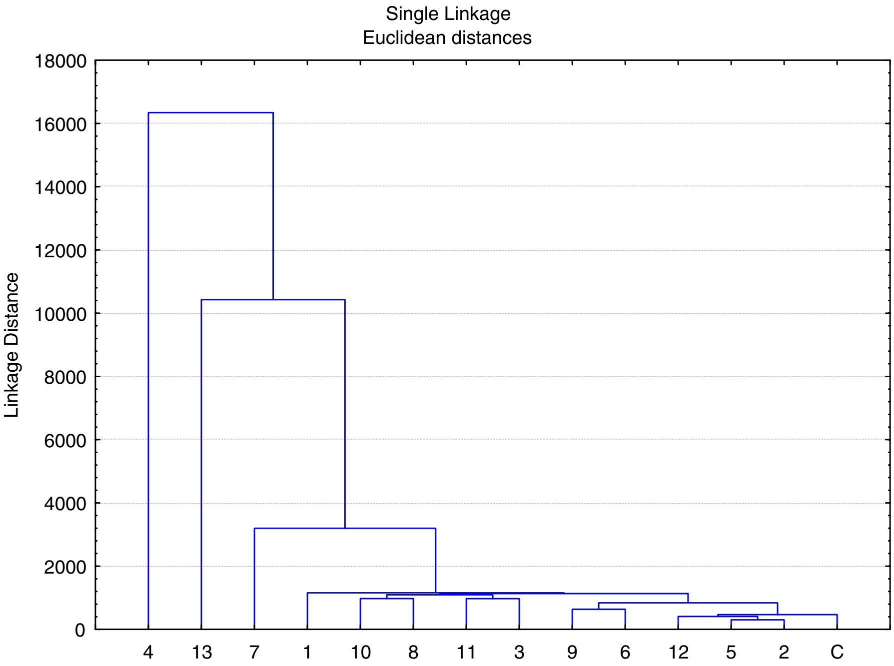

Fig. 2 Dendrogram showing station groups formed by group averaging cluster analysis of elemental concentrations

eigenvalues are higher than 1 accounting for 67% of the cumulative variance, were distinguished for the analysed data. Factor 1 accounted for 49.5% of the total variance and is mainly characterised by high levels of OC, TN, TP, Cu, Zn, Cd and Hg (Fig. 3a); this can be explained by the significant role of organic matter to the binding of certain heavy metals (Murray et al. 1999; Eimers et al. 2002). Factor two accounted for 18% of the total variance, which mainly consists of data of CO_3^{2-}, HEM and Mn and low positive loadings to Cd (Fig. 3b). Generally, the results of correlation analysis and factor analysis coincide with each other. Their results demonstrate the lack of clustering between Mn, Cr and Ni, and the sediment components including organic matter and carbonate content confirm the complicated behaviour of these pollutants, which can be influenced by many factors.

Table 4 Factor analysis of Cádiz and Sancti Petri sediments loading with chemical parameters

Variable	Factor 1	Factor 2
CO_3^{2-}	−0.252	0.684
OC	0.639	−0.544
TN	0.932	0.009
TP	0.864	−0.091
HEM	0.412	0.408
Ni	−0.652	−0.179
Cu	0.904	−0.191
Zn	0.963	0.012
Cr	−0.552	−0.366
Pb	−0.399	−0.503
Cd	0.925	0.088
Hg	0.708	−0.518
Mn	0.430	0.811
Eigenvalue	6.432	2.327
% total variance	49.48	17.90
% cumulative	49.48	67.37

Geo-accumulation index

Geo-accumulation index (I_{geo}) was introduced by Muller (1969) and allows the contamination of the investigated sediment with organic and inorganic pollutants to be determined by comparing present concentrations with pre-industrial levels. Concentrations of geochemical background are multiplied each time by 1.5 in order to allow content fluctuations of a given substance in the environment as well as very small anthropogenic influences. Values of geoaccumulation index can be defined as follows:

$$I_{geo} = \log_2 \left[(C_n / (1.5 \times B_n) \right],$$

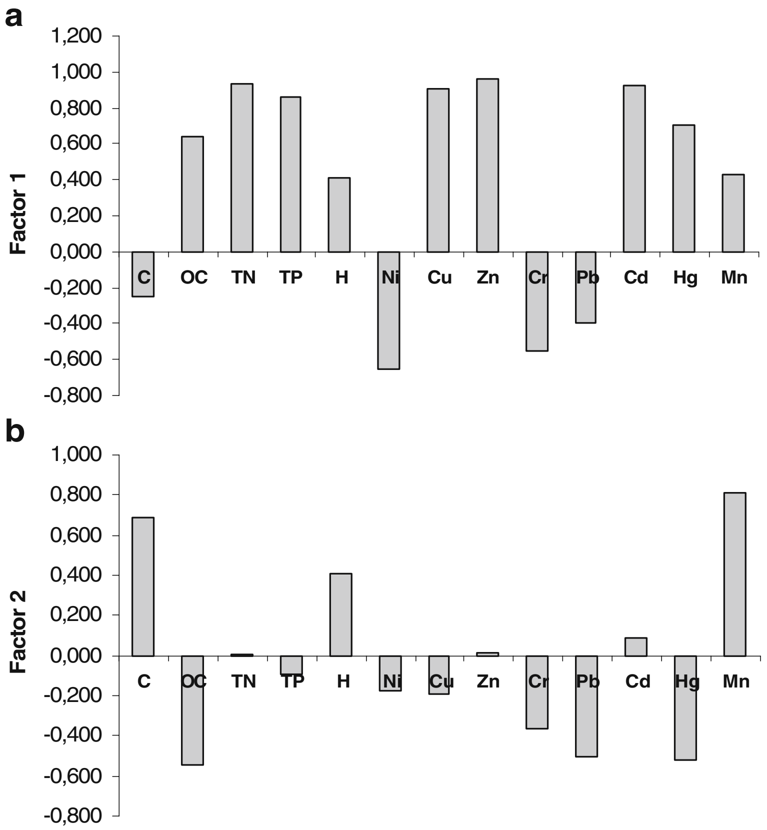

Fig. 3 Results of factor 1 (**a**) and factor (**b**) in sediments of the south of Spain. *C* represents (CO_3^{2-} and HEM is represented by *H*)

where C_n is the measured concentration of the heavy metal (n) in the examined bottom sediment and B_n is the geochemical background value in average shale (Turekian and Wedepohl 1961) of element n; 1.5 is the background matrix correction factor due to lithogenic effects. The index of geoaccumulation includes even grades, from 0 (non-contaminate) until 6 (very strong). The I_{geo} values calculated for heavy metal concentrations in Cádiz Bay and Sancti Petri channel reveal that the sediments are unpolluted with respect to the total of analysed metals. Authors that used this index register sediments strongly polluted, as Chen et al. (2007) at the vicinity of the mouths of major rivers that flow into Kaohsiung harbour, Taiwan. Also, Ghrefat and Yusuf (2006) found sediments very strongly polluted with Cd in a dam of Jordan.Rodríguez-Barroso et al. (2009b) detected sediments moderately contaminated with Fe and Hg in rivers from the north of Morocco.

Metal pollution index

The overall metal contents of sediments at the sites investigated in this study were compared using the metal pollution index (MPI) calculated according to Usero et al. (2000) with the formula:

$$\text{MPI}_n = (Cf_1 \times Cf_2 \times \ldots \times Cf_n)^{1/n}$$

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

The MPI values of the eight heavy metals in sediments of the area under investigation are summarised in Table 2. The overall average MPI_8 in Cádiz area (15.3) was lower than that recorded in Sancti Petri Channel (19.3). The lowest values were recorded at stations 2, 5, 6 and 12, in agreement with the first group defined in cluster analysis, whilst the highest values were very similar ($\text{MPI}_8 \sim 25$) and were found in stations

1, 3, 4, and 7 from Cádiz area and sites 8, 11 and 13 from Sancti Petri channel. These are considered not polluted areas, even though those stations were very near to urban and industrial discharges. In another work, bigger values of MPI were found, e.g. in a river from the north of Morocco. Rodríguez-Barroso et al. (2009b) found a maximum value of 73.0 nearest to an industrial complex. Khaled et al. (2006) registered values between 35.7 and 144.2 next to a miner and industrial outlet.

Conclusions

Identification and quantification of heavy metal sources, as well as the fate of those heavy metals, are important environmental scientific issues. The present study presents useful tools, methods and indices for the evaluation of sediment contamination. This study also provides a powerful tool for processing, analysing and conveying raw environmental information for decision-making processes and management involving natural resources.

Stations 7 and 13 host harbour and shipbuilding activities and may justify some high values in nearby sediments, with particularly high Zn contamination. The secondary maxima of Hg at Cádiz and Sancti Petri channel may be attributed to the past as a result of the role of organic matter in the sorption of Hg on marine sediments.

Multivariate analyses, including the correlation matrix analysis and factor analysis used in this study, provide an important tool for better understanding the complex dynamics of pollutants. The correlation analysis of concentrations data shows important positive correlations among OC, TP, Cu, Zn, Cd and Hg, otherwise, weak correlations among Mn, Cr, Ni and CO_3^{2-}, indicating that these metals have complicated geochemical behaviours. The use of statistical factor analysis also confirms these results.

Sediment pollution in the present study was assessed using geoaccumulation and metal pollution indexes values. The results of geoaccumulation index reveal that sediments of Cádiz Bay and Sancti Petri channel are unpolluted with respect to the total of analysed metals. The calculation of metal pollution index showed that the highest values ($MPI_8 \sim 25$) are considered not polluted sediments; therefore, both areas are catalogued as not contaminated.

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