Determining contamination sources in marine sediments using multivariate analysis

T.Á. DelValls, J.M. Forja, E. González-Mazo, A. Gómez-Parra*
Departamento de Química-Física, Facultad de Ciencias del Mar, Universidad de Cádiz, 11510 Puerto Real, Cádiz, Spain

J. Blasco
Departamento de Oceanografía, Instituto de Ciencias Marinas de Andalucía, CSIC, 11510 Puerto Real, Cádiz, Spain

The problem of identifying sources of anthropogenic pollutants in a local marine environment has been intensively studied during the last two decades. An approach is descibed for tracing anthropogenic pollutant sources, and for characterizing various geochemical and chemical processes related to contamination by anthropogenic heavy metals and surfactants in the marine coastal environment, which uses a multivariate technique of principal components analysis (PCA). This approach was applied to study two selected littoral ecosystems in the Gulf of Cádiz. The multivariate analysis approach can be used successfully for contamination source assessments. From this information, it was possible to identify current superficial sources of contamination and it might be possible to determine the areas where further toxicological testing is required. ©1998 Elsevier Science B.V.

Keywords: Marine sediments; Multivariate analysis; Principal component analysis; Contamination source assessment

1. Introduction

The geochemical cycle of most anthropogenic chemicals in the marine environment is determined to a large degree by their interactions with sediments. Sediments act as integrators and amplifiers of the concentrations of these elements in the waters which pass over and transport them, and play an important role in the shallow water estuarine areas. For this reason, sediments have been widely used to identify sources of contamination, to measure their extent, and to diagnose the environmental quality of aquatic systems [1,2]. One of the problems relating to contamination of the continental margin and estuarine environment is the identification of sources of pollutants. This problem for a local marine environment has been discussed by several authors [3,4]. Their approaches were based on the assumption that if anthropogenic pollutants for any particular area had originated from the same source, then the pairwise relationships between the concentrations of these pollutants in sediments from various stations in the contaminated area would be linear. Nevertheless, this linear assumption could not always be real, because more than one source could occur in any one area. For this reason, we propose the use of a multivariate analysis tool – principal component analysis (PCA) – which does not need the above linear assumption. This PCA analysis establishes and quantifies the correlations among the original variables in a data set, when the goal is to reduce the number of variables to a smaller set of components which can allow an easier interpretation. There are several monographs on the uses of PCA in the examination of multivariate data [5,6].

The objectives of the present work were to examine the results of a screening-level study of superficial

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*Corresponding author.

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sediments within two littoral ecosystems from the Gulf of Cádiz and to determine the spatial distribution of 14 heavy metals and the surfactant linear alkylbenzenesulfonate (LAS), by measuring the physico-chemical characteristics of sediments. Based on this spatial distribution and using the multivariate analysis (PCA) approach it should be possible to identify sources of contamination. It should also help to establish those areas in which further toxicological testing should be conducted, by comparing the chemical concentration results with sediment quality guidelines proposed by North American agencies and government bodies [7–10].

2. Sampling and sample preparation strategies

The present study was performed at seven stations in two shallow littoral ecosystems in the Gulf of Cádiz in the south-west of Spain (Fig. 1). Five sampling stations (CB1, CB2, CB3, CB4, and CB5) were selected in the Bay of Cádiz and two stations (BR1 and BR2) in the area of the salt marsh from the Barbate River. Stations were chosen on the best available information to represent presumed low, moderate and high levels of chemical contamination [11]. The stations chosen, in order of decreasing potential anthropogenic influences, were: CB2, CB3, CB5, CB4, and CB1 in the Bay of Cádiz, and BR2 and BR1 in the Barbate River (Fig. 1).

Sediment samples from each station were collected with a 0.025 m^2 Van Veen grab and transferred to a cooler. Prior to sample collection, all beakers for the collection and storage of sediment samples were thoroughly cleaned with acid (10% HNO_3) and then rinsed in reagent grade water (Milli-Q). Sediment used for determining the grain size distribution was maintained in the dark as wet samples whereas the rest of the sediments were air-dried for 24 h prior to chemical analysis, using an oven at 60°C (to avoid loss of any volatile Hg and of As). Coarse material > 2 mm, such as pebbles, coarse organic fibers and shell debris, was removed. Wet sediment was oxidized (1:10 v/v H_2O_2) and dispersed in distilled water during 48 h with a magnetic stirring by the addition of a 2 g l^{-1} solution of H_2PO_4.

For trace metal analysis (Fe, Mn, Zn, Cu, Pb, Cd, Cr, Ag, V, Ni, Co, and Sn) sediments dried at 60°C were totally dissolved following the recommendations of Loring and Rantala [12]. For the other two metals (As, and Hg), sediments were digested with HNO_3 (10 ml) followed by H_2SO_4 (20 ml) in a Winkler bottle placed in a water bath for 1 h at 60°C.

The grain size distribution was determined by laser diffraction using an Analysette 22 particle size analyzer following ultrasonic (Cole-Palmer, model 8891) dispersal in distilled water during 15–20 min at 200 MHz intensity. Next, the percent fractions were determined of coarse sand (> 200 μm), fine sand (200–20 μm), silt (20–2 μm), and clay (< 2 μm), as well as the parameters average grain size (η) and specific surface (σ). The organic carbon content was determined using the method of Gaudette et al. [13] with the El Rayis modification [14]. Elemental analysis for CHN was performed with a Carlo Erba machine (model 1106). Surfactants (LAS) were measured using the methods outlined by González-Mazo et al. [15].

The concentrations of the heavy metals Fe, Mn, Zn, and Cu in the extracts were determined by flame atomic absorption spectrophotometry with a Perkin-Elmer 2100. The heavy metals Hg and As in the extracts were determined by means of Perkin-Elmer MHS–FIAS coupled with a Perkin-Elmer 4100 ZL spectrophotometer. The remaining trace metals were measured by graphite furnace atomic absorption spectrophotometry (Perkin-Elmer, 4100 ZL) with the operating conditions shown in Tables 1–3.

The accuracy of the heavy metal analytical procedure was assessed by carrying out analyses of certified reference material (marine sediment MESS-1, National Research Council of Canada, and estuarine sediment BCR RM-277, Commission of the European Communities, Community Bureau of Reference) (Table 4). It can be seen that, apart from vanadium, the analytical procedures allow agreement with the certified values higher than 85%.

3. Measured levels of contamination

The sediment samples had relatively similar textures, being dominated by the clay fraction with a dark color, and a specific surface of 7.0–8.0 m^2 cm^{-3}. Station BR1 was the only station analyzed for which the sand proportion (grain size > 20 μm) was higher (7%) than the others (1%) and the specific surface was lower than the others (5.8 m^2 cm^{-3}). Also, this station presented the highest average grain size value (4.5 ± 0.7 μm). The levels of organic carbon were similar among the sediments and in the normal range for shallow littoral ecosystems (1–3% by dry

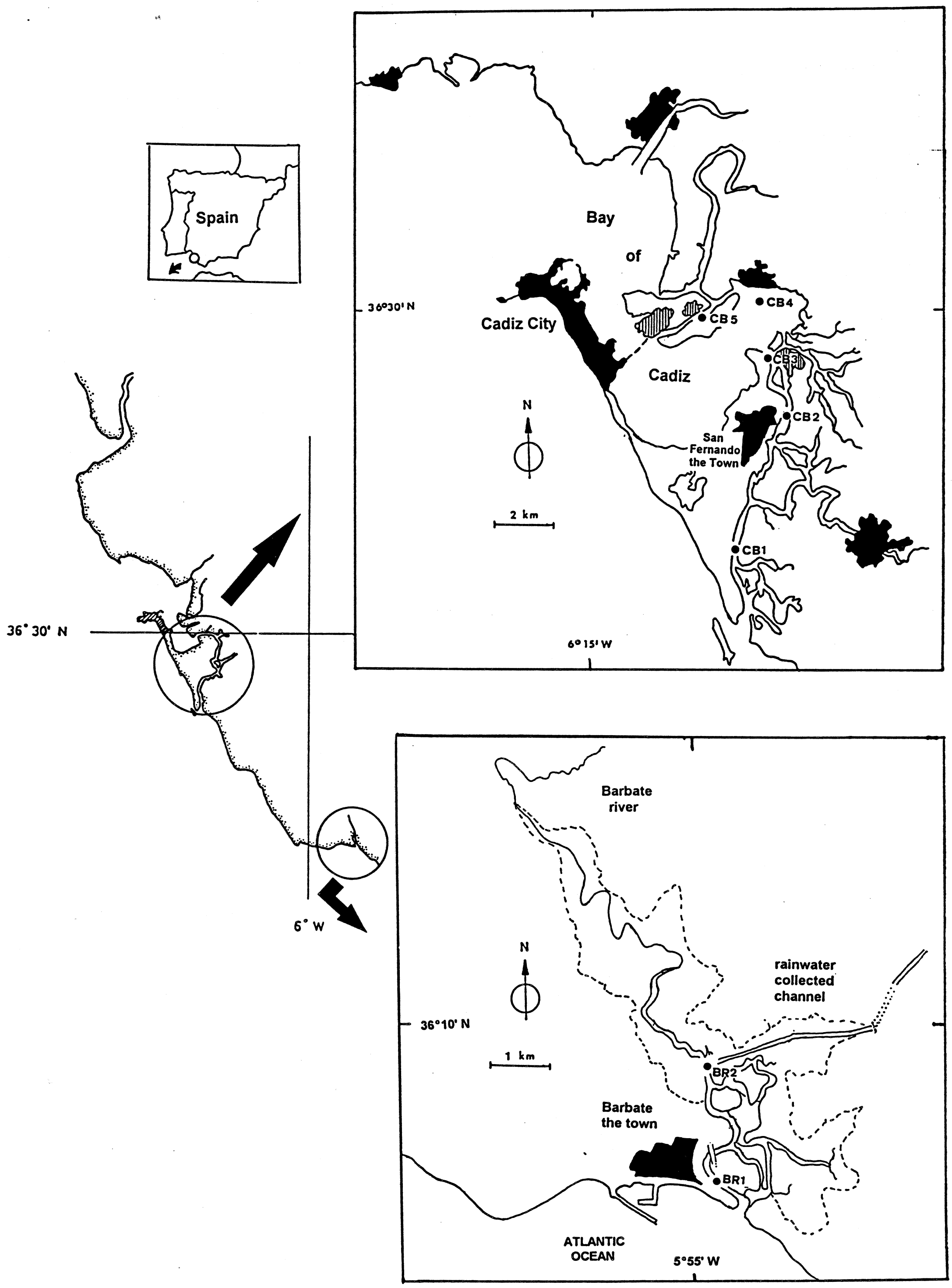

Fig. 1. Map of the two littoral ecosystems (Bay of Cádiz, and salt marsh of the Barbate River) selected in the Gulf of Cádiz, showing locations of sampling stations. Urban locations are represented by filled areas and industrial locations by hatched areas.

Table 1
Summarized operating conditions for the analysis of the heavy metals Fe, Mn, Cu, and Zn using flame atomic absorption spectrophotometry (Perkin-Elmer 2100) in digested sediment extracts

Metal	λ (nm)	S (nm)	Flame composition
Fe	248.3	0.2	Air–acetylene
Mn	279.5	0.2	Air–acetylene
Cu	324.8	0.7	Air–acetylene
Zn	213.9	0.7	Air–acetylene

λ is the incident radiation wavelength and S is the slit setting.

Table 2
Summarized operating conditions for the analysis of the heavy metals Cd, Pb, Cr, Ag, Co, Ni, V, and Sn using graphite furnace atomic absorption spectrophotometry (Perkin-Elmer 4100 ZL) in digested sediment extracts

Metal	λ (nm)	S (nm)	T_P (°C)	T_A (°C)	Matrix correctors
Cd	228.8	0.7	700	1400	$NH_4H_2PO_4$+$Mg(NO_3)_2$
Pb	213.6	0.7	1300	2500	$NH_4H_2PO_4$+$Mg(NO_3)_2$
Cr	357.9	0.7	1500	2300	$Mg(NO_3)_2$
Ag	328.1	0.7	800	1500	Pd+$Mg(NO_3)_2$
Co	242.5	0.2	1400	2400	$Mg(NO_3)_2$
Ni	232.0	0.2	1100	2300	–
V	318.4	0.7	1200	2400	–
Sn	286.3	0.7	1200	2100	Pd+$Mg(NO_3)_2$

λ is the incident radiation wavelength, S is the slit setting, and T_P and T_A are the pyrolysis and atomization process temperatures, respectively. Matrix interference correctors used for some heavy metals are described.

weight) except for station BR1 where the value was lower (0.59%). A few differences in the concentrations of the major elements (Fe and Mn) were observed between stations. Of all the stations, BR1 showed the lowest values for both metals. In general, chemical concentrations were higher in the sediments from the Bay of Cádiz than those in the Barbate River and similar to the concentrations measured in previous studies performed in both ecosystems [11,16]. From the obtained data, it was apparent that station CB2 was highly enriched in domestic detergents (LAS) compared to other sites: the inorganic contaminants were principally high levels of Pb and Ag, typical of urban effluents. Stations CB3 and CB5 were more contaminated with Hg, As, and Sn, and station CB5 also with Cr. Station CB4 showed three heavy metals (Cd, Ag, and Hg) more concentrated in sediments than in the reference station (CB1), but with an absence of apparent contamination.

4. Identifying contamination sources (multivariate analysis)

In order to identify the contamination sources in the ecosystems studied we applied PCA to explore the distribution of variables ($n = 19$). The PCA was performed on the correlation matrix, i.e., the variables were auto-scaled (standardized) so as to be treated with equal importance. All analyses were performed using the PCA option of the FACTOR procedure, followed by the basic set-up for the factor analysis procedure (P4M) from the BMDP statistical software package [17]. The application of PCA to the variables in this study indicates that 19 variables can be represented by five new variables or principal components. These new variables explain 97.5% of the variance in the original data set. The sorted rotated factor loadings (patterns) are coefficients correlating the original variables and the principal components in this analysis. The variables are re-ordered, so the rotated factor loadings for each factor are grouped together. In the present study, we elected to interpret a group of variables as those associated with a particular component where the loadings were 0.6 or greater, corresponding

Table 3
Summarized operating conditions for the analysis of the heavy metals Hg and As using Perkin-Elmer MHS–FIAS coupled with a graphite furnace atomic absorption spectrophotometer (Perkin-Elmer 4100 ZL) in digested sediment extracts

Metal	λ (nm)	S (nm)	Carrier	Reductor	Cell temperature
Hg	253.7	0.7	3% v/v HCl	0.2% $NaBH_4$ 0.05% NaOH	100°C
As	193.7	0.7	10% v/v HCl	0.2% $NaBH_4$ 0.05% NaOH	900°C

λ is the incident radiation wavelength, and S is the slit setting. The carrier and reductor mixtures are also shown for each metal as well as the cell temperature.

to an associated explained variance of more than 60%. This improves the approximation of Comrey's [18] cut-off of 0.65 for a good association between an original variable and a component, and also takes into account discontinuities in the magnitudes of the loadings of the original variables. Based on these results, each component is described according to the dominant group of variables, as follows.

4.1. Component 1. Geochemical sediment matrix and background levels

This component, accounting for 45.31% of the total variance, has positive loadings on the concentrations of the heavy metals Ni, V, Co, Fe, Zn, and Cu, the specific surface (σ), and the total organic carbon concentration. Based on this association, this component describes the geochemical matrix composition of the studied sediments, represented by the organic carbon (OC), specific surface (σ), and the metal Fe. Also, the other association could be related to background levels of these heavy metals in the studied area [11] and with low levels of these chemicals when compared to other areas in the world [19,20].

4.2. Component 2. Urban contamination

High loadings are observed for the chemical concentrations in sediments of the heavy metals Ag and Pb, the surfactant LAS, and the total of all carbon, nitrogen, and organic carbon (OC) for this component, accounting for 22.29% of the total variance. These correlations suggest a contamination source associated with untreated urban discharge from the town of San Fernando. This affirmation is based on the allochthonous origin of the organic matter measured [21], and the high levels of the chemicals Ag and Pb associated with an anthropogenic origin from urban effluents [20], as well as the surfactant LAS, which is the anionic surfactant most used in domestic detergents, its daily consumption rate calculated for Spain is 5.5 g per inhabitant.

4.3. Component 3. Contamination associated with nautical activity sources

High positive loadings are observed for the chemical concentrations in sediments of Sn and As, and for the specific surface, but the loading is negative for Cd in this component, accounting for 12.90% of the total variance. This positive relationship between the heavy metals and the specific surface could reflect an adsorption process on the surface controlling the Sn and As bound in the studied sediments. On the other hand, the incorporation of Cd into sediments could be controlled by other processes not measured in this study, but not related to adsorption (e.g., sulfide associations [22]). Since the traditional formulas based on copper oxide as the active component in anti-fouling paints were changed to use Sn and As compounds [19,23], the association described above could relate to paints used for boats mostly used for nautical recreation.

Table 4
Summarized concentration results (mg kg^{-1} dry weight; except for Fe, % dry weight) of heavy metals in certified sediment standards

Metal	This study	Certified value (MESS-1)	This study	Certified value (CRM-277)
Fe	27.45 ± 1.59	–	42.34 ± 1.56	45.50[a]
Mn	284 ± 41	513 ± 25	1400 ± 0	1600[a]
Zn	179 ± 29	191 ± 17	485 ± 1	547 ± 12
Cu	40.6 ± 6.1	25.1 ± 3.8	120.5 ± 4.5	101.7 ± 1.6
Pb	39.8 ± 1.7	34.0 ± 6.1	153.5 ± 8.5	146.0 ± 3.0
Cd	1.41 ± 0.25	0.59 ± 0.10	12.84 ± 0.5	11.9 ± 0.9
Cr	52 ± 4	71 ± 11	170 ± 6	192 ± 7
Ag	0.42 ± 0.06	–	3.19 ± 0.02	3.30[a]
Hg	–	–	1.33 ± 0.24	1.77 ± 0.06
V	161.0 ± 76.9	72.4 ± 17.0	–	–
Ni	29.1 ± 0.9	29.5 ± 2.7	47.8 ± 2.7	43.4 ± 1.6
Co	10.1 ± 0.7	10.8 ± 1.9	12.8 ± 0.3	17.0[a]
As	–	10.6 ± 1.2	35.1 ± 2.2	47.3 ± 1.6
Sn	9.18 ± 3.70	3.98 ± 0.44	–	–

Mean values and standard deviations (MESS-1, $n = 3$; CRM-277, $n = 2$; this study, $n = 3$) for the quality control of measurements.
[a] Values not certified (orientatives).
– Not available from CRMs.

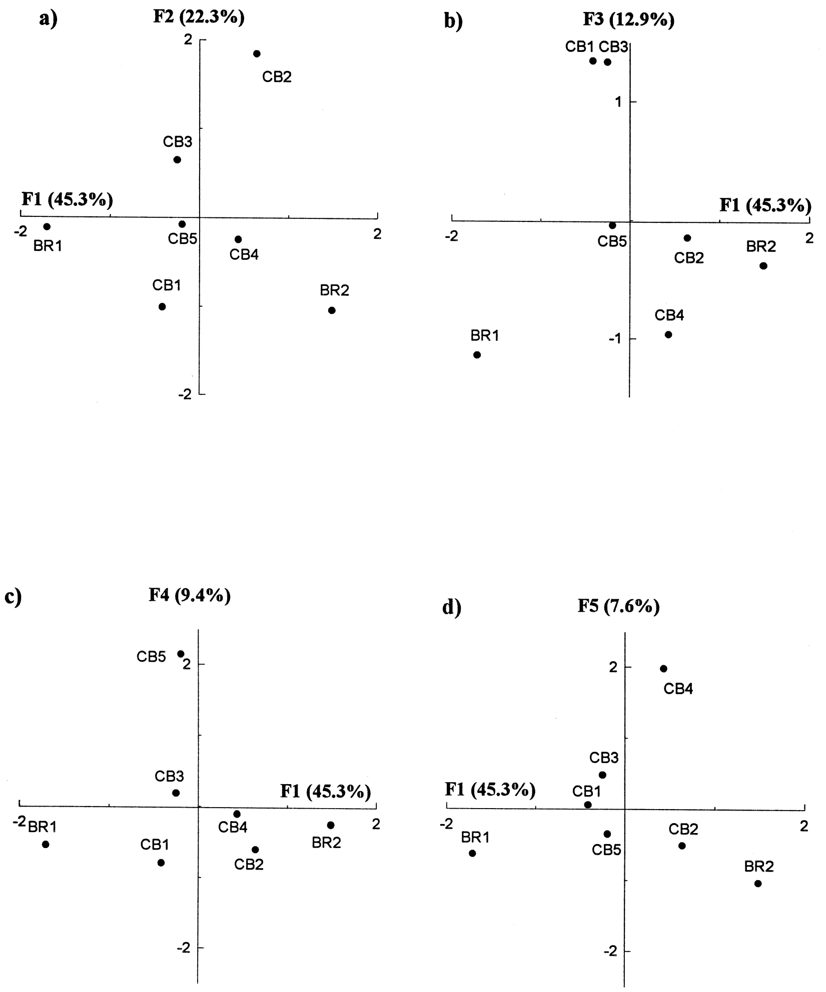

Fig. 2. Results of the multivariate analysis (PCA; estimated factor scores) used for the station distribution in the space defined by factor couples: F1 versus the other factors, F2, F3, F4, and F5. The explained variance for each factor is reflected in each axis.

4.4. Component 4. Cr and Hg contamination related to industrial sources

This component, accounting for 9.36% of the total variance, has positive loadings on the sediment concentrations of the two heavy metals Cr and Hg. Cr is widely used in metallic surface treatments and other industrial activities (aircraft and car components) close to some of the studied areas. The other component, Hg, is widely used in several industrial processes [19,20]. Although Hg is being replaced in most of the industrial processes because of its toxicity, it is still being used in some of them.

4.5. Component 5. Geochemical matrix of sediments associated with manganese hydroxides

The lowest eigenvalue component (7.26% of the total variance) gives a high loading only on Mn concentrations. Because Mn is included in the geochemical matrix in marine sediments it could associate this component with changes in the geochemical matrix. Furthermore, the vertical Mn distributions show that the superficial sediments have the lowest values [24], related to diagenesis processes. The maximum value is measured at depths of 5–10 m depending on the sedimentation rates in the area [25]. The unusually high

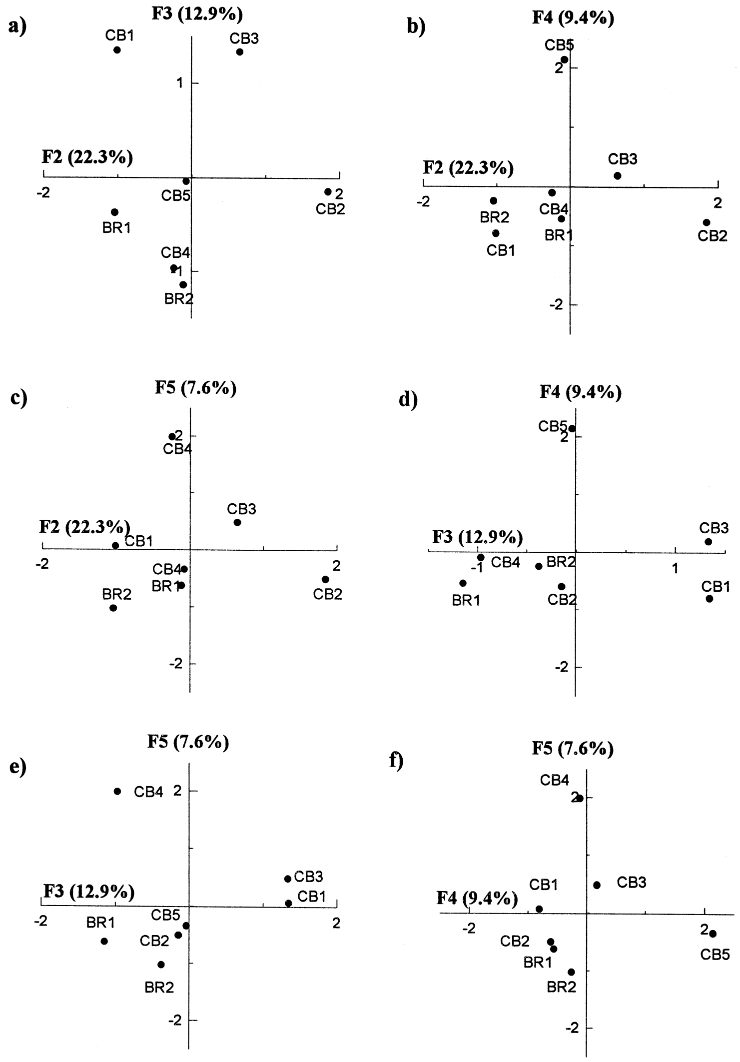

Fig. 3. Results of the multivariate analysis (PCA; estimated factor scores) used for the station distribution in the space defined by factor couples. a–c: F2 versus the factors F3, F4, and F5, respectively. d, e: F3 versus F4 and F5, respectively. f: F4 versus factor F5. The variance explained for each factor is reflected in each axis.

Mn levels in the superficial sediments could therefore be related to dredging processes which take place periodically at the Bay entrance areas.

Only two variables account for two different factors: the specific surface (σ) for factors 1 and 3, and the organic carbon (OC) for factors 1 and 2. These facts can easily be understood in both cases because the specific surface is geochemically characterized for the sedimentary matrix and is also the controlling parameter for adsorption processes involving bound chemicals in sediments. The OC association in factor 1 occurs naturally as a sedimentary matrix component, whereas the associations measured in factor 2 clearly represent this variable as a characteristic of organic enrichment in sediments originating from untreated urban discharge.

Fig. 2 represents the estimated factor scores and their Mahalanobis distances (χ^2) for each case (station) to the centroid of all cases for the original data. We use the prevalence (factor scores) of principal components for each of the cases studied to make the contamination source assumptions for each studied station. Furthermore, these prevalences are represented against each component (Figs. 3 and 4) to better understand the contamination sources proposed. On the basis of the above representations we could identify and describe the contamination phenomena occurring at each station.

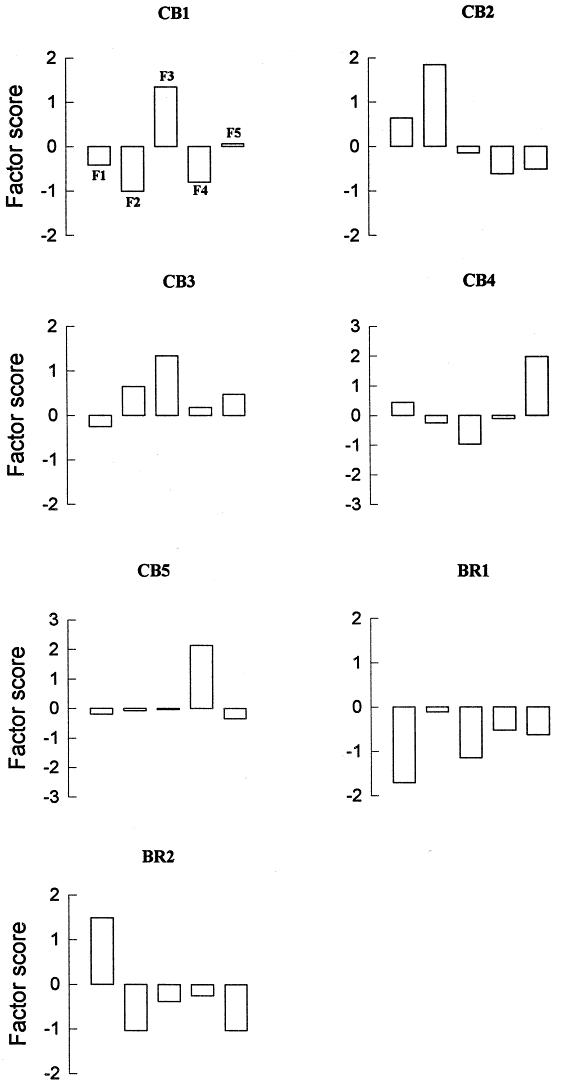

Fig. 4. Estimated factor scores from each of seven cases (five stations at the Bay of Cádiz: CB1, CB2, CB3, CB4 and CB5, and two stations at the salt pond of the Barbate River: BR1 and BR2) to the centroid of all cases for the original data. The factor scores quantify the prevalence of every component for each station and are used to establish the chemical level sources in sediments.

Station CB1 presents a high factor 3 prevalence (−1.344, see Fig. 2). Also, the station presents a positive prevalence of factor 5, but close to zero (−0.059, Fig. 2), this station being situated in the x,y-positive quadrant in Fig. 4e. This fact, and the knowledge that the station is situated near a recreational nautical pier, allows us to identify this station as suffering a nautical recreational effect, represented by relatively high levels of the heavy metals Sn and As. In adition, although this should be taken cautiosly, it could suffer from dredging (positive prevalence of factor 5).

Station CB2 has high positive prevalences of factors 1 (1.844) and 2 (0.644), shown in Fig. 2, and is clearly strongly affected by both factors (Fig. 3a). The higher prevalence of factor 2 shows a contamination phenomenon associated with untreated urban discharge, related to the urban effluents from the nearby town of San Fernando. The high OC concentrations in their sediments and the fact that OC is highly correlated in factor 1 could explain the positive influence of this factor.

Station CB3 has positive prevalences from all except factor 1 (factor 2: 0.645; factor 3: 1.334; factor 4: 0.182; factor 5: 0.478) (Fig. 2). The highest prevalence was associated with factor 3. From the six graphics represented in Fig. 4 we could establish the complex contamination description measured in this station. Since CB3 is presented as the only one of the six figures to be associated with a first-positive quadrant, and because the maximum relationship was measured between factors 2 and 3, we can classify the origin of contamination in this station as having a number of sources, the most important ones to the sediment being those sources associated with nautical recreational activities. Less important are those associated with close (less than 2 km) urban effluents, and least important are those from industrial and dredging processes.

Station CB4 has positive prevalences from factors 5 (1.981) and 1 (0.435), shown in Figs. 2 and 3. This could be explained by dredging processes in this area five years ago [26]. Nevertheless, the prevalence of factor 1 could give information about the recovery of the ecosystem to the original sedimentary matrix usual for the Bay of Cádiz and represented by the factor 1 associations.

Station CB5 had only an important contribution from factor 4 (2.139), which is associated with an industrial source of contamination. This, and the fact that the station is situated near a historic industrial discharge point [12,16], allows us to identify it as suffering from an industrial source, represented by high levels of the heavy metals Cr and Hg.

Station BR1, located in the Barbate salt marsh area, has a negative prevalence of all the factors. In general, the chemical levels measured in its sediments were lower than for the rest of the stations. Also, the sedimentary matrix was different from those at the Bay of Cádiz and the other station selected in the area, possibly because the station situation is close to a beach area. We consider this station as not contaminated

Table 5
Summary of benchmark sediment quality guidelines ($mg\,kg^{-1}$ dry weight) proposed to evaluate potential sediment toxicity for Pb, Ag, Cr, Zn, Cu, Cd, Ni, As, and Hg by different North American agencies and government bodies

Chemical	Sediment quality guideline		
	'Not polluted'	'Moderately polluted'	'Highly polluted'
Pb			
A)	<40	40–60	>60
B)	<23	31	>250
C)	<35	35–110	>110
D)	–[a]	–[a]	>450
Ag			
C)	1.0	1.0–2.2	>2.2
Cr			
A)	<25	25–75	>75
B)	<22	22–111	>111
C)	<80.0	80–145.0	>145.0
Hg			
A)	<1.0	–	>1.0
B)	<0.12	0.12–2.0	>2.0
C)	<0.15	0.15–1.3	>1.3
D)	–[a]	–[a]	>0.41
Zn			
A)	<90	90–200	>200
B)	<65	65–800	>800
C)	<120	120–270	>270
D)	–[a]	–[a]	>410
Cu			
A)	<25	25–50	>50
B)	<15	5–114	>114
C)	<70	70–390	>390
D)	–[a]	–[a]	>390
Cd			
A)	–[a]	–[a]	>6
B)	<0.6	0.6–10	>9
C)	<5	5–9	>10
D)	–[a]	–[a]	>5.1
Ni			
A)	<1.0	<1.0	<1.0
B)	<0.1	<0.1	<0.1
C)	<0.15	<0.15	<0.15
As			
A)	<3	3–8	>8
B)	<4	4–33	>33
C)	<33	33–85	>85
D)	–[a]	–[a]	>57

A: USEPA [7]; B: Ontario Ministry of the Environment [8]; C: US NOAA [9]; D: WADOE [10]. Guidelines for the heavy metals V, Co, and Sn, and the surfactant LAS were not available.

[a] Guideline not available.

by the chemicals measured in the present study and not influenced by dredging processes.

The last station, BR2, has only a positive prevalence from factor 1 (1.488). This can be related to the absence of contamination sources in its sediments, although they have the same sedimentary matrix as those measured in the Bay of Cádiz.

5. Potential adverse effects associated with contamination phenomena

The potential for adverse effects on biological organisms of chemical levels measured in the studied sediments was evaluated, based on comparisons with available benchmark sediment quality criteria and tox-

Table 6
Ratio of the average Pb, Ag, Cr, Hg, Zn, Cu, Cd, Ni, and As concentrations (mg kg^{-1} dry weight) in superficial sediments from two littoral ecosystems in the Gulf of Cádiz to benchmark sediment quality criteria and guidelines

Chemical	CB1	CB2	CB3	CB4	CB5	BR1	BR2
Pb							
A)	0.51	**1.41**	**1.07**	0.41	0.85	**1.11**	0.50
B)	0.12	0.34	0.26	0.10	0.20	0.27	0.12
C)	0.28	0.77	0.59	0.22	0.46	0.61	0.27
D)	0.07	0.19	0.14	0.05	0.11	0.15	0.07
Ag							
C)	0.22	0.61	0.55	0.35	0.48	0.34	0.28
Cr							
A)	0.66	**1.03**	0.71	0.55	**3.79**	0.57	**1.35**
B)	0.45	0.69	0.48	0.37	**2.56**	0.38	0.91
C)	0.34	0.53	0.37	0.28	**1.96**	0.29	0.70
Hg							
A)	0.11	0.25	0.46	0.25	0.57	0.06	0.15
B)	0.06	0.13	0.23	0.13	0.29	0.03	0.08
C)	0.08	0.19	0.35	0.19	0.44	0.05	0.12
D)	0.27	0.61	**1.12**	0.61	**1.39**	0.15	0.37
Zn							
A)	0.41	0.79	0.82	0.37	0.53	0.17	0.70
B)	0.10	0.20	0.20	0.09	0.13	0.04	0.18
C)	0.30	0.58	0.60	0.27	0.39	0.13	0.52
D)	0.20	0.38	0.40	0.18	0.26	0.08	0.34
Cu							
A)	**1.03**	**1.39**	**1.33**	0.70	0.99	0.75	**1.47**
B)	0.45	0.61	0.58	0.31	0.44	0.33	0.65
C)	0.13	0.18	0.17	0.09	0.13	0.10	0.19
D)	0.13	0.18	0.17	0.09	0.13	0.10	0.19
Cd							
A)	0.09	0.11	0.13	0.17	0.14	0.18	0.11
B)	0.06	0.07	0.08	0.11	0.09	0.12	0.08
C)	0.05	0.07	0.08	0.10	0.08	0.11	0.07
D)	0.10	0.13	0.15	0.19	0.16	0.22	0.13
Ni							
A)	0.50	0.71	0.56	0.69	0.65	0.16	0.86
B)	0.28	0.39	0.31	0.38	0.36	0.09	0.48
C)	0.50	0.71	0.56	0.69	0.65	0.16	0.86
As							
A)	**1.41**	0.97	**1.71**	**1.07**	**1.66**	0.65	**1.21**
B)	0.34	0.23	0.41	0.26	0.40	0.16	0.29
C)	0.13	0.09	0.16	0.10	0.16	0.06	0.11
D)	0.20	0.14	0.24	0.15	0.23	0.09	0.17

A: USEPA [7]; B: Ontario Ministry of the Environment [8]; C: US NOAA [9]; D: WADOE [10]. Ratios shown in bold are 1.0 or greater and are potentially associated with an adverse effect on benthic biota.

icity guideline values. In the absence of sediment criteria specific for the two littoral ecosystems studied, our results were compared with values derived from several proposed approaches (Table 5). Sediment management guidelines proposed by the US Environmental Protection Agency, using site-specific sediment bioassays [7], by the Ontario Ministry of the Environment, using the screening level concentration (SLC) approach [8], by the Washington State Marine Sediment Quality Standards derived for Puget Sound, using a combination of the apparent effects threshold (AET) and equilibrium partitioning (EqP) methodologies [10], and by the National Oceanic and Atmospheric Administration (NOAA), from a compilation of the results of acute and chronic bioassays in several aquatic species [9], were used for comparative purposes. Although many of those values are considered site-specific and are not intended for use as regulatory guidelines, they provide useful benchmarks for assessing the potential toxicity of contamination.

Table 7
Summarized characteristics determined for each station selected in this study

Station	Contamination phenomena
CB1	- Contamination source: nautical activities. - Chemical levels: high levels of the heavy metals Sn and As. Low levels of the other measured chemicals. - No potential adverse effect measured.
CB2	- Contamination source: untreated urban disposal. - Chemical levels: high levels of the surfactant LAS, and the heavy metals Ag and Pb. Intermediate to high levels of the other measured chemicals. - No potential adverse effect measured. No guidelines available for organic chemicals (LAS).
CB3	- Contamination source: mixture of activities. Nautical > urban > industrial > spills. - Chemical levels: high levels of the heavy metals Sn, As, Hg, and Cr. Intermediate levels of the other measured chemicals. - Potential adverse effect associated with Hg concentrations.
CB4	- Contamination source: not detected. - Chemical levels: low levels of most measured chemicals. - No potential adverse effect measured.
CB5	- Contamination source: historic and uncontrolled industrial disposal. - Chemical levels: high levels of the heavy metals Cr and Hg. Intermediate levels of the other measured chemicals. - Potential adverse effect associated with the Cr and Hg concentrations.
BR1	- Contamination source: not detected. Cádiz Bay, different geochemical sedimentary matrix. - Chemical levels: intermediate levels of the heavy metal Cd and low levels of the other measured chemicals. - No potential adverse effect measured.
BR2	- Contamination source: not detected. Similar geochemical sedimentary matrix to that in the Bay of Cádiz. - Chemical levels: low levels of most measured chemicals. - No potential adverse effect measured.

In order to quantify the relative hazards to aquatic biota posed by the presence of some heavy metals (those with benchmark sediment quality guidelines: Pb, Ag, Cr, Hg, Zn, Cu, Cd, Ni, and As) in superficial sediments, hazard indices were calculated (Table 6) by dividing the average concentrations found at each station by various sediment quality criteria and guideline values (Table 5). Since each benchmark sediment quality value was determined on the basis of effects observed during sediment toxicity testing, a ratio of 1.0 or higher was assumed to indicate a sediment metal concentration potentially associated with an adverse effect on benthic biota.

Based on comparisons with sediment quality guidelines and toxicity values, the metal concentrations in superficial sediments are of great concern in station CB5 (associated with the high levels of Cr and Hg related to industrial sources of contamination), followed by CB3 station (associated with the relatively high levels of Hg related to nautical recreational activities and industrial sources of contamination). Chromium concentrations in CB5 sediments exceeded the benchmark values set by all the agencies evaluated, and Hg was higher at CB3 and CB5 than the benchmark values set by WSDOE [10]. Note that some metals (Pb in CB2, CB3, and BR1; Cr in CB3, CB5, and BR2; Cu in CB1, CB2, CB3, and BR2; and As for all stations except BR1) were found in sediments at concentrations exceeding their respective benchmarks set by the US Environmental Protection Agency [7]. However, since the lowest effect level is defined as the threshold for metal toxicity in freshwater organisms, the sensitivity of aquatic biota in estuarine and littoral ecosystems such as those studied here in the Gulf of Cádiz could be similar, due to differences in sediment and water chemistry. For the rest of the heavy metals, the calculated ratios were below 1.0, and are not associated with adverse biological effects. In summary, the chromium concentrations measured in sediments from station CB5 (283.9 mg kg^{-1}) are of most concern, followed by the mercury concentrations measured in sediments from stations CB5 (0.57 mg kg^{-1}) and CB3 (0.46 mg kg^{-1}). The presence of these metals in surface sediments must be considered potentially significant in the overall environmental quality of the littoral ecosystems from the Bay of Cádiz. Consequently, sediment toxicity should be conducted on these sediments to certify this potential biological effect. Recent related studies have shown that some metal and surfactant concentrations in interstitial waters [27,28] and in sediments [29–31] have a significant effect on the bioavailability and toxicity of those chemicals in sediments.

6. Final remarks

The main conclusions from the data obtained from each station in this study are summarized in Table 7. The chemicals selected for measurement in the sediments studied, as well as the statistical tools (multivariate analysis by PCA), and the sediment quality guidelines have been successful in establishing the following conclusions.

It has been possible to establish three different sources of contamination – nautical recreational activities (Sn and As sediment concentrations), industrial discharges (Cr and Hg sediment concentrations), and urban effluents (OC, LAS, and Pb and Ag sediment concentrations). Also, different compositions of the sedimentary matrix were evident between station BR1 and the other stations, and effects of dredging processes were detected in some of them.

As a result of comparisons with benchmark sediment quality criteria and guidelines proposed by several environmental agencies and government bodies, some sediment concentrations (of Cr and Hg) were concluded to have potential for adverse effects for aquatic biota. Although site-specific sediment toxicity tests would be required to evaluate the adverse biological effects, the comparisons with sediment quality guideline values indicate that site-specific conditions in stations CB5, CB3, and CB2 warrant further study.

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References

[1] W. Salomons, Environ. Technol. Lett. 6 (1985) 315.

[2] S.N. Luoma, Hydrobiologia 176/177 (1989) 379.

[3] B.S. Krumgalz, Estuaries 16 (1993) 488.

[4] P.K. Hopke, Anal. Asp. Environ. Chem. 64 (1983) 219.

[5] J.W. Einax (Editor), Chemometrics in Environmental Analysis, VCH, Weinheim, 1997.

[6] O. Hutzinger (Editor), Chemometrics in Environmental Chemistry, Springer, Berlin, 1995.

[7] Army Corps of Engineers (US), Misc. Paper D-76-17, Vicksburg, MS, 1-EZ.

[8] D. Persaud, R. Jaagumagi and A. Hayton (Editors), Development of Provincial Sediment Quality Guidelines, Ontario Ministry of the Environment, Toronto, Ont., 1989, p. 19.

[9] E.R. Long and L.G. Morgan (Editors), The Potential for Biological Effects of Sediment-sorbed Contaminants Tested in the National Status and Trends Program, US National Oceanic and Atmospheric Administration (NOAA), Seattle, WA, 1991 p. 228.

[10] Washington State Department of Ecology (Editor), Sediment Management Standards, Sediment Management Unit, Olympia, WA, 1991, Ch. 173, p. 204.

[11] A. Gómez-Parra, R. Establier, D. Escolar, Mar. Pollut. Bull. 15 (1984) 307.

[12] D.H. Loring, R.T.T. Rantala, Earth-Sci. Rev. 32 (1992) 235.

[13] H.E. Gaudette, W.R. Flight, L. Torner, D.W. Folger, J. Sedim. Petrol. 44 (1974) 249.

[14] O.A. El Rayis, Rap. Commun. Int. Mer Medit. 29 (1985) 45.

[15] E. González-Mazo, J.M. Quiroga, D. Sales, A. Gómez-Parra, Toxicol. Environ. Chem. 59 (1997) 77.

[16] R. Establier, A. Gómez-Parra, J. Blasco, Bull. Environ. Contam. Toxicol. 35 (1985) 348.

[17] J. Frane, R. Jennrich and P. Sampson, in W.J. Dixon (Editor), BMDP Statistical Software, University of California Press, Berkeley, CA, 1985, p. 480.

[18] A.L. Comreys, A First Course in Factor Analysis, Academic Press, New York, 1973, p. 342.

[19] G.W. Bryan, W.J. Langston, Environ. Pollut. 76 (1992) 89.

[20] M. Sadiq (Editor), Toxic Metal Chemistry in Marine Environments, Marcel Dekker, New York, 1992, p. 390.

[21] A. Gómez-Parra, M. Frutos, Inv. Pesq. 51 (1987) 107.

[22] G.T. Ankley, G.L. Phipps, E.D. Leonard, D.A. Benoit, V.R. Mattson, P.A. Koisan, A.M. Cotter, J.R. Dierkes, J.D. Mahony, Environ. Toxicol. Chem. 10 (1991) 1299.

[23] J.M. Azcue and J.O. Nriagu, in J.O. Nriagu (Editor), Arsenic in the Environment, Part I, Wiley, New York, 1994, pp. 1–15.

[24] R.C. Aller, Geophysics 22 (1984) 351.

[25] A. Mangini, A. Eisenhauer, P. Walter, Math.-Naturwissensch. Klasse 4 (1990) 267.

[26] J.M. Forja, J. Blasco, A. Gómez-Parra, Estuar. Coast. Shelf Sci. 28 (1994) 417.

[27] T.A. DelValls, L.M. Lubián, M. González delValle, J.M. Forja, Hydrobiologia 341 (1996) 159.

[28] T.A. DelValls, L.M. Lubián, J.M. Forja, A. Gómez-Parra, Environ. Toxicol. Chem. 16 (1997) 2323.

[29] T.A. DelValls, J.M. Forja and A. Gómez-Parra, Environ. Toxicol. Chem., in press.

[30] T.A. DelValls, J.M. Forja and A. Gómez-Parra, Ciencias Marinas, in press.

[31] T.A. DelValls and P.M. Chapman, Ciencias Marinas, in press

Drs. Ángel DelValls, Eduardo González-Mazo, and Jesús M. Forja, as well as Professor Abelardo Gómez-Parra are at the Departamento de Química-Física, Facultad de Ciencias del Mar, Universidad de Cádiz, and Dr. Julián Blasco is at the Departamento de Oceanografía, Instituto de Ciencias Marinas de Andalucía, CSIC, all at 11510 Puerto Real, Cádiz, Spain.