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Assessment of urban and industrial contamination levels in the bay of Cádiz, SW Spain

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Abstract

Measuring the amount of pollution is of particular importance in assessing the quality and general condition of an ecosystem. In this paper, some of the results obtained as a consequence of the specific agreement between the Environmental Agency (*Consejería de Medio Ambiente, Junta de Andalucía*) and the University of Cadiz to assess the environmental condition of the marine bottom and waters are showed. Physical and chemical analyses in water and sediments were undertaken at various sampling sites close to urban and industrial locations. Later on, these results were studied under statistical analysis to reveal any possible relationships between the parameters employed, and to identify any analogous behaviour between the sampling sites. Physical–chemical data revealed that sediments and waters analysed were moderately contaminated and, in addition, no great differences were found between in rising and ebbing tide conditions. Finally, considering only the pollution level, from the cluster analysis of sediments two major groups appear, one of which corresponded to those sites located in the outer bay, and the other to those situated in the inner bay. However, number 6 and 14 sampling sites cannot be associated to those groups due to be related to points with important local discharges.

Keywords: Seawater quality; Sediment quality; Bay of Cadiz; Urban pollution; Industrial pollution; Uncontrolled discharges

1. Introduction

Over the past 50 years industry has released more waste into the natural environment than over the whole of the preceding centuries. Agricultural, chemical, textile or metallurgic industries consume large amounts of water which, subsequent to processing, is released into the environment together with dissolved toxic substances: acid, base or toxic chemical compounds and heavy metals, which are prejudicial to the coastal environment. As a general rule, the release of this type of waste does not affect offshore areas except as the result of an accident involving a vessel transporting substances of this nature. In general, the effects are stronger along the coastline than offshore (Campbell, 1988).

In Spain, 66% of industries are located in coastal areas. Consequently, 80% of significant industrial waste (more than 2000 point sources) goes directly into the sea. Article 4 of the Regulation governing the Quality of Coastline Waters of the Autonomous Community of Andalusia (Decree 14/1996) sets authorized limits for waste discharges in Andalusian coastal waters. Thus, the discharge of waste over the levels established is forbidden. These levels may be exceeded provided that appropriate monitoring demonstrates that the aquatic environment in question will continue to meet, and maintain, the required quality objectives. Therefore, the Bay of Cadiz is an area with great significance to industry, the population and the environment. This fact proves the importance of assessing environmental conditions.

2. Study area

This research has been carried out in the Bay of Cadiz. The Bay of Cadiz, and the eastern area of tidal-marshes which forms part thereof, covers an area of

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approximately 30,000 ha and is located at the south-western end of Europe (W–NW of the province of Cadiz), between 36°23′ and 36°37′ north latitude and 6°08′ and 6°15′ west latitude. Of this surface area, 12,000 ha correspond to the strip of water and 18,000 to the emerged areas. From a purely hydrological point of view, the area may be divided into four regions, namely: (1) The outer bay, with markedly oceanic characteristics: this area is the most exposed to the action of waves, winds and tides. (2) The inner bay, located to the S and SE of the aforesaid outer bay: the marine dynamics of this area are strongly influenced by the tides and it is the area least exposed to the action of the waves. Its shallow waters also characterise it. (3) The amphibious bay, corresponding to the area of tidalmarshes: this area has foreshore characteristics and offers a rich and varied ecosystem, although currently this is somewhat deteriorated due to human intervention. (4) The terrestrial bay, corresponding to those parts which are permanently emerged, and are of vital importance as the biotype for a multitude of organisms: this area constitutes a significant source of sediment to maintain the sedimentary balance of the coastal environment.

400,000 people live around the bay and a part of the wastewater is adequately treated. The main industries located in this zone are related with ship, offshore, car and aerospace manufacturing.

3. Material and methods

Six sampling sites were chosen to study the water quality, whereas a total of 19 were selected for the study of the sediments (Fig. 1). The sampling sites were located both near to, and away from, industries which are representative of the area. Two samples were collected using 2-l capacity Nansen bottles on consecutive days, with rising and ebbing tides and at two different depths (the top 15 cm of surface water and 5–10 cm from the bottom). In the case of the sediments, a top-layer sedi-

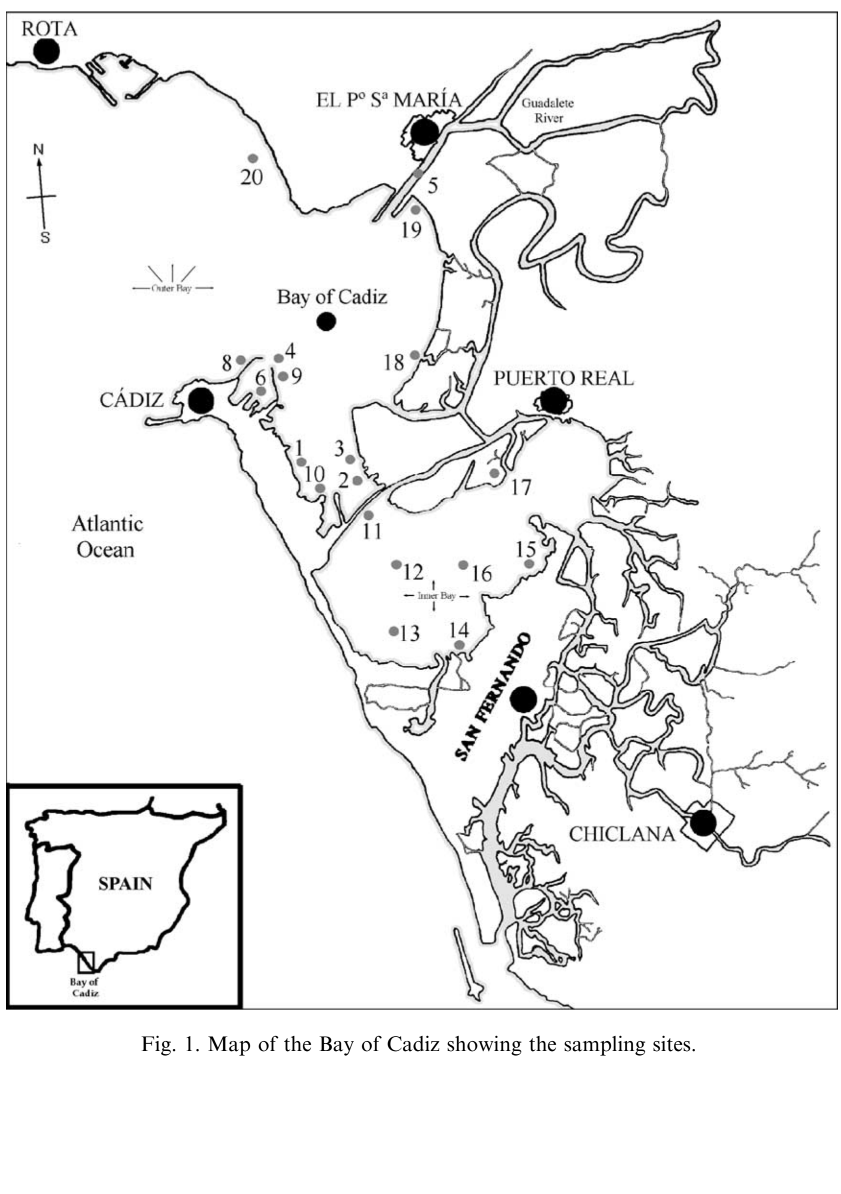

Fig. 1. Map of the Bay of Cadiz showing the sampling sites.

ment sample was taken with a Van Veen grab. The following parameters were analysed: pH, salinity, conductivity, suspended solids (SS), BOD_5, dissolved organic carbon (DOC), ammonium, nitrates, nitrites, iron, selenium, lead, cadmium, zinc, mercury and total chromium and, as indicators of microbiological contamination, faecal coliforms. The methods of analysis employed were the standard methods expressly indicated for seawaters (Strickland and Parsons, 1972; Grashoff et al., 1983). Characterisation of the sediments was made by granulometric (mechanical sieve and laser measurement of the <63 μm particle size fraction, including specific surface determination) and mineralogical (XRD, powder method) analyses, organic carbon determination by K_2CrO_4 oxidation in sulphuric acid medium (Gaudette et al., 1974), together with chemical analysis of selenium, chromium, iron, lead, zinc and mercury. Before the acid digestion of the sediment samples, particles less than 200 μm were separated with a nylon fibre sieve. Following digestion in a strongly acidic medium (Sturgeon et al., 1982; Conde, 1993), heavy metal concentration levels were determined by atomic absorption spectrometry: in the case of selenium, chromium, iron, lead and zinc, the furnace technique (FAAS) was employed, for cadmium, the graphite furnace technique (GFAAS) was used, and the cold vapour technique (CVASS) for mercury.

The chemical data obtained in sediments were normalized using the concentration/specific surface ratio, based on the fact that it is a parameter controlling the physicochemical adsorption process responsible for most chemical incorporation into sediments (Luoma, 1990).

The statistical techniques of cluster and factorial analysis were applied to the results obtained in order to determine the internal structure of the system, using a software package: Statistica 6.0© for Windows.

4. Results and discussion

To assist in the task of overall comprehension, the results are presented in two stages: waters and sediments.

4.1. Seawater

Physical–chemical and bacteriological parameters are shown in Table 1. In general, water contamination level was low, although there were differences between the various sampling sites. Salinity and pH in the Guadalete river estuary were slightly lower than elsewhere. DOC and BOD_5 did not exceed the established hazard limits and showed significant differences between rising and ebbing tidal conditions; these are the result of a residual tidal current (Álvarez et al., 1999) which removes the contaminated water from the inner bay, which is then subsequently renewed, to some extent, over the course of the next rising tide. A previous paper (González-Mazo et al., 1998) included data on different concentration levels in waters of the inner and outer bay.

Values recorded for inorganic nitrogen (ammonium, nitrites and nitrates) indicated that no threat is posed to the marine ecosystem, although at two sites the levels slightly exceeded the limits imposed for "special" waters according to the Regional Laws (Orden Consejería Medio Ambiente, 14 febrero 1997): Guadalete river (site 5) and the dry dock (site 6). The faecal coliforms values are below the special water levels for bathing waters, with the exception of the surface water sample collected at site 6. At site 5, although still below the required level, the faecal coliforms values are higher than the others. This fact, in conjuction with the results of the physical–chemical analyses, confirm the existence of domestic and industrial uncontrolled discharges.

4.1.1. Heavy metal content in the waters

Table 2 shows average metal content in the seawater at the different sites. No significant differences between tidal conditions were found. The table reveals that the values of mercury, chromium, cadmium and selenium are below the threshold limit established by the quality objectives for coastal waters, in the section dealing with "special" waters.

Zinc content was high at all sites, in some cases, the values were markedly high, particularly at sites 5 (Guadalete river), 4 (Delta Plant) and 2 (Shipyard), which would imply a direct link with discharges of an anthropic nature. Lead values were high in samples collected on an ebbing tide, exceeding the limit set by quality objectives at four of the sampling sites, and most notably at site 5 (Guadalete river) and site 3 ("Dragados offshore" Company).

4.2. Statistical analysis of the results

To establish relationships between the different parameters under study, a statistical analysis was undertaken of the results obtained from the seawater collected in different tidal conditions. A cluster analysis was carried out to identify any analogous behaviour patterns between the different sites. Few differences may be detected between the behaviour of the sampling sites during rising or ebbing tides (Figs. 2 and 3). Sites number 5 (Guadalete river estuary) and 6 (Dry dock), however, are clearly differentiated from the rest. Site 5 showed the lowest saline and conductivity levels (located in a river estuary). Microbiological and other contamination levels are high due to the fact that this site is the main receiving point for waste generated in the upstream regions of the province. Site 6 is similar in nature to site 5, displaying high levels of microbiological and

Table 1
Parameters analysed in the waters of the Bay of Cadiz

	pH	Conductivity (mS/cm)	SS (mg/l)	DOC (mg C/l)	BOD_5 (mg O_2/l)	NH_4^+ (mg NH_4^+/l)	NO_2^- (mg NO_2^-/l)	NO_3^- (mg NO_3^-/l)	Faecal coliforms (UFC/100 ml)
Ebbing tide surface collection, day 1									
Threshold value	7–9	–	1, 15	2	–	0, 6	0, 6	0, 7	–
Site 1	8.27	50.2	0.39	2.590	6.2	0.03	0.07	0.3	0
Site 2	8.34	50.1	0.28	2.809	2.7	0.01	0.05	0.3	0
Site 3	8.33	50.0	0.24	2.917	4.1	0.01	0.05	0.2	1
Site 4	8.27	50.0	0.24	2.772	4.0	0.01	0.06	0.2	0
Site 5	8.11	48.5	0.26	3.604	4.5	0.04	0.17	0.3	600
Site 6	8.14	49.1	0.32	2.861	4.0	0.06	0.30	0.2	2600
Ebbing tide deep collection, day 1									
Site 1	8.35	50.2	0.29	2.38	4.2	0.03	0.05	0.3	2
Site 2	8.36	50.1	0.26	2.571	3.4	0.01	0.06	0.2	0
Site 3	8.31	50.0	0.26	3.56	3.8	0.02	0.06	0.4	10
Site 4	8.32	50.0	0.36	1.766	4.2	0.01	0.05	0.3	0
Site 5	8.19	48.6	0.36	2.605	3.5	0.07	0.16	1.1	751
Site 6	8.19	50.0	0.27	2.763	4.0	0.02	0.07	0.3	36
Rising tide surface collection, day 2									
Site 1	8.23	50.2	0.25	2.718	2.4	0.01	0.07	0.2	6
Site 2	8.25	50.3	0.39	3.459	3.0	0.01	0.05	0.3	32
Site 3	8.21	50.1	0.35	1.220	2.8	0.02	0.05	0.1	55
Site 4	8.21	50.1	0.27	1.451	2.6	0.01	0.06	0.2	0
Site 5	8.08	48.0	0.23	1.799	2.2	0.16	0.17	0.2	494
Site 6	8.2	49.9	0.26	0.884	2.4	0.01	0.30	0.2	445
Rising tide deep collection, day 2									
Site 1	8.21	50.1	0.34	3.164	2.2	0.01	0.05	0.4	26
Site 2	8.29	50.3	0.33	2.338	2.3	0.02	0.06	0.2	35
Site 3	8.23	50.1	0.26	1.785	2.3	0.02	0.06	0.5	54
Site 4	8.22	50.1	0.32	1.658	2.4	0.01	0.05	0.3	3
Site 5	8.13	48.8	0.24	0.749	2.2	0.02	0.16	0.3	445
Site 6	8.19	50.0	0.24	0.928	1.8	0.01	0.07	0.3	712

Table 2
Average metal content in the seawater at the different sites

Site	Hg (μg/l)	Se (μg/l)	Cd (μg/l)	Pb (μg/l)	Zn (μg/l)	Cr (μg/l)	Fe (μg/l)
1	<1	1.3	1.0	6.8	30	<3	18.0
2	<1	0.8	2.0	9.6	69	<3	40.7
3	<1	1.7	1.3	109.0	37	<3	15.0
4	<1	1.4	1.0	13.3	101	<3	14.4
5	<1	1.2	1.3	118.0	242	<3	45.2
6	<1	1.0	1.0	3.5	23	<3	36.2
Threshold values[a]	0, 3	1, 0	2, 5	10	60	10	–

[a] Threshold values to "Special Waters" (Consejería Medio Ambiente Junta de Andalucía, 1997).

organic pollution, together with lower conductivity values, which would suggest the proximity of a faecal water discharges. This would appear to be corroborated by the fact that the conductivity levels are lower at this site than elsewhere. The other four sites form one overall group; this may be further divided into two sub-groups, which are differentiated on the basis of the results recorded in rising or ebbing tidal conditions.

1. Rising tide:
   - Group 1: sites 2 and 3
   - Group 2: sites 1 and 4
2. Ebbing tide:
   - Group 1: site 3
   - Group 2: sites 1, 2 and 4

The results of the factorial analysis applied to the physical–chemical parameters of the seawater are illustrated in Fig. 4. Factor 1 accounts for 56.6% of the total variance of the data, affecting the following variables in decreasing order of importance: nitrate, conductivity, total coliforms, nitrite, ammonium, zinc and lead. The remaining variables may be partially accounted for by this factor. Factor 2 accounts for 24% of the total variance of the data, affecting (in decreasing order of importance): cadmium, BOD_5, iron and selenium. The remaining variables do not affect this factor in any significant way. Table 3 shows the results obtained in the study of the communalities, which indicates as a fraction of one the amount of information of each of the variables which has been employed in the factorial analysis.

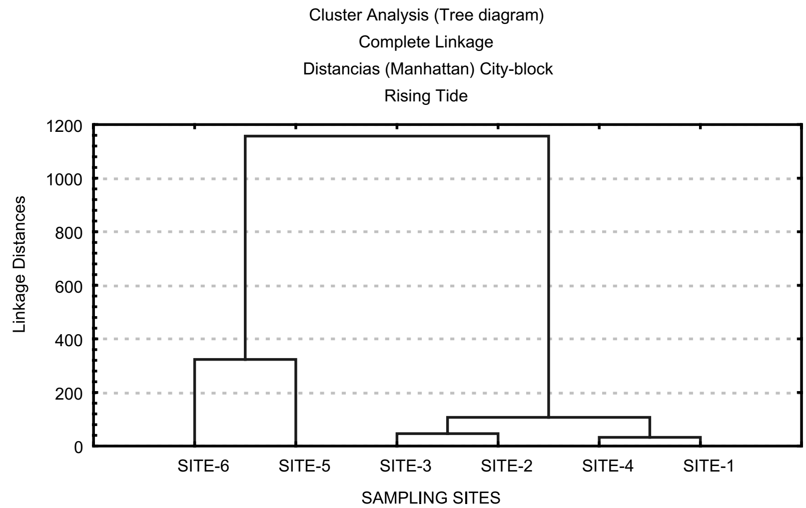

Fig. 2. Cluster analysis of the sampling sites at rising tide.

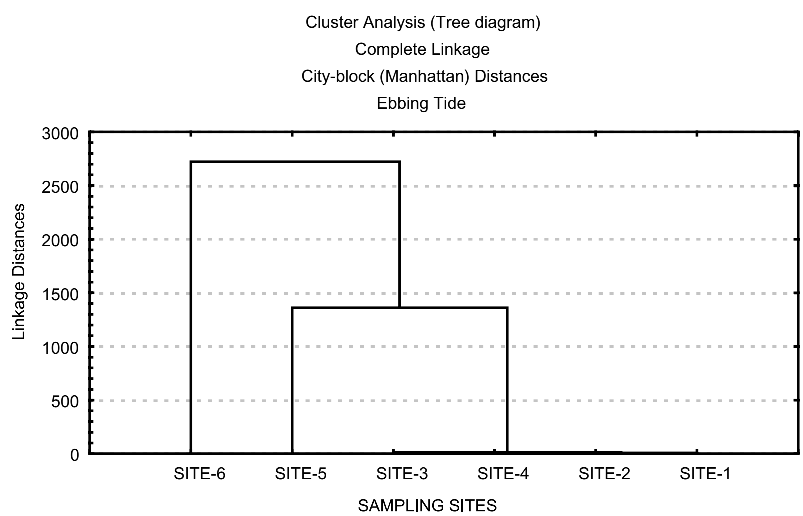

Fig. 3. Cluster analysis of the sampling sites at ebbing tide.

With respect to these results, it is worth pointing out that, in general, large fractions have been used of the majority of the variables used in the factorial analysis. On the other hand, it is also worth highlighting that cadmium, selenium and iron exert very little influence on factor 1.

Fig. 4 illustrates how the different variables are grouped. On the one hand there are the variables of conductivity and pH, and, on the other, nitrite, nitrate, ammonium, faecal coliforms, SS, zinc and lead. The association of conductivity and pH is to be expected, since the pH of water in an estuarine environment is influenced, amongst other things, by the injection of river waters into the area, and accordingly, pH is linked to the ionic concentration of the water.

With regards to the second grouping of parameters, it is worth remembering that these variables are typical indicators of urban contamination (nitrite, nitrate, ammonium, faecal coliforms), which would point to the existence of waste discharges in the area. The presence of zinc and lead in this group would suggest possible sources of industrial contamination in the vicinity. Factor 2 is composed of the variables cadmium, iron and selenium. This factor corroborates the hypothesis regarding possible sources of industrial contamination in the area, since it reveals a difference in the behaviour of cadmium, on the one hand, and zinc on the other. This deviation would suggest the existence of anthropic additions of the latter element, which break the natural balance between the two.

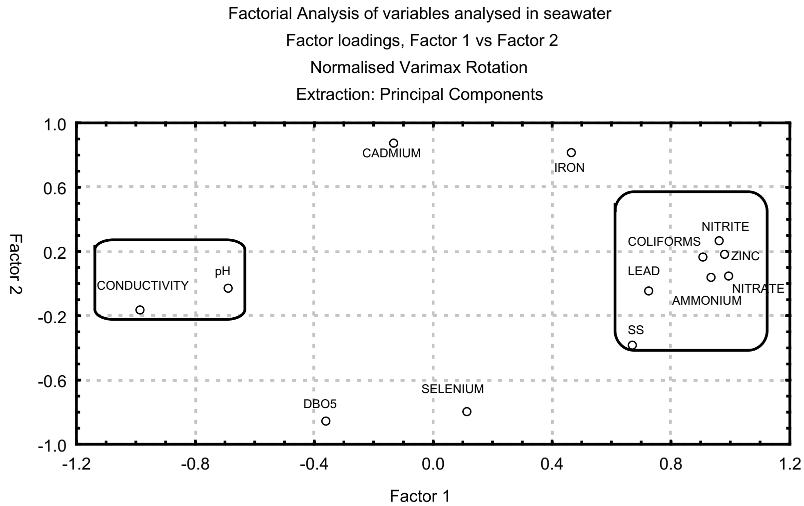

Fig. 4. Factorial analysis of the variables analysed in the seawater.

Table 3
Study of the communalities corresponding to the factorial analysis of the variables

	Factor 1	Factor 2
pH	0.472	0.473
Conductivity	0.971	0.997
Suspended solids	0.451	0.597
BOD_5	0.129	0.859
Ammonium	0.872	0.874
Nitrite	0.944	0.994
Nitrate	0.984	0.989
Total coliforms	0.958	0.992
Selenium	0.012	0.784
Cadmium	0.017	0.652
Lead	0.525	0.527
Zinc	0.823	0.851
Iron	0.215	0.885

4.3. Sediment quality

4.3.1. Granulometric analysis

With the textural sedimentary information it is possible to establish the risk levels of increased water turbidity in the event of marine bottom removal. Moreover, numerous authors have acknowledged grain size to be one of the most significant factors in the capacity to retain trace elements: finer fractions having greater capacity to adsorb contaminants on their surfaces (Horowitz and Elrick, 1987; Jenne et al., 1980). The results of the granulometric analysis indicate that, despite a certain granulometric variability in the bay bottoms at the sites chosen for sampling, two overall groupings predominate, with essentially clayed silt sediments on the one hand (sites, 1, 2, 4, 5, 10, 11, 12, 13, 14, 15, 16, 17) and typically sandy sediments with a fairly significant gravel and sand content on the other (sites 3, 6, 8, 9, 18, 19 and 20). However, the granulometric analysis of the 3 and 6 samples present a bimodal distribution with two maximums on the gravel and <63 μm size fractions, indicating probably that these samples are mixtures resulting from anthropogenic processes. Both two samples are located in the "Bajo de la Cabezuela" and the dry dock in the Cadiz harbour respectively.

Table 4
Results of the granulometric analysis of representative sites (mean values)

Sites	Fraction < 63 μm (%)	Fraction < 63 μm (%)	Specific area σ (m^2/cm^3)
1, 2	96.95	3.05	2.91
3, 6	7.54	92.46	3.6
8, 18, 19, 20	0.61	99.39	0.59
12, 13, 14, 15, 16, 17	96.33	3.67	2.52
4, 5, 9, 10, 11	90.84	9.16	1.83

Table 4 presents the textural results of the representative sites of the different textures found and its specific surface.

4.3.2. Organic matter

Unlike metallic compounds, non-conservative elements (C, N, P) pose no toxic threat to biota; nevertheless, an excess of these elements in an estuarine environment (system overload) may be gravely detrimental to the ecosystem, causing eutrophication or anoxia (Establier et al., 1984). With regards to the levels of organic matter (Table 5), it is worth mentioning that the values recorded ranged between 1.2 and 5.2 (%) respectively, and that these are normal values in marine bottoms of this type (Del Valls, 1994; Ponce, 1996).

Table 5
Organic matter concentrations (%)

Sites	O.M. (%)	Sites	O.M. (%)
1	1.24	11	1.57
2	2.52	12	3.05
3	2.88	13	4.53
4	5.20	14	3.55
5	4.16	15	3.82
6	4.40	16	3.72
7	1.70	17	2.42
8	0.37	18	0.11
9	0.35	19	0.07
10	2.11	20	0.21

4.3.3. Mineralogical analysis

The most abundant mineral is quartz (between 20% and 60%) and, consequently, these sediments may be considered to be siliciclastic. The quartz content recorded in this research reflects the overall level recorded in the sandy sediments of the Bay of Cadiz by Gutiérrez Más (1992). After quartz, the second most prevalent terrigenous component in these sandy sediments are the feldspars, although, due to their instability, their concentration levels are markedly lower (between 5% and 8%). Clay minerals (phillosilicates) are the most prevalent terrigenous components of the fine sediments (silt and clay). The concentration levels recorded in the sediments analysed ranged between 10% and 20%. Calcite is the most abundant carbonate mineral in these sediments; its origin is bioclastic, corresponding to the carapaces and shell rests. Calcite concentration levels ranged between 15% and 20%. The remaining minerals (plagioclases, dolomite, aragonite, etc.) were found in minor quantities in the sediments. Table 6 shows the mineralogical composition results obtained from the analytical procedure performed at some of the chosen sampling sites.

4.3.4. Heavy metal concentrations in the sediments

There are no provisions in respect of required quality levels for sediments in Andalusian, Spanish or European regulations. In Spain there only exists "Recommendations to the management of dredged materials at the Spanish Harbours" (CEDEX, 1994). However, the regulations of the Ministry of the Environment of Ontario, Canada (Donze et al., 1990)) and the United States Environment Protection Agency (Hamdy and Post, 1985) are more restrictive and suitable than the recommendations to the dredged materials of the CEDEX (Spain). For this reason, these two regulations have been chosen to evaluate the contamination of sediments of the Bay of Cadiz.

The results of the metal analyses performed in the course of this research are shown in Table 7. In the case of mercury, the vast majority of the sediments may be classed as "not contaminated" according to the reference regulations. At only one of the 13 sites analysed were the levels of concentration found to exceed the set limits: site number 17. According to USEPA recommendations, the sediment at this site would be classified as "moderately contaminated". In reference to the cadmium levels, the zone may be classed as "not contaminated". The lead levels obtained show that, in accordance with USEPA recommendations, only site number 6 may be considered "contaminated"; this site is located in the dry dock. Sites 5, 8, 9, 18, 19 and 20 recorded the lowest levels of zinc, and may be classed as "not contaminated". The remaining sites, however, registered zinc levels in excess of the permitted limit for non-contaminated sediments. Consequently, sites 1, 2, 4, 10, 11, 12, 13, 14, 15, 16 and 17 may be classified as "moderately contaminated" by this metal. These sites correspond to locations within the inner bay (11, 12, 13, 14, 15, 16 and 17) with high <63 μm content and others close to areas of strong anthropic influence (1, 2, 4 and 10). Finally, sites 3 and 6 recorded very high concentrations of zinc, and may be deemed "contaminated" in accordance with USEPA criteria. These sites are located in areas markedly affected by shipbuilding activities (maintenance, sand blasting and vessel painting) and consequently they should be a mixture of natural sediments and very fine anthropogenic discharges, this could be the explanation for the high values of the specific surface in these samples.

Chromium levels were measured at six places. The values recorded reveal the existence of a problem of chromium contamination in the area, since the results at

Table 6
Mineralogical composition of the sediments (%)

Site	Calcite	Dolomite	Quartz	Potassium feldspars	Plagioclase	Clay minerals	Aragonite
1	27	<5	20	<5	–	47	–
2	17	<5	40	20	<5	16	–
3	25	<5	63	<5	<5	6	–
4	25	<5	45	<5	<5	19	–
5	25	<5	41	6	8	20	–
6	18	<5	55	<5	12	11	–
9	22	<5	57	5	<5	11	–
11	14	<5	43	8	<5	21	8

Table 7
Results of the metal analyses performed on the sediments (normalized data are also included)

	Hg (µg/kg)	Normalized data	Se (mg/kg)	Normalized data	Cd (mg/kg)	Normalized data	Pb (mg/kg)	Normalized data	Zn (mg/kg)	Normalized data	Cr (mg/kg)	Normalized data	Fe (%)	Normalized data
1	32.6	11.20	2.3	0.79	0.30	0.10	34.0	11.6	152	52.23	249	85.57	2.4	0.84
2	55.5	18.07	2.3	0.79	0.29	0.10	24.0	8.25	110	37.80	278	95.53	2.8	0.96
3	21.2	8.22	3.6	1.39	0.65	0.25	44.0	17.0	348	134.8	129	50	1.5	0.58
4	78.5	42.9	2.9	1.58	0.30	0.16	20.0	10.9	155	84.70	206	112.5	2.0	1.09
5	89.9	49.13	1.2	0.65	0.65	0.35	18.0	9.84	72	39.34	245	133.8	2.2	1.20
6	44.1	17.09	4.4	1.71	0.95	0.37	167	64.7	1749	677.9	241	93.41	3.0	1.16
8	–		–		0.02	0.03	5.5	9.32	22	37.28	–		–	
9	<20.0	10.93	–		0.02	0.02	5.7	3.11	66	36.06	–		–	
10	–		–		0.29	0.16	11.1	6.06	139	75.96	–		–	
11	–		–		0.30	0.16	8.6	4.70	95	51.91	–		–	
12	240.0	95.24	–		0.29	0.11	29.6	11.7	125	49.60	–		–	
13	300.0	119.04	–		0.50	0.20	35.3	14.0	141	55.95	–		–	
14	150.0	59.52	–		0.21	0.08	35.8	14.2	129	51.19	–		–	
15	–		–		0.36	0.14	42.6	16.9	156	61.90	–		–	
16	320.0	126.98	–		0.41	0.16	35.8	14.2	132	52.38	–		–	
17	510.0	202.38	–		0.21	0.08	43.5	17.2	97.9	38.85	–		–	
18	–		–		0.39	0.66	<0.9	1.52	<3.5	5.93	–		–	
19	–		–		<0.01	0.02	2.0	3.39	21.9	37.12	–		–	
20	–		–		<0.01	0.02	3.6	6.10	6.3	10.68	–		–	
N. pol. (*)	<300				<1		<40		<90		<25			
Polluted (*)	>1000				>6		>60		>200		>75			

(–) = Not analysed.
(*) Threshold values proposed by USEPA and Ontario Ministry of Environment (Canada).

all the sites were in excess of the maximum established limit, in accordance with the recommendations of the USEPA.

Comparison was made among raw data, because USEPA data are not normalised. However, using normalised data (Table 7), as indicative of metal availability, the results do not seem to lead to substantial changes in interpretation of the obtained data, ruling out a granulometric effect in metal distribution.

4.4. Statistical analysis of the results of heavy metal content in the sediments

The variables used as grouping criteria were zinc, cadmium, lead and mercury, and only those sites in which the concentration of all these metals were determined were included in the statistical analysis. Fig. 5 illustrates the results of the cluster analysis of the sediment samples and shows two different groups. The first major grouping is formed by sites 17, 15, 16, 13 and 12, with site 17 somewhat separated from the others; this group of sites corresponds to those located in the inner bay, an area characterized by its shallow waters, low rate of water renewal and the preponderance of sedimentation phenomena, associated with very fine sediment. The second group is composed of sites 1, 2, 3, 4, 5 and 9 and corresponds to those sites located in areas of greater anthropic influence and which, consequently, are closer to sources of contamination.

A factorial analysis was undertaken of the parameters analysed at each of the sampling sites and for each of the other sites (Fig. 6). Two procedural options were therefore available: (1) to use the greatest number of parameters for the factorial analysis, thus requiring the use of data from a small number of sites, (2) to use the greatest number of sites possible, thus including in the factorial analysis only a limited number of parameters.

In this research, an intermediate solution was applied, namely, an average number of sites and an average number of parameters. As a result, a factorial analysis was undertaken using the data relating to the following parameters: mercury, selenium, cadmium, lead, zinc, chromium, iron and organic material, from sites 1, 2, 3, 4, 5, and 6; a second factorial analysis was also undertaken, with the data relating to the parameters: mercury, cadmium, lead, zinc and organic material, from sites 1, 2, 3, 4, 5, 6, 9, 12, 13, 14, 16 and 17 (Tables 8 and 9). The results of this first factorial analysis reflect the existence of two main factors. Factor F1 is affected by almost all of them, and in order of importance, by zinc, lead, cadmium, selenium and iron. Factor F2, on the other hand, is represented only by the variables chromium, mercury and iron. The existence of two groups of metal associated with two different factors may indicate a

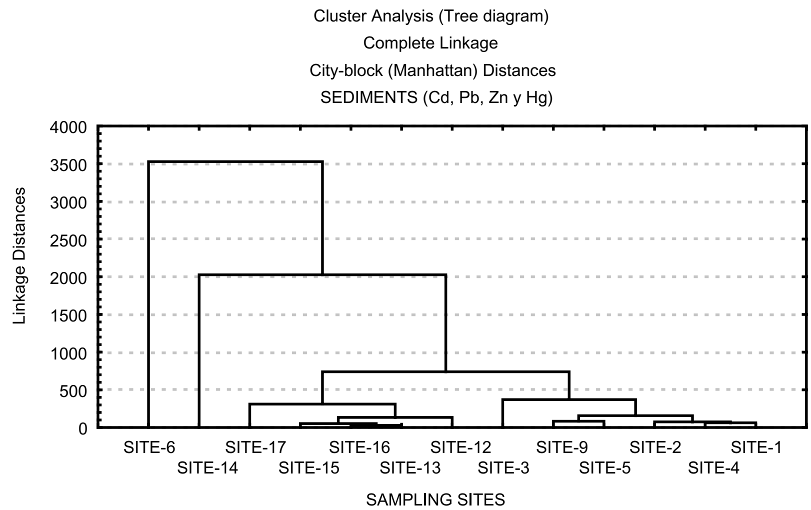

Fig. 5. Cluster analysis of the variables analysed in sediment.

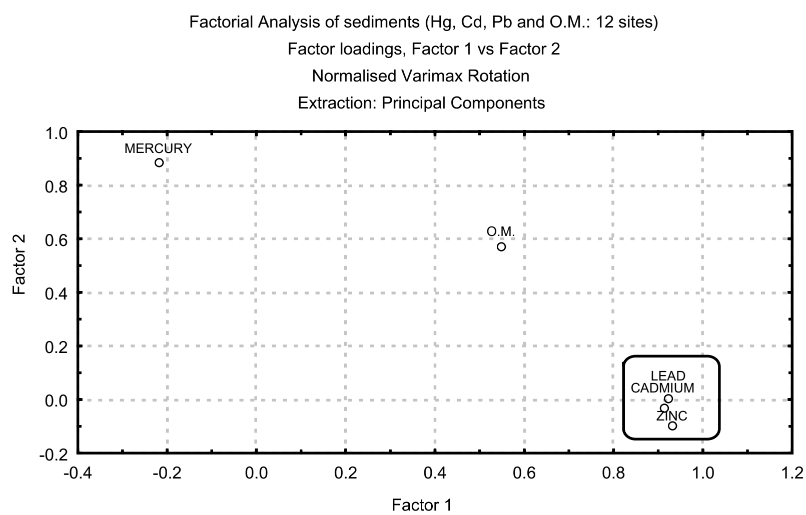

Fig. 6. Factorial analysis of the variables analysed in the sediments of sites 1, 2, 3, 4, 5, 6, 9, 12, 13, 14, 16 and 17.

Table 8
Study of the loading factors corresponding to the factorial analysis of the variables analysed at sites 1–6

	Factor 1	Factor 2
Mercury	−0.314	0.682
Selenium	0.816	−0.441
Cadmium	0.814	−0.102673
Lead	0.992	0.047
Zinc	0.997	0.052
Chromium	−0.034	0.930
Iron	0.508	0.764
Organic matter	0.310	0.216

different industrial origin for each group of metals. Consequently, mercury and chromium, normally linked to industrial contamination, are clearly separated from

Table 9
Study of the loading factors corresponding to the factorial analysis of the variables analysed at sites 1, 2, 3, 4, 5, 6, 9, 12, 13, 14, 16 and 17

	Factor 1	Factor 2
Mercury	−0.218	0.882
Cadmium	0.913	−0.032
Lead	0.925	0.003
Zinc	0.931	−0.097
Organic matter	0.550	0.572

the other group of metals. The results of the second factorial analysis confirm the existence of two principal factors (F1 and F2). Factor F1 includes the following variables, in order of importance: lead, zinc, cadmium and organic matter. On the other hand, factor

2 is represented only by the variable mercury and, to a lesser extent, organic matter. The fact that organic matter should be similarly involved in both factors may imply that it has an transport role in the final distribution, both in the first group of metals (Cd, Pb and Zn) and with mercury.

The coincidences in both cases are significant, since the same elements are grouped with the same factors. The differences lie in the relative importance of the organic matter, a fact that may be related to the speciation of the elements and their availability in the sediment. From the results of the first factorial analysis, it would appear that oxides are the principal carriers of heavy metals, whereas the second analysis, in the absence of iron, would indicate the relative importance of organic matter in the fixation of these elements.

5. Conclusions

Based on the experimental results obtained and the discussion thereof, the following conclusions may be reached:

1. The results obtained from the different physical–chemical analyses of seawater, in conditions of both rising and ebbing tides, revealed that, in general, the level of contamination in the waters of the outer bay is low, although there are differences between some sampling sites.
2. The values recorded for inorganic nitrogen in its various forms (ammonium, nitrites and nitrates) pose no threat to the marine ecosystem; however, at two sites, the limits set for special waters are exceeded slightly: Guadalete river (site number 5) and the dry dock in the fishing quay in Cadiz (site number 16).
3. Cluster analysis of all the parameters studied in the seawater revealed few differences between rising and ebbing tidal waters. In addition, the grouping of the sites identified two in particular which displayed different characteristics from the rest (sites 5 and 6) for the existence of domestic and industrial discharges.
4. Although contamination levels in sediments are among low and moderate, the most contaminated sites are those which present a modified granulometric distribution (sites 3 and 6), probably due to fact that these two sites are a mixture of natural sand and gravel sediments and fine materials from uncontrolled industrial discharges.
5. Sediment analysis revealed that virtually none of the sites suffered contamination by mercury, cadmium or lead. Zinc was found in greater concentrations at thirteen of the 19 sites, and these affected sites may be classified as ‘‘moderately contaminated’’ by this metal. Finally, the chromium concentration levels recorded would suggest that sources of chromium contamination exist in the area, since at all six sites studied, the level exceeded the recommended limits set by the USEPA for ‘‘contaminated’’ sediments.
6. The cluster analysis performed on the parameters analysed in the sediments revealed the existence of two groups of sites with analogous characteristics. One of these corresponded to those groups located in the inner part of the bay (sites 12, 13, 15, 16 and 17), and the other to those situated close to the areas of the bay which are subject to greater anthropic influence (sites 1, 2, 3, 4, 5 and 6).

Finally, it must be highlighted that this study has discovered uncontrolled discharges in samples 3, 5 and 6 and other threats for the environment that have previosuly not been monitored and assessed.

References

Álvarez, O., Izquierdo, A., Tejedor, B., Mañanes, R., Tejedor, L., Kagan, B.A., 1999. The influence of sediment load on tidal dynamics, a case study: Cadiz Bay. Estuarine Coastal Shelf Sci. 48, 439–450.

Campbell, P.G.C., 1988. Biologically available metals in sediments. NRCC div. Chem. Pub, Otawa, 296 pp.

CEDEX, 1994. Recomendaciones para la gestión del material dragado en puertos españoles. Ministerio de Obras Públicas, Transportes y Medio Ambiente, Madrid.

Conde, B., 1993. Metales Pesados en los Sedimentos de la Zona Intermareal de la Ría del Tinto. Tesis Doctoral. Universidad de Sevilla.

Del Valls, A., 1994. Aplicación de un Método Integrado para la Medida de la Calidad Ambiental en Ecosistemas Litorales del Golfo de Cádiz. Tesis Doctoral. Universidad de Cádiz, 389 pp.

Donze, M., Nievwendijk, C., Boxtel, A., Quaak, M., 1990. Aquatic pollution and dredging in the European Community. Delwel Publishers, La Haya.

Establier, R., Blasco, J., Gómez, A., Escolar, D., 1984. Materia Orgánica de los Sedimentos de la Bahía de Cádiz y de sus Zonas de Marismas y Salinas. Inv. Pesq. 48 (2), 285–301.

Gaudette, H.E., Flight, W.R., Torner, L., Folger, D.W., 1974. An inexpensive titration method for the determination of organic carbon in recent sediments. J. Sediment. Petrol. 44 (1), 249–253.

González-Mazo, E., Pajares, J.M.F., Gómez-Parra, A., 1998. Identifying the processes involved in the hydrochemistry and environmental quality system (Bay of Cádiz, Spain). A case-study using factor analysis. TRAC-Trends in Analytical Chemistry, vol. 17, p. 58-69.

Grashoff, K., Ehrhardt, M., Kremling, K. (Eds.), 1983. Methods of Seawater Analysis, 2nd ed. Verlag-Chimie, Alemania.

Gutiérrez Más, J.M., 1992. Estudio de los sedimentos recientes de la plataforma continental Bahía de Cádiz. Tesis doctoral, Universidad de Cádiz, 364 pp.

Hamdy, Y., Post, L., 1985. Distribution of mercury, trace organics, and other heavy metals in Detroit river sediments. J. Great Lake Res. 11, 353–365.

Horowitz, A., Elrick, K., 1987. The relation of stream sediment surface area, grain size and composition to trace element chemistry. Appl. Geochem. 2, 437–451.

Jenne, E., Kennedy, V., Burchard, J., Ball, J., 1980. Sediment collection and processing for total metal analysis. in: Baker,

R. (Ed.), Contaminants and sediments, vol. II, Ann Arbor Sciences.

Luoma, S.N., 1990. Processes affecting metal concentrations in estuarine and coastal marine sediments. In: Fürness, R.W., Rainbow, P.S. (Eds.), Heavy metals in the environment. CRC, Boca Ratón, FL, USA, pp. 51–56.

Orden de la Consejería de Medio Ambiente de 14 de Febrero de 1997, por la que se clasifican las aguas litorales andaluzas y se establecen los objetivos de calidad de las aguas afectadas directamente por los vertidos, en desarrollo de decreto 14/1996, de 16 enero, por el que se aprueba el reglamento de calidad de las aguas litorales. BOJA n° 27 de 4 de marzo de 1997.

Ponce, M.R., 1996. Distribución de Zn, Cd, Pb y Cu en Sedimentos Marinos Costeros. Tesis de Licenciatura. Universidad de Cádiz.

Strickland, J.D.H., Parsons, T.R., 1972. A practical handbook of Seawater Analysis. Fisheries Research Board of Canada. Canada.

Sturgeon, R.E., Desaulniers, J.A.H., Berman, S.S., Russell, D.S., 1982. Determination of trace metals in estuarine sediments by graphite-furnace atomic absorption spectrometry. Anal. Chim. Acta. 134, 283–291.