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Seasonality of contamination, toxicity, and quality values in sediments from littoral ecosystems in the Gulf of Cádiz (SW Spain)

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Abstract

To seasonally evaluate littoral contamination, toxicity and quality values of sediments from the Gulf of Cádiz, we measured chemical concentrations and conducted toxicity tests in winter and summer and linked these results by means of multivariate analysis. Sediment samples were subjected to two separate, replicated sediment toxicity tests (*Microdeutopus gryllotalpa* amphipod survival, and *Ruditapes philippinarum* clam reburial), and to comprehensive sediment chemistry analyses (grain size, organic carbon, 14 heavy metals, and the surfactant linear alkylbenzenesulfonate (LAS)). Only sediments associated with an untreated urban discharge were toxic and related to high levels of surfactant LAS, Ag, and Pb. Multivariate analysis indicated that variables and chemicals associated with geochemical matrix and background levels (specific surface, Fe, Zn, Cu, V, Ni, and Co), chemicals associated with untreated urban discharge sources, and toxicity effects showed no seasonal variability. Only copper concentrations showed seasonal differences, being toxic during the winter and not toxic during summer. Multivariate analysis permits us to derive sediment quality values (SQVs); in terms of concentrations at or below which biological effects were not measured (mg kg^{-1} dry sediment), are: LAS, 2.6; lead, 66.8; silver, 0.78; copper, 69.6. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Marine pollution; Ecotoxicology; Multivariate analysis; Gulf of Cádiz; Sediment quality values

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1. Introduction

It has long been demonstrated that sediments can adsorb persistent and toxic chemicals to levels many times higher than water column concentrations. This fact is particularly important in littoral ecosystems affected by different contamination sources. Understanding of the ecological significance of marine sediment contamination has been advanced by the use of sediment toxicity tests (see reviews in Lamberson et al., 1992; Luoma and Ho, 1992; DelValls and Conradi, 2000). Further, linking sediment chemical concentrations and endpoints obtained from laboratory toxicity tests by means of multivariate analysis have been used to establish those chemical ranges associated with adverse effects by proposing sediment quality values (SQVs) (Long et al., 1995; DelValls et al., 1997, 1998a,b; DelValls and Chapman, 1998). Normally contamination and toxicity evaluations over in-place sediment are performed either once or over a limited period of time, with no indication of seasonal fluctuations in both sediment toxicity and contamination phenomena.

The objectives of this study were to assess the seasonality of:

1. Sediment contamination by measuring the levels of heavy metals originating from various anthropogenic

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sources and the surfactant linear alkylbenzenesulfonate (LAS) with an origin associated with urban disposal.

2. Sediment toxicity by performing two sediment toxicity tests, using lethal (amphipod 10 d survival) and sublethal (clam 48 h reburial) responses.
3. To calculate SQVs calculated by linking both chemical and biological measurements using multivariate analysis. The study was conducted by synoptically collecting sediment samples during two different seasons in the same year (winter and summer).

2. Materials and methods

2.1. Approach

The present study was performed at seven stations in two shallow littoral ecosystems in the Gulf of Cádiz located in the SW Spain (Fig. 1). Approximately half of each area (20 km^2) has a water depth of less than 3 m. Five sampling stations (CB1-5) were established in the Bay of Cádiz. The other two stations (BR1 and BR2) were selected in the uncontaminated area of the salt-marshes from the Barbate river (Fig. 1). Stations were chosen on best available information from previous studies to represent presumably low, moderate and high levels of chemical contamination (Gómez-Parra et al., 1984; Establier et al., 1985). Stations chosen, in the 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). *Clean* sediment (NC) from Cádiz beach (Fig. 1) was used as a negative control (NC) reference. Also, *polluted* sediment (PC) collected from the untreated sewage discharge point located in the town of San Fernando (Fig. 1) was used as positive control (PC) (DelValls et al., 1996).

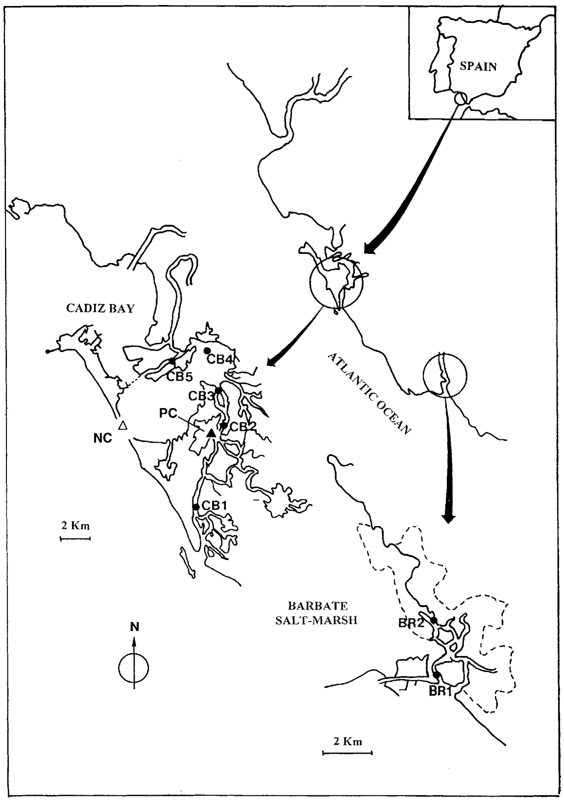


Fig. 1. Map of the two littoral ecosystems (Bay of Cádiz and salt-marsh of the Barbate river) selected in the Gulf of Cádiz showing locations of sampling stations. NC and PC, respectively, used in toxicity tests are represented by triangles (△ – NC; ▲ – PC).

All stations were synoptically sampled for sediment chemical and toxicity test analyses during winter (W) and summer (S) in the same year. Detailed chemical analyses and two separate sediment bioassays on the homogenized surface sediment were conducted for each season. The results of these analyses were used to establish those ranges in the chemical concentrations associated with biological effects.

2.2. Sample collection

Sediment samples from the seven stations and the two controls for toxicity tests were collected with a 0.025 m^2 Van Veen grab. Only grabs that had achieved adequate penetration (2/3 of total volume) to collect the first 5 cm of the sediment and that showed no evidence of leakage or surface disturbance were retained and transferred to a cooler. When sufficient sediment had been collected from a particular station, the contents of the cooler were homogenized with a Teflon spoon until no color or textural differences could be detected. Then the coolers, chilled with ice were transported to the laboratory. Samples were received at the laboratory 6–7 h after collection. The sediments were subsampled (1.5 l aliquots) for chemical quantification and toxicological characterization. After that sediment samples were maintained in the cooler at 4 °C in the dark until they were used for toxicity testing (carried out the day after the final sample collection). Sediment was filtered (0.5 mm) prior to the performance of toxicity tests. Prior to sample collection and storage, all beakers were thoroughly cleaned with acid (10% HNO_3), and rinsed in double-deionized (Milli-Q) water.

2.3. Chemical analyses

For sediment grain size and specific surface, an aliquot of wet sediment was analyzed using a laser particle sizer Fritsch (model Analysette 22) following the method reported by DelValls et al. (1998c). The remaining sediment was dried at 60 °C prior to chemical analysis.

Dried sediments were gently homogenized. Organic carbon content was determined using the method reported by El Rayis (1985). Elemental analysis was carried out with a CHN Carlo Erba (Model 1106). The surfactant LAS was analyzed in isocratic regime using high-performance liquid chromatography equipped with a fluorescence detector using the procedure outlined by González-Mazo et al. (1997). For trace metal analysis, the sediments were digested as described by Loring and Rantala (1992). Fe, Mn, Zn, and Cu concentrations in the extracts were determined with a Perkin–Elmer 2100 flame atomic absorption spectrophotometer. Hg and As concentrations were determined by means of Perkin–Elmer MHS-FIAS coupled with a Perkin–Elmer 4100 ZL spectrophotometer. The other trace metals were measured by graphite furnace atomic absorption spectrophotometry (Perkin–Elmer 4100 ZL). Results are expressed as mg kg^{-1} dry sediment. The analytical procedures were checked using reference material (MESS-1 NRC and CRM 277 BCR) and allow agreement with the certified values higher than 90%.

2.4. Sediment toxicity

Two separate bioassays were used to measure sediment toxicity during winter and summer seasons on two benthic species widely distributed in the studied area: the amphipod *Microdeutopus gryllotalpa* and the clam *Ruditapes philippinarum*.

The test using the estuarine clam *R. philippinarum* was developed in whole sediment using a 1:2 v/v sediment–water relation. Temperature was controlled at 20 °C. The rate of burial of the clams was measured during a 48 h exposure period (McGreer, 1979). The amphipod test was performed in whole sediments using a 1:4 v/v sediment–water relation. Temperature was controlled at 20 °C and survival of the amphipod after 10 days of exposure was the endpoint selected (ASTM, 1991a).

NCs were included in both sediment toxicity tests. PCs were used only for the amphipod tests. All the tests and controls were performed in duplicate. The resulting parameters calculated from the sediment test and control duplicates: % amphipod survival, clam reburial rates (ET_{50} $\langle h \rangle$ – the time required for 50% of the population to burial) were compared using ANOVA and Scheffe's *F* tests to identify significant differences in sensitivity among toxicity tests and controls ($p < 0.01$). The parameter ET_{50} was calculated by linear regression of log toxicant time on declining probit values, using a probit modified from the classic methodology following the method reported by DelValls et al. (1997).

The contamination and toxicity data were analyzed by factor analysis using the principal component as the extraction procedure, a multivariate statistical technique, to explore chemical concentrations ($n = 19$ chemicals $\times$ 2 periods) and toxicity data ($n = 2$ tests $\times$ 2 periods) distributions. The factor analysis was performed on the correlation matrix, i.e., the variables were autoscaled (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 setup for factor analysis procedure (P4M) from the BMDP statistical software package (Frane et al., 1985). All biological data were treated similarly, assuming that the significance of each type of toxicity test was equal.

Adequate quality assurance/quality control (QA/QC) measures were followed in all aspects of the study, from field sampling through to laboratory and data entry as per Chapman (1988), and ASTM (1991a,b).

3. Results and discussion

3.1. Sediment contamination

Summarized concentrations of selected contaminants and parameters analyzed are shown in Table 1 for winter and summer, respectively. Sediment samples had relatively similar texture, being dominated by the clay fraction with a dark color, and with a specific surface from 7.03 to 7.96 m^2 cm^{-3}. Station BR1 was the only station analyzed in which the sum of the silt and the sand proportion (grain size higher than 20 μm) was higher (7%) compared with the others (1%) and the specific surface was lower than the others (5.78 m^2 cm^{-3}). The granulometry did not change between both periods of time considered in this study. Levels of organic matter in sediments were similar among stations and between winter and summer. These values were in the normal range for shallow littoral ecosystems (1–3% dry weight) except for station BR1 which had lower values (0.59% and 0.62%) during winter and summer, respectively. Chemical data showed an organic and inorganic contamination gradient among studied stations similar in both winter and summer periods of sampling. These data were ideal to allow identification of the main contamination sources (DelValls et al., 1998c). A few differences in the concentration of the major elements (Fe and Mn) were observed between stations. Of all the stations, BR1 showed the lowest values for both metals. At station CB5 Cr appears to be very high in both summer and winter relative to other stations. In general, chemical concentrations were relatively higher in 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 (Gómez-Parra et al., 1984; Establier et al., 1985).

Although these data were ideal for identifying the origin of contamination in the studied area, they offer a limited picture of the changes that may have occurred as a result of anthropogenic impacts in the Gulf of Cádiz.

Table 1
Values of organic carbon (%), total carbon (%), total nitrogen (%), specific surface (σ $\langle \mathrm{m}^2\ \mathrm{cm}^{-3} \rangle$), 14 heavy metals (mg kg^{-1}, %, dry sediment), and (LAS mg kg^{-1} dry sediment), analyzed in sediments from the selected stations in the Gulf of Cádiz at both seasons

Contaminants	CB1	CB2	CB3	CB4	CB5	BR1	BR2
Summer							
Organic carbon	1.49	3.01	2.71	3.03	2.76	0.62	1.56
Total carbon	3.06	3.73	4.19	4.91	3.89	5.21	2.01
Total nitrogen	0.10	0.23	0.19	0.20	0.21	0.01	0.11
σ	7.89	7.27	7.78	7.33	6.98	5.95	7.57
Fe	29 650	36 170	34 970	27 440	28 530	1350	37 370
Mn	329	201	324	396	293	79	255
Zn	107	185	188	149	128	19	125
Cu	49.4	92.4	71.2	48.8	43.9	13.2	45.3
Pb	25.7	64.7	50.3	51.2	52.5	6.9	26.7
Cd	0.52	0.93	0.87	0.84	1.24	0.94	0.39
Cr	64.1	90.2	67.9	60.3	164.9	39.7	86.2
Ag	0.38	1.59	1.01	0.60	0.64	0.68	0.5
Hg	0.14	0.32	1.02	0.47	0.45	0.27	0.10
V	75.3	125.4	100.4	85.3	75.3	3.1	134.2
Ni	25.5	43.8	34.3	30.5	26.3	1.2	43.6
Co	6.97	8.56	8.48	8.39	6.95	0.40	11.33
As	8.70	7.42	10.88	11.31	9.18	5.12	7.89
Sn	23.4	12.4	14.1	8.1	15.1	1.1	7.4
LAS	1.9	26.7	8.7	1.2	2.3	1.7	2.5
Winter							
Organic carbon	1.39	2.96	2.21	1.82	2.46	0.59	1.86
Total carbon	2.98	3.75	3.79	3.49	3.61	3.17	1.96
Total nitrogen	0.10	0.19	0.14	0.07	0.10	0.03	0.12
σ	7.63	7.35	7.96	7.16	7.03	5.78	7.77
Fe	27 734	33 426	31 872	33 380	27 759	1271	39 820
Mn	333	278	332	452	272	262	295
Zn	82	157	163	73	105	34	140
Cu	51.4	69.6	66.4	34.8	49.6	37.4	73.7
Pb	30.5	84.6	64.4	24.4	51.1	66.8	30.0
Cd	0.51	0.67	0.75	0.99	0.81	1.10	0.68
Cr	49.6	77.1	53.0	41.1	283.9	42.5	101.2
Ag	0.48	1.34	1.20	0.78	1.06	0.75	0.61
Hg	0.11	0.25	0.46	0.25	0.57	0.06	0.15
V	79.1	106.5	77.0	80.7	83.3	17.9	147.5
Ni	24.9	35.5	27.9	34.4	32.5	8.2	42.8
Co	7.29	9.16	7.64	10.92	7.78	3.40	11.50
As	11.27	7.72	13.69	8.53	13.24	5.19	9.67
Sn	19.8	17.0	24.0	9.9	18.8	7.4	10.3
LAS	2.2	62.1	12.8	2.6	1.2	1.7	2.5

This also demonstrates the difficulty of using chemical data alone to define "problem areas", because the resulting data provide little or no evidence of any biological consequences of contamination.

3.2. Sediment toxicity

The results of each sediment toxicity test are summarized in Figs. 2 and 3 for the clam reburial test and Fig. 4 for the amphipod test. In Fig. 5 are shown the summarized results of the toxicity tests to identify significant differences among stations and period.

Clam reburial: There were no clam mortalities in the test or control sediment over the 48 h exposure period. The ET_{50} values were fastest in the salt-marsh of the Barbate river stations (BR#) and in the CB1 and CB4 stations in the Bay of Cádiz, slowest in the CB2 station, and intermediate in the CB3 and CB5 stations for both winter and summer periods. The ET_{50} values were generally faster in winter than in summer for all the stations except for the controls and for the CB2 stations in which the clams never buried more than 20–30% during the 48 h exposure period. It might inform about a potential seasonal difference between both periods of time.

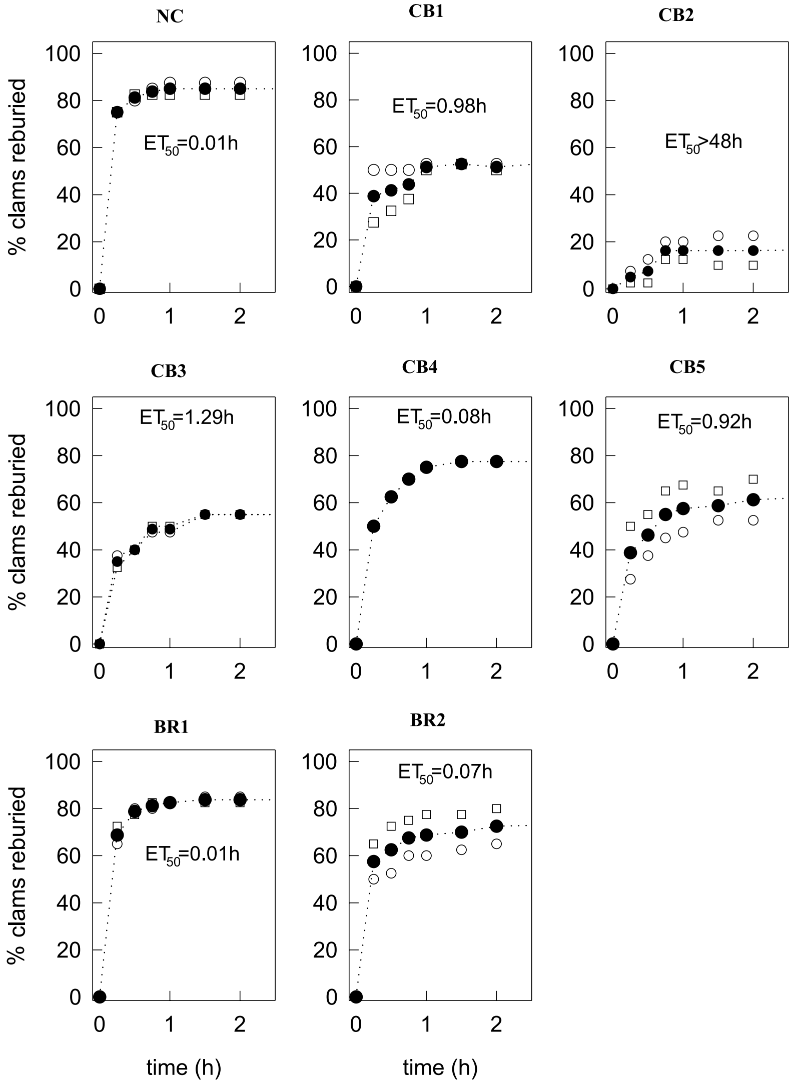


Fig. 2. Sediment toxicity results for the clam reburial tests during winter. The percentage of clams buried for each replicate (empty figures) and the average value (filled circle) are presented versus the first 2 h of the total 48 h of exposure. The average ET_{50} value calculated from the plots is also presented in the figures.

Amphipod survival: Mean survival during the 10 d amphipod toxicity test ranged from a low value of 0% in the PC (used only during the summer period) to a high value of 97.5% (for winter and summer, Figs. 4 and 5) in the NC. The lowest survival measured (16%), at contaminated sites was associated with sediments form CB2, while highest survival (85%) was associated with sediments from station CB1. From Fig. 5 survival in sediments from CB3, CB5 and CB2 was significantly different from the NC ($p < 0.05$). CB2 station survival was not significantly different from the PC ($p < 0.05$). From this figure some general trends can be observed among stations for winter and summer. Station CB2 was toxic for both periods and for both bioassays. Stations BR#, CB4 and CB1 were similar to the NC in all the cases and not toxic. Stations CB5 and CB3 show different trends depending on the bioassay and the period tested, they can be considered as moderately toxic.

3.3. Seasonality of sediment contamination, toxicity and SQVs

The results obtained following factor analysis to link the chemical and biological variables for winter and summer are shown in Table 2. No significant differences were determined for any of the endpoints measured in the toxicity tests between winter and summer. The two biological parameters (% of amphipod survival – Morty

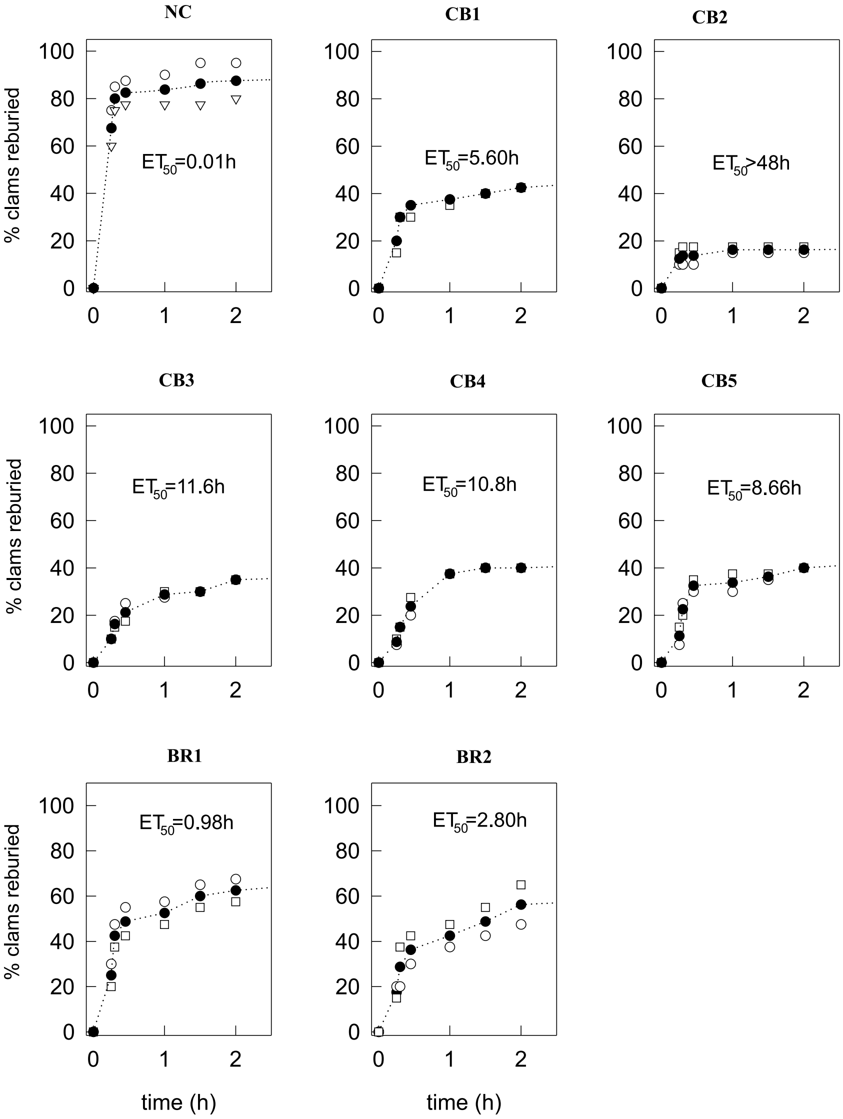


Fig. 3. Sediment toxicity results for the clam reburial tests during summer. The percentage of clams buried for each replicate (empty figures) and the average value (filled circle) are presented versus the first two hours of the total 48 h of exposure. The average ET$_{50}$ value calculated from the plots is also presented in the figures.

and ET$_{50}$) were together in factor 2 with loadings higher than 0.8 for winter and summer. This suggests that there was no influence of season on sediment toxicity. In general, from Table 2 the same groups of chemicals appear to be grouped for winter and summer. Only a few differences in the loading values between seasons were observed. For Mn in winter two different loadings are for factors 1 (0.475) and 4 (0.710) because this high difference in loading could be associated predominantly with factor 4. On the other hand, As and Cd were included in different groups in winter than in summer. This fact makes it complicated to establish a trend in their association for both periods. This could be explained by the heterogeneity of the sampling processes, the analytical errors and may be by the seasonal component. Unfortunately, with the set of data used in this study it cannot determine a clear association of these two metals with a factor for both periods. It is not the objective of this study to establish the geochemical behavior of these metals and further studies should be carried out to determine their seasonal component in their trends. It is important to note that they were not included in factor 2, related to the toxicological effects so the uncertainty in their trends will not affect the deri-

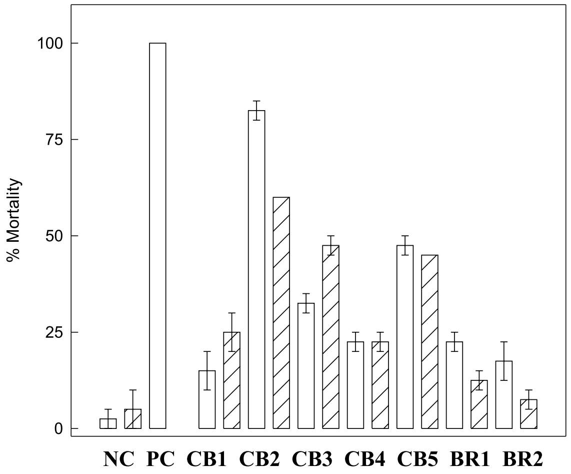
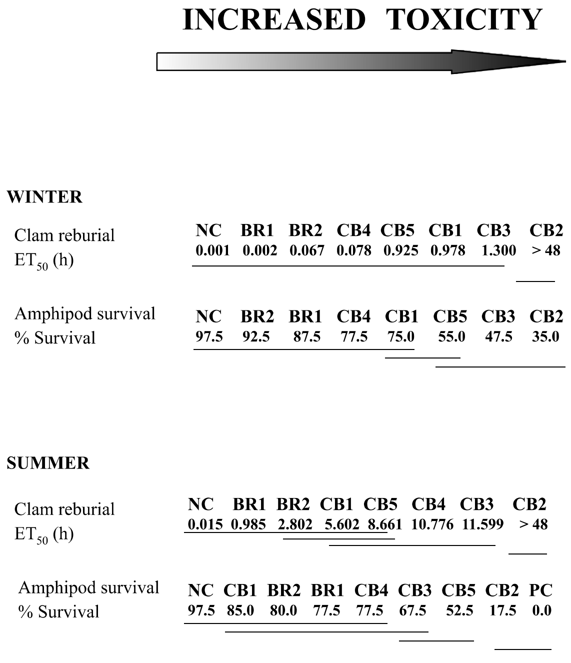


Fig. 4. Histogram of the percent of the amphipod mortality measured for sediments collected in winter (crossed bars) and summer (empty bars). The error bars represent the standard deviation from duplicates for each sediment station and in both periods.

vation of SQVs. Three chemicals (LAS, Pb, and Ag) were in both periods of time grouped together with the toxicity parameters. These chemicals are of concern in the studied area. Also, Cu measured in winter was grouped with these three chemicals. The chemical Zn was associated with the factor 2 but it was not included in the derivation of SQVs because its loading in this factor was lower (0.510) than in factor 1 (0.617) not associated with toxicological effect. Also the OC concentration was included in factor 2 for winter and summer but it was not included to derive SQVs because their values were in the normal range for littoral ecosystems and its contribution to this factor could be explained as the variable that controls the incorporation of the chemicals to the sediment instead of a chemical associated with the biological effect measured (DelValls et al., 1998c; DelValls and Chapman, 1998). The description of the meanings for factors 1, 3, 4 and 5 are out of scope of this paper because the chemicals included in them are considered absent of effect in the concentrations measured in this study.



WINTER

Clam reburial ET_{50} (h)	**NC**	**BR1**	**BR2**	**CB4**	**CB5**	**CB1**	**CB3**	**CB2**
	0.001	**0.002**	**0.067**	**0.078**	**0.925**	**0.978**	**1.300**	**> 48**

Amphipod survival % Survival	**NC**	**BR2**	**BR1**	**CB4**	**CB1**	**CB5**	**CB3**	**CB2**
	97.5	**92.5**	**87.5**	**77.5**	**75.0**	**55.0**	**47.5**	**35.0**

SUMMER

Clam reburial ET_{50} (h)	**NC**	**BR1**	**BR2**	**CB1**	**CB5**	**CB4**	**CB3**	**CB2**
	0.015	**0.985**	**2.802**	**5.602**	**8.661**	**10.776**	**11.599**	**> 48**

Amphipod survival % Survival	**NC**	**CB1**	**BR2**	**BR1**	**CB4**	**CB3**	**CB5**	**CB2**	**PC**
	97.5	**85.0**	**80.0**	**77.5**	**77.5**	**67.5**	**52.5**	**17.5**	**0.0**

Fig. 5. Summary of the toxicity test results (average results) carried out in winter and summer. Treatments not underlined by the same line are significantly different at $p < 0.05$ (Scheffe's *F* tests).

For the four chemicals (LAS, Pb, Ag and Cu) we developed SQVs following the procedures reported by DelValls and Chapman (1998) and the factor scores shown in Table 3 for the studied stations. In this approach we used the prevalence (factor scores) of factors for each of the cases studied to make the three operative definitions based on the data obtained from the toxicity tests. It should be emphasized that this approach is based on comparing those chemicals that group under the same factor as the toxicity parameters (in this study, under factor 2). The assumption is that these chemicals are correlated presumably in a cause-and-effect manner. In this sense, when the factor score from factor #2, which suggests a correlation between the above chemicals and biological adverse effects, is 0 or below with respect to all the cases (stations) (Table 3), the maximum concentrations of toxic chemicals at any of those stations represent the maximum chemical concentrations that are not associated with adverse effects. These are considered to be the concentrations below which biological effects are low or minimal and are here indicated as "not polluted". In contrast, to establish the minimal concentrations above which biological effects are always high, those minimal concentrations at stations where factor scores from factor #2 were higher than 0 were selected and described here as "highly polluted". Also, an intermediate range of chemical concentrations representing an area of uncertainty, or a break point between the high and low concentrations, is shown and described as "moderately polluted".

To facilitate the understanding of the mentioned process to derive SQVs we have described the calculation method for the case of Pb. The metal is included in factor 2 so correlated to biological effect. Also, this factor is positive in the cases (stations) CB2 and CB3 and negative for the rest of stations in both periods (summer and winter). To derive the guideline not polluted (Table 4: for Pb = 66.8) we should find the higher concentration of Pb measured in the sediments from the

Table 2
Sorted rotated factor loadings (pattern) of 38 variables on the five principal factors[a]

	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
Variance (%):	43.96	21.51	12.40	7.59	6.82
Summer					
Organic carbon	0.552	0.621	0.429	–	–
σ	0.742	–	–	–	0.585
Fe	0.939	–	–	–	–
Mn	–	–	–	0.821	–
Zn	0.617	0.510	–	–	–
Cu	0.621	–	–	–	–
Pb	–	0.832	–	–	–
Cd	−0.569	–	–	–	−0.691
Cr	–	–	0.959	–	–
Ag	–	0.843	–	–	–
Hg	–	–	0.767	0.445	–
V	0.959	–	–	–	–
Ni	0.934	–	–	–	–
Co	0.922	–	–	–	–
As	–	–	0.462	–	0.744
Sn	–	–	–	–	0.889
LAS	–	0.932	–	–	–
ET_{50}	–	0.914	–	–	–
Morty	–	0.895	–	–	–
Winter					
Organic carbon	–	0.480	–	0.660	–
σ	0.685	–	–	–	0.610
Fe	0.842	–	–	–	–
Mn	0.475	–	–	0.710	–
Zn	0.598	–	–	0.480	–
Cu	0.495	0.728	–	–	–
Pb	–	0.610	–	0.521	–
Cd	−0.523	–	0.651	–	–
Cr	–	–	0.917	–	–
Ag	–	0.972	–	–	–
Hg	–	–	–	0.663	–
V	0.907	–	–	–	–
Ni	0.893	–	–	–	–
Co	0.931	–	–	–	–
As	–	–	–	0.844	–
Sn	–	–	–	–	0.803
LAS	–	0.943	–	–	–
ET_{50}	–	0.896	–	–	–
Morty	–	0.804	–	–	–

[a] The loading matrix has been rearranged so that the columns appear in decreasing order of variance explained by factors. Only loadings greater than 0.4 are shown in table. Factors (#) are numbered consecutively from left to right in order of decreasing variance explained.

stations (cases) with factor score negative (Table 3): CB1, CB4, CB5, BR1 and BR2 from Table 1. This value is that measured at sediments from the station BR1 (66.8) during summer. Note that the concentrations of Pb in winter are lower than that and then the toxicity measured in winter could not be related to Pb but to other chemical with higher loadings than Pb (LAS, Ag and/or Cu). To develop the guideline highly polluted we should find the lower concentration of the chemical from the stations with factor score positive, CB2 or CB3 from Table 1. This value is that measured at sediments from the station CB2 (84.6). The moderately polluted value is considered as the uncertainty area between these two calculated values.

Following this method and from Tables 2 and 3 only three heavy metals Pb, Ag and Cu and the surfactant LAS could be used to define SQVs. The guidelines proposed for these four chemicals according to the above three toxicity designations are shown in Table 4. The rest of the measured chemicals in the different sed-

Table 3
Factor scores estimated for each of the seven stations evaluated in the Gulf of Cádiz to the centroid of all cases for the original data[a]

	CB1	CB2	CB3	CB4	CB5	BR1	BR2
Factor 1	−0.0384	0.4977	−0.2654	0.3139	−0.2302	−1.8346	1.5570
Factor 2	−0.8236	2.1098	0.4235	−0.4456	−0.2504	−0.2060	−0.8077
Factor 3	−0.8604	−0.2058	−0.1732	−0.4361	2.2344	−0.4540	−0.1049
Factor 4	−0.4103	−0.4539	0.9481	1.7800	0.0101	−0.8360	−1.0380
Factor 5	1.3208	−0.2593	1.3685	−1.1901	0.1553	−0.9286	−0.4666

[a] The factor scores quantify the prevalence of every factor for each station and are used to calculate the site-specific SQVs in sediment.

iments selected in this study appear in concentrations below the biological effect detected for both winter and summer and were not associated with adverse effect.

Determining sediment quality guidelines is a difficult task and comparative evaluation of broad-scale data sets encompassing complex interactions based on sediment toxicological data provides a promising alternative method for developing site-specific sediment quality guidelines. Furthermore, this method of deriving guideline concentrations provides an estimation based on interactions between complex chemical mixtures that may, individually or in combination, be responsible for the observed effects.

The guidelines developed in the current study were compared to values derived from several proposed approaches (Table 4). Sediment management guidelines proposed by the US Environmental Protection Agency using site-specific sediment bioassays (US Army Corps of Engineers, 1977), Ontario Ministry of the Environment using the screening level concentration (SLC) approach (Persaud et al., 1989), Washington State Marine Sediment Quality Standards derived for Puget Sound using a combination of the apparent effects threshold (AET) and equilibrium partitioning (EqP) methodologies (WADOE, 1991), National Oceanic and Atmospheric Administration (NOAA) from a compilation of the results of acute and chronic bioassays in several aquatic species (Long et al., 1995), and DelValls and Chapman from the sediment quality triad and a similar approach here described (DelValls and Chapman, 1998)

Table 4
Summary of benchmark sediment quality guidelines (mg kg^{-1} dry weight) proposed to evaluate sediment quality guidelines obtained in the Gulf of Cádiz[a]

Chemical		Sediment quality guideline		
		Not polluted	Moderately polluted	Highly polluted
Pb	(A)	<66.8	66.8–84.6	>84.64
	(B)	<40	40–60	>60
	(C)	<23	23–250	>250
	(D)	<35	35–110	>110
	(E)	–[b]	–[b]	>450
	(F)	<66.8	66.8–84.6	>84.64
Cu	(A)	<69.6	69.6–71.2	>71.2
	(B)	<25	25–50	>50
	(C)	<15	15–114	>114
	(D)	<70	70–390	>390
	(E)	–[b]	–[b]	>390
Ag	(A)	<0.78	0.78–1.34	>1.34
	(D)	<1.0	1.0–2.2	>2.2
	(F)	<1.2	1.2–1.3	>1.3
LAS	(A)	<2.6	2.6–8.7	>8.7
	(F)	<12.8	12.8–62.0	>62.0

[a] (A) This study for Pb, Cu, Ag, and LAS and by different North American agencies, government bodies and authors. (B) Environmental Protection Agency (US Army Corps of Engineers, 1977). (C) Ontario Ministry of Environment (Persaud et al., 1989). (D) National Oceanic and Atmospheric Administration (Long and Morgan, 1991). (E) Washington State (WADOE, 1991). (F) DelValls and Chapman (1998) for the Gulf of Cádiz.

[b] Guideline not available.

were used for comparative purposes. The results from the previous study in the Gulf of Cádiz determine the same guidelines for Pb being different for the rest of chemicals. In this sense, DelValls and Chapman found the heavy metals Cr and Hg as of concern and not during the current study. On the other hand, the current study determines Cu as of concern and not in the previous study. In general, the guidelines although similar for those common chemicals in both studies are more restricted for Cu, Ag and LAS. The values obtained in this study compared very closely with those proposed by the various agencies. This suggests that the sediment quality data from the Gulf of Cadiz, which are supported by substantial synoptic and available biological effects data, could therefore be applied for comparison proposes as a first step of a tier testing during environmental risk assessment (Gómez-Parra et al., 2000; Riba et al., 2002).

This study presents the results of a combined chemical and biological assessment of sediment toxicity at two different periods in one year to evaluate the potential influence of seasonality on sediment contamination and toxicity, and the derivation of SQVs in two littoral ecosystem from the Gulf of Cádiz. These conclusions are summarized below, based on the utilization of the two samples as NC or baseline condition, and one for PC or toxicity condition, for the adverse effect.

(a) Only association of chemicals such as LAS, Pb, and Ag were correlated in both periods of time with toxicity. Also Cu was correlated with adverse effects in winter. Overall, our data did not indicate effects due to seasonality so it could be concluded that sediment quality was the same in winter and summer.

(b) The multivariate statistical method (factor analysis) used in this study provides a deeper insight into the structure of complex and diverse data. For example, this multivariate tool revealed groupings of varying degrees of correlation between chemical concentrations in sediment and biological effects for winter and summer. Moreover, the relationships between lead, silver, copper and LAS concentrations in sediment and biological effects using different organisms, assessed in two different periods of time, are strong enough to permit the establishment of site-specific sediment quality guidelines.

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