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SPECIATION OF HEAVY METALS IN RECENT SEDIMENTS OF THREE COASTAL ECOSYSTEMS IN THE GULF OF CÁDIZ, SOUTHWEST IBERIAN PENINSULA

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Abstract—A five-step sequential extraction technique was used to determine the partitioning of Cr, Mn, Fe, Cu, Zn, Cd, and Pb among the operative sedimentary phases (exchangeable ions, carbonates, manganese and iron oxides, sulfides and organic matter, and residual minerals) in coastal sediment from three locations in the southwest Iberian Peninsula. Two sites are located close to industrial areas, the salt marshes of the Odiel River and Bay of Cádiz, and one in a nonindustrial area, the Barbate River salt marshes. The Odiel River salt marshes also receive the drainage from mining activities in the Huelva region. In the sediments from the Bay of Cádiz and Barbate River salt marshes, Cr, Cu, Fe, and Zn were extracted from the residual fraction at percentages higher than 60%. In the sediments from the Odiel River salt marshes, concentrations of all the metals, except Cu, Zn, and Cd, exceeded 60% in the residual fraction as well. In the sediments from the Bay of Cádiz and Barbate River salt marshes, the main bioavailable metals were Mn and Cd; in those from the Odiel River salt marshes, the main bioavailable metals were Zn and Cd, respectively. The environmental risk was determined by employing the environmental risk factor (ERF), defined as ERF = (CSQV − Ci/CSQV), where Ci is the heavy metal concentration in the first four fractions and CSQV is concentration sediment quality value (the highest concentration with no associated biological effect). Our results showed that the sediments from the Cádiz Bay and Barbate River salt marshes do not constitute any environmental risk under the current natural conditions. In contrast, in the Odiel River salt marshes, Cu, Zn, and Pb yielded ERFs of less than zero at several sampling stations and, consequently, pose a potential threat for the organisms in the area. This is a consequence of the high levels of metals in the area derived from the mining activity (pyrite) and industrial activities and the association of these heavy metals with more labile fractions of the sediments.

Keywords—Speciation   Sediment   Heavy metals   Salt marshes

INTRODUCTION

Throughout history, estuaries have been favored sites for human settlements and their associated industrial activities and have therefore received heavy contaminant inputs. Estuarine sediments show a strong tendency to accumulate contaminants, especially heavy metals; thus, analysis of these sediments constitutes a rapid means of obtaining time-integrated information concerning a range of sedimentological variables [1]. In addition, estuaries often include wetland sites of internationally recognized ecological importance as well as economic importance for their shellfish production. Heavy metals are ecologically relevant, mainly because of their toxicity and their nonbiodegradable character [2].

Sediments act as sinks for trace metals; thus, they become a more or less permanent part of the ecosystem. Remobilization processes reintroduce them into the ecosystem in bioavailable forms [3]. Metals can be released into the water phase when conditions such as pH, redox potential, ionic strength, and the concentration of organic complexing agents are appropriate; therefore, sediments also act as sources of the metals [4].

The biogeochemical and ecotoxicological significance of a given element is determined not only by its concentration in a natural or terrestrial system but also by its chemical form, which in turn is controlled by the physical, chemical, and biological characteristics of that system [5]. Knowledge regarding the chemical speciation of heavy metals in sediments is important for assessing the capacity of those sediments to act as sources of the potentially toxic metals. The determination of the total concentrations of metals is not, on its own, sufficient for prediction of such behavior [6].

Currently, the methods used most frequently to study the distribution of metals in a solid phase are based on partition techniques using different chemical extractants in sequence (i.e., the use of selective chemical extraction is widespread) [7–14]. It is generally recognized that the partitioning of trace metals achieved by such procedures is operational, and the results are determined by several experimental factors, such as the nature of the reagents used, time, temperature, mixing rates, the ratio of reagent to sediment, and the physicochemical characteristics of the sample (especially its chemical composition). The chemical composition of a sample could cause heterogeneous chemical reactions, leading to changes in the distribution of metals during extraction, such as the precipitation of newly formed compounds and readsorption of released metals [15–21].

Speciation is very useful, not only for determining the degree of association of the metals to the sediments and the extent to which they might be remobilized into the environment but also for differentiating metals with a lithogenic origin from those with an anthropogenic origin [22]. Metals associated with any of the following four fractions—the adsorptive or exchangeable fraction, the carbonate fraction, the reducible fraction, and the organic fraction—are considered to be more mobile and, therefore, more easily released from the sediment

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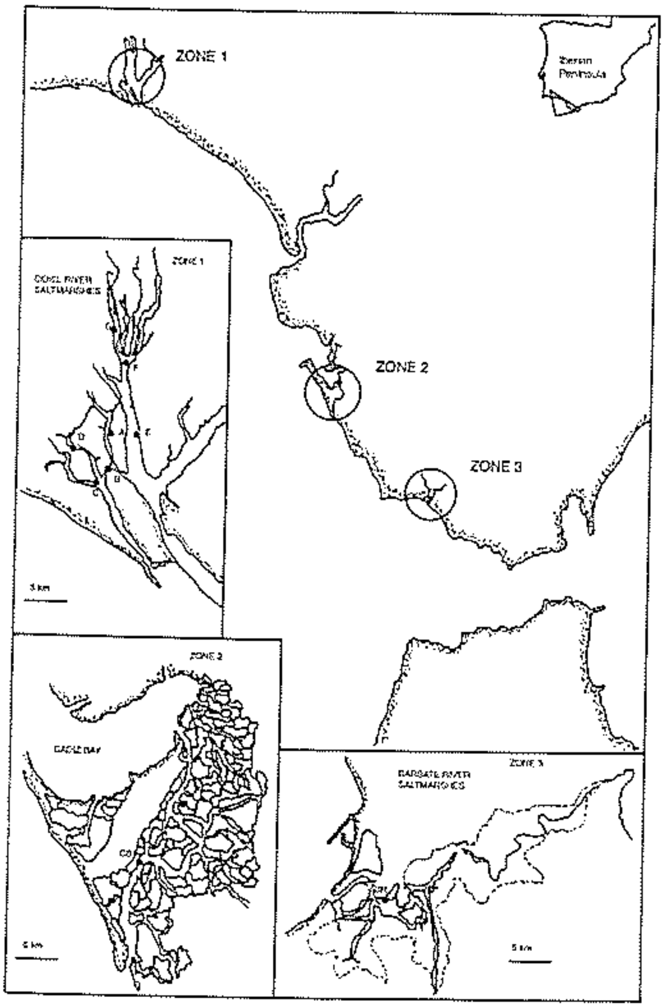

Fig. 1. Map of the Odiel River salt marshes (A–G), Cádiz Bay (CB), and Barbate River (BR) salt marshes (Andalucia, southwest Iberian Peninsula). Locations of sampling stations are shown.

and potentially more dangerous. These four fractions cover metals from anthropogenic sources and, therefore, give information regarding the type and severity of the pollution to which a particular environment has been exposed. Metals reporting to the inert fraction may be interpreted as having originated from geochemical or natural sources (i.e., of lithogenic origin) [3].

In the present study, we investigated the partitioning of seven metals (Cr, Mn, Fe, Cu, Zn, Cd, and Pb) among different fractions in superficial sediments from three coastal areas in the southwest (SW) Iberian Peninsula: The salt marshes of the Odiel River (OR), the Bay of Cádiz (CB), and the Barbate River (BR). All three areas are of considerable ecological relevance, and the aim of this work is to provide information concerning the distributions of heavy metals in the sediments sampled in these three valuable ecosystems to predict the environmental risks associated with these metals.

MATERIALS AND METHODS

Study area

The salt marshes of the OR, CB, and BR are located on the SW coast of the Iberian Peninsula (Fig. 1). The OR was declared a biosphere reserve because of its large population of migratory birds. The CB hosts a wide diversity of aquatic species, and many areas have been transformed for the development of aquaculture activities [23]. (It is also cataloged as a nature park.) The BR is also cataloged as a nature park and has commercial activities of bivalve cultivation (mainly shellfish and oysters). Despite their status as administratively protected areas, these zones are exposed to different types and levels of contamination. The OR marshes are affected by inputs of contaminants from the Huelva industrial area and the OR itself, which flows through a well-known mining area called the Iberian Pyrite Belt. The CB includes an international port with heavy maritime traffic and for decades has supported a major industrial activity in the marine construction sector; in recent years, this industrial activity has been diversified by the incorporation of other industries using metals, such as the manufacture of vehicle and aircraft components. The BR is an area relatively free from domestic and industrial contaminants, and its pollution inputs are derived more from agricultural activities. Therefore, it is included in the present study as a reference against which the zones subjected to metal pollution can be evaluated.

Sampling and sample pretreatment

Sediments were collected from June through July 1996 from nine sampling stations: A, B, C, D, E, F, and G in the OR (zone 1), CB, (zone 2), and BR (zone 3). Their locations are shown in Figure 1. A Van Veen grab was used to collect approximately 1 kg of superficial sediment (0–5 cm) at each of the sampling points. Samples were transferred to polyethylene bags and stored under a N_2 atmosphere at −4°C. A portion of each sediment sample was air-dried at 70°C to a constant weight and passed through a 500-μm sieve. Those subsamples of dried sediment were subjected to a selective chemical extraction. The sediment characteristics (percentages of sand, silt, clay, organic carbon, and total carbon) of sampling stations are shown in Table 1. The grain-size distribution in the fine fraction less than 63 μm was carried out in a Coulter Channelyzer C1000 (Coulter Electronics, Hertfordshire, UK). Organic carbon was determined by the method of Gaudette et

Table 1. Granulometric distribution and organic carbon (OC) and total carbon (TC) in the three sampling ecosystems[a]

	Odiel River salt marshes								
	A	B	C	D	E	F	G	CB	BR
% Clay	8.53	9.17	13.04	18.57	11.36	1.10	4.19	5.11	16.76
% Silt	41.51	37.63	76.62	69.01	35.40	0.83	8.24	24.83	49.47
% Sand	49.96	53.20	10.34	12.42	53.24	98.07	87.57	70.06	33.77
% OC	1.97	1.29	2.69	2.73	1.67	0.34	1.14	1.65	1.71
% TC	1.52	1.12	2.17	2.04	1.15	0.19	0.33	3.07	2.37

[a] Sampling stations (A–G) are located in the Odiel River salt marshes (Huelva, Spain) and Bay of Cadiz (CB) and Barbate River (BR) in Cadiz Bay and Barbate River salt marshes (Cadiz, Spain).

Table 2. Reagents and conditions for fractioning the sediment simples

Fraction	Reagents and conditions	Extracted sediment components
F1: Exchangeable metals	1 M $MgCl_2$, 1 h of shaking at room temperature	Exchangeable ions
F2: Metals bound to carbonates	1M NaOAc, pH 5 (HOAc), 5 h of shaking at room temperature	Adsorbed ions, carbonates, and some oxyhydroxides
F3: Metals bound to Fe-Mn oxides	0.04 M $NH_2OH{\cdot}HCl$ in 25% (v/v) HOAc, 6 h of occasional agitation at 96°C	Amorphous and oxyhydroxides of Fe and Mn
F4: Metals bound to organic matter	0.02 M HNO_3, 30% H_2O_2, pH 2 (HNO_3), 5 h of occasional agitation, extracted with 3.2 M NH_4OAc in 20% (v/v) HNO_3	Sulfides and organic matter
F5: Residual metals	Microwave acid digestion with aqua regia-HF	Lithogenic crystalline materials
Total digestion	Microwave acid digestion with aqua regia-HF	All sediment components

al. [24], and total carbon was determined with an elemental analyzer (Carlo Erba 1106, Milano, Italy).

Chemical analysis

The extraction procedure used in the present study is a modification of the sequential extraction procedure proposed by Tessier et al. [8]. The modification involves determining the inert or residual fraction using the method described by Loring and Rantala [25]. Extraction with a mixture of aqua regia (HNO_3:HCl, 1:3 [v/v]) and hydrogen fluoride (HF) provides an estimate of the residual and total metal content in the sample. This procedure is necessary to ensure the complete solution of aluminum. This mixture has also been shown to be effective in breaking down organic matter, and HF decomposes silicates [26,27]. Volumes of 0.5 ml of aqua regia and 3.0 ml of HF were added to the aliquot of oven-dried sediment in a 120-ml Teflon® bomb, and the mixture was heated in a 700-W microwave oven (Panasonic NN 6200, Mississauga, ON, Canada) and further treated with boric acid [28]. A description of the five fractions obtained with this method as well as the operative conditions used for each extraction are given in Table 2. This procedure was carried out in triplicate. The sample:reagent ratios were 1:40 (w/v) in fraction (F)1, F2, and F3, 1:80 (w/v) in F4, and 1:20 (w/v) in F5. Reactive blank and reference sediment (estuarine sediment 277 CRM certified by the Bureau Community of Reference [BCR], Brussels, Belgium) were used to ensure quality control. Trace metals were determined by graphite furnace atomic absorption spectrometry or by flame atomic absorption spectrometry (Perkin-Elmer 4100 ZL and Perkin-Elmer 3110, respectively, Norwalk, CT, USA), depending on the trace metal concentration and the fraction analyzed.

All reagents employed were from Merck (Darmstadt, Germany) and of analytical grade or Suprapur quality. Standard working solutions of the different elements analyzed were prepared from the corresponding 1,000 mg/L of Merck Titrisol solutions.

Comparisons between sampling stations were performed by cluster analysis using the biomedical statistical package. The algorithm used was the normalized euclidean distance between the centered clusters.

RESULTS AND DISCUSSION

Table 3 shows the sum of the five fractions of the sequential extraction procedure and the heavy metal concentration found by applying the total digestion procedure [25]. When the sediment samples undergo the sequential extraction procedure, a high recovery for all the heavy metals is obtained. The results are particularly satisfactory for Cr and Cu, whereas the recovery observed for Mn and Pb is not so high.

Heavy metal concentrations for the five fractions of the sediment at each of the nine stations studied is presented in Figure 2. The concentration is expressed in μg/g, except for Fe, which is expressed in mg/g. The concentrations of the heavy metals (Cu, Zn, Cd, Pb, and Fe) from anthropogenic sources (corresponding to the first four fractions) are higher at OR than at CB or BR.

In Figure 3, the partitioning patterns for Cr, Mn, Fe, Cu, Zn, Cd, and Pb corresponding to each sampling site are presented as bar diagrams. The quantity of metal extracted in each step of the leaching scheme is given as a percentage of total metal content. The behavior of Cr and Fe was similar in all samples. Both metals were most abundant in the residual fraction and in the most highly polluted samples (OR). The third fraction was approximately 16.5% for Cr and 12 to 17% for

Table 3. Comparison between the heavy metal concentrations in the sediment of the studied stations obtained by adding the concentrations in the five fractions obtained by the sequential extraction procedure and the metal levels obtained by the sediment total digestion procedure of Loring and Rantala [25][a]

	Odiel River salt marshes								
	A	B	C	D	E	F	G	CB	BR
Cr	99.99	98.26	99.72	99.10	93.46	82.87	102.97	97.35	92.24
Mn	85.63	77.96	87.57	91.13	84.35	102.12	74.64	98.29	90.75
Fe	103.21	102.66	117.96	106.38	80.57	89.96	88.84	111.08	92.94
Cu	110.02	117.17	95.90	103.45	96.32	107.37	103.17	77.64	96.03
Zn	90.31	86.86	86.35	82.81	92.36	94.98	103.37	108.86	102.02
Cd	112.47	80.71	118.83	98.11	90.39	83.41	104.38	104.38	89.43
Pb	98.40	82.26	90.80	88.60	97.78	84.31	83.54	101.30	87.66

[a] Results are expressed as the percentage with respect to total digestion procedure. Sampling stations (A–G) are located in the Odiel River salt marshes (Huelva, Spain) in Cadiz Bay (CB) and Barbate River (BR) salt marshes (Cadiz, Spain).

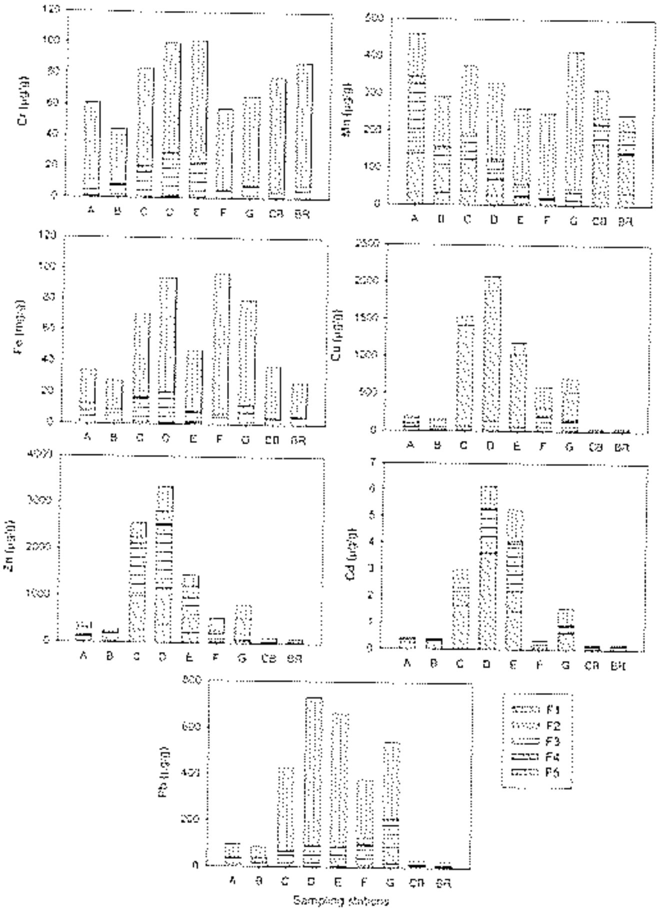

Fig. 2. Speciation of trace metals in the sediments of the Odiel River (A–G), Cádiz Bay (CB), and Barbate River (BR) salt marshes (see Fig. 1). Results are expressed as µg/g dry sediment, except for Fe (mg/g dry sediment). Fraction (F) 1 to F5 correspond to fractions of the Tessier sequential procedure.

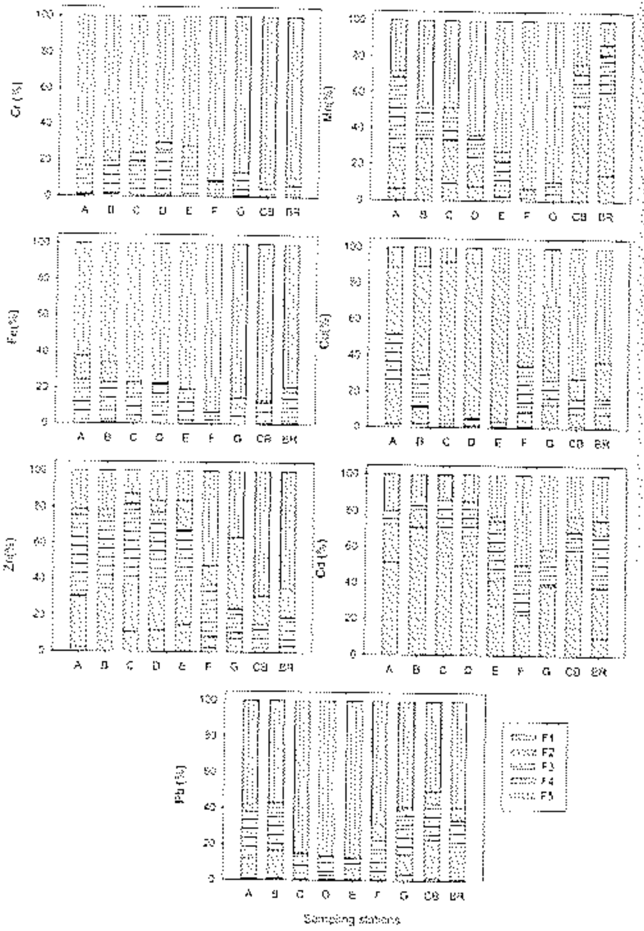

Fig. 3. Speciation of trace metals in the sediments of the Odiel River (A–G), Cádiz Bay (CB), and Barbate River (BR) salt marshes (see Fig. 1). Results are expressed as a percentage with respect to total digestion. Fraction (F) 1 to F5 correspond to fractions of the Tessier sequential procedure.

Fe. This behavior is in agreement with the partitioning found in other coastal ecosystems (Table 4).

The partitioning patterns of Mn, Cu, and Zn at CB and BR are similar and differ from those observed at OR. At the first two sites, Mn was extracted mainly in the second fraction, related to metal bound to carbonates, and the third fraction, related to metal bound to Fe and Mn oxyhydroxides. In the same two areas, substantial amounts of Mn were also extracted in the exchangeable (F1) and residual (F5) fractions. In these two areas, Mn speciation coincides with the results reported in the Acheloos River estuary [29] and in CB [22]. The Mn has an affinity to carbonates in both lacustrine and coastal sediments [30]. At OR, Mn was extracted mainly in the residual fraction, but F1, F2, and F3 (in that order) were also well represented. This partitioning pattern is similar to that found in the Huelva estuary [31]. The high percentage of Mn previously reported, associated with the residual fraction (F5) in the sediments of OR, is in agreement with previous observations [32] that in sediments contaminated by mine drainage waters, as is the case with OR, Mn is mainly concentrated within the crystalline structure of the primary and secondary minerals.

Regarding Cu, in the samples from CB and BR the residual fraction (F5) was approximately 62.9 to 72.3%. This indicates the mineralogical origin of this metal in these zones and its reduced mobility from the water–sediment interface. However, in the samples from OR, copper was extracted mainly in F4 (21.4–87.9%) and was related to the solubilization of oxidizable phases from sediments (organic matter and sulfide). The amount of residual metal (F5) was low in comparison to the total metal content (8.2–44.1%). This indicates the anthropogenic source of this metal as a consequence of the industrial and mining activities as well as from moderate urban pollution.

In the CB and BR sediments, Zn was mostly concentrated in the residual fraction (64.8–69%). The distribution of nonresidual metal species was between the fractions dissolved by reducing or oxidizing reagents (F3 and F4, respectively). On the contrary, in all the samples from OR, the percentages of total metal extracted from the residual minerals (F5) were lower and ranged from 12.5 to 52.4%. The distribution of nonresidual Zn in decreasing order was in F3, F2, and F4. The distribution pattern in the OR coincides with that reported by other authors in this area, and the speciation pattern found in CB and BR is also similar to that presented for CB (Table 4).

The Cd behaved similarly in all samples. Being a mobile heavy metal, it was present in F1 (20–70% in most samples) and was mainly distributed among the first three fractions (>70% of total Cd). At OR, it was principally extracted in F1 and, at CB and BR, in F2 and F3. Small amounts of metal remained in F4 and F5.

The Pb was mainly present in the residual fraction in all samples, although the percentage of this metal bound to re-

Table 4. Speciation of the analyzed heavy metals in the sediment of different coastal systems[a]

Metal	Ecosystem	F1	F2	F3	F4	F5	References
Cr	Acheloos River estuary, Greece	2	1.5	7.1	1.1	88.3	[29]
	Coastal sediment, Baja California, USA	0.25	0.26	5.3	4.1	90	[38]
	Huelva estuary, Spain	0	0	15	10.7	74.3	[31]
	Odiel River salt marshes, Spain	0	0	0	8.8	91.2	[22]
	Cádiz Bay	0	6.9	6.4	8.3	78.4	[22]
	Odiel River salt marshes	0.3	0.7	16.5	3.5	79.0	Present study
	Cádiz Bay salt marshes	0	0.5	3.6	3.3	92.6	Present study
	Barbate River salt marshes	0	0.6	5.5	4.5	89.4	Present study
Mn	Acheloos River estuary, Greece	1.1	72.1	11.2	13.4	13.4	[29]
	Huelva estuary, Spain	9.3	0	25	58.6	58.6	[31]
	Cádiz Bay	11.7	41.1	16.2	22.8	22.8	[22]
	Odiel River salt marshes	5.3	12.9	16.2	63	63	Present study
	Cádiz Bay salt marshes	11.1	42.3	17.3	23.7	23.7	Present study
	Barbate River salt marshes	14.5	44.6	22.4	12.6	12.6	Present study
Fe	Acheloos River estuary, Greece	0.3	5.2	12.2	4.2	78.1	[29]
	Coastal sediment, Baja California, USA	0	0.4	6	1.6	92	[38]
	Huelva estuary, Spain	0	0.6	14	0.9	84.5	[31]
	Odiel River salt marshes, Spain	0	3.5	34	11.5	51	[22]
	Odiel River salt marshes	<0.1	0.9	17.3	4.4	77.3	Present study
	Cádiz Bay salt marshes	<0.1	0.6	11.6	1.3	86.4	Present study
	Barbate River salt marshes	<0.1	0.8	17.4	2.8	79	Present study
Cu	Humber estuary, UK	2	6.1	8.2	53.1	30.6	[41]
	Mersey estuary, UK	1.8	12.9	10.5	37.4	37.4	[41]
	Vigo estuary, Spain	1.2	1.7	0.6	58	38	[42]
	Coastal sediment, Baja California, USA	1.7	0	2.3	16	80	[38]
	Huelva estuary, Spain	13.3	0	2.9	60.9	22.9	[31]
	Odiel River salt marshes	1.4	7.5	14	58.9	18.2	Present study
	Cádiz Bay salt marshes	1.4	6.8	8.2	11.3	72.3	Present study
	Barbate River salt marshes	1.1	6.9	8.8	20.3	62.9	Present study
Zn	Vigo estuary, Spain	0	10	34	11	39	[42]
	Huelva estuary, Spain	15.7	18.9	28.8	12.9	24.3	[31]
	Cádiz Bay	3.5	9.5	20	7	60	[22]
	Odiel River salt marshes	7.9	19.5	35.1	12.3	25.2	Present study
	Cádiz Bay salt marshes	0	2.5	12.6	15.9	69	Present study
	Barbate River salt marshes	0	3.6	15.4	16.1	64.8	Present study
Cd	Humber estuary, UK	31.9	37.7	26.1	4.3	0	[41]
	Mersey estuary, UK	34.2	29.1	22.8	6.3	7.6	[41]
	Huelva estuary, Spain	46.1	9.9	16.3	14.9	12.8	[31]
	Odiel River salt marshes	45.7	10.5	17.7	2.2	24.9	Present study
	Cádiz Bay salt marshes	15.5	38.5	14.6	8.8	22.6	Present study
	Barbate River salt marshes	9.9	27.6	30	7.7	24.8	Present study
Pb	Mersey estuary, UK	5.3	16.8	55	9.2	13.7	[41]
	Vigo estuary, Spain	0	9	31	8	53	[42]
	Huelva estuary, Spain	0	10	10.7	2.9	77.1	[31]
	Odiel River salt marshes	0.9	7.6	17.3	2.6	71.5	Present study
	Cádiz Bay salt marshes	1.4	21.7	20	6.8	50	Present study
	Barbate River salt marshes	1.1	13.8	18.9	7	59.2	Present study

[a] Results are expressed as the percentage of total metal concentration. Fraction (F) 1 to 5 correspond to the fractions of the sequential extraction technique of Tessier et al. [8].

sidual minerals (F5) differed widely among stations (50–90%). After the residual fraction, F3 and F2 had the greatest abundances of Pb (6–26% for F3 and 2–22% for F2). In all samples, the exchangeable metal content was very low (<2% of the total metal concentration). In the sediments from OR, the percentages of Pb associated with the residual fraction (F5) are the same as those found in the sediments of CB and BR except for locations C, D, and E, where the percentages are higher. Despite qualitative similarities, at all the OR sites Pb content was high and characteristic of contaminated sediments (Fig. 2). Samples from OR showed that Pb is present in the residual fraction [33]. At sites C, D, and E, where the percentages of this metal in the residual fraction (F5) are relatively high, the Pb origin in the sediment is mainly lithogenic. In anthropogenic polluted sediments [34], Pb is principally associated with F3 (iron–manganese oxyhydroxides); therefore, CB and BR and locations A, B, F, and G in OR represent the areas with the greatest severity of Pb pollution.

A cluster analysis was carried out to classify the sampling stations according to their heavy metal content and speciation. The dendogram (Fig. 4) allows three groups to be established. Group 1 corresponds to all the stations of CB and BR as well as to sampling stations A and B of OR; all of these show the lowest values for heavy metals. Group 2 includes stations F and G of OR, both of which display high levels of metals as a consequence of a chronic pyritic contamination from the mining activities of this area. Group 3 comprises stations C, D, and E of the OR salt marshes, which are moderately contaminated by mining activities and also affected by the chemical industries of Huelva.

The degree of environmental risk can be predicted by the use of the environmental risk factor (ERF), defined as CSQV

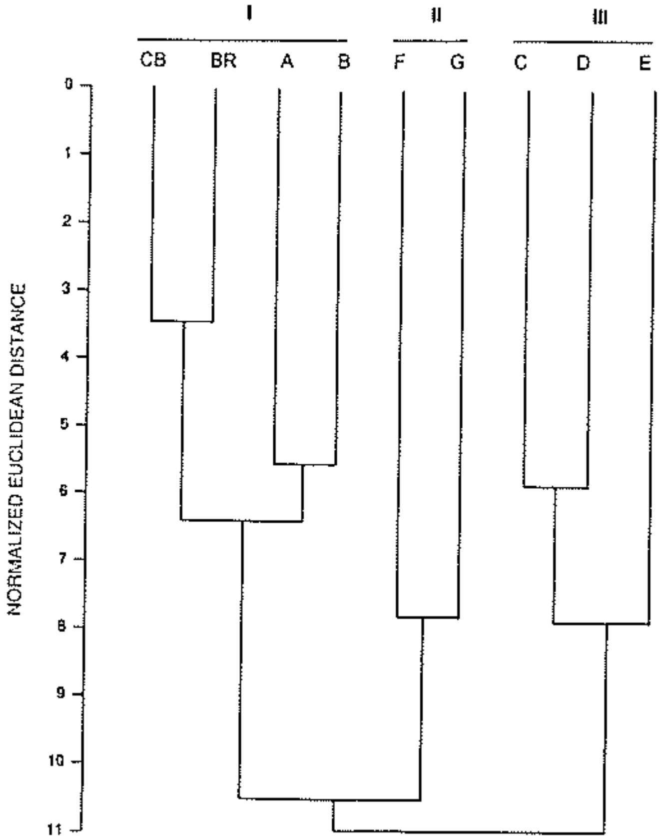

Fig. 4. Dendogram showing clustering of sampling sites (A–G) for Odiel River, Cádiz Bay (CB), and Barbate River (BR) salt marshes (see Fig. 1).

– Ci/CSQV [35], where Ci is, in our case, the heavy metal concentration corresponding to the first four fractions (reactive fractions) and CSQV is the concentration sediment quality value, which corresponds to the highest concentration with no associated biological effect. The SQV data selected in the present study correspond to site-specific values for the Gulf of Cadiz [36,37]. For Cd, a value of 1.2 mg/kg, obtained from the biological effects database–sediments, was selected as the SQV. This value corresponds to effects range low, because site-specific values were not available. The definition of F1 to F4 as the bioavailable fractions was made following previously reported criteria [38]. Other authors [35] define F1 to F3 as the reactive fractions. However, we prefer the first definition, because the metal of the first four fractions can be mobilized. In any case, the ERF values were similar for most cases, regardless of whether the first three or four fractions are considered. F4 is included in our case to calculate Ci. All sampling stations of OR showed an ERF of less than zero for Cu and Zn, for Pb at stations E to G, and for Cd at stations C, D, E, and F. The stations of CB showed an ERF of greater than zero for all metals analyzed. The Fe and Mn were not considered because of their very limited toxicity when they are associated with sediments. Although the parameter SQV has limitations [39], the use of site-specific values allows us to avoid some of the drawbacks in their application for ecological risk assessment. The different operative fractions obtained by the procedure of Tessier et al. [8] or other proposed speciation schemes, such as the BCR [12] or acid-volatile sulfide [40], can also be useful for measuring the bioavailability of contaminants. In short, the ERF values calculated as the sum of the different operative fractions from the speciation procedure can be employed to predict the potential adverse effects of contaminated sediment on the ecosystem.

In summary, the highest proportions of metals in the sediments of CB and BR salt marshes occurred in the residual fraction, which means that they cannot be solubilized and, therefore, do not pose a threat to their environment. Although anthropogenic inputs are higher in CB than in BR salt marshes, the similarity in the heavy metal concentrations is related to different granulometric distribution; thus, the silt–clay size percentage represents approximately 30% in CB and 60% in BR salt marshes. However, the metals found in sediments of the OR salt marshes showed not only a considerably higher total metal content but also lower percentages associated with the residual fraction because of the mining activities (copper and pyrites) in this area since the times of the Tartesians and Romans and the nearby industrial area of Huelva. In general, this level of metal pollution does represent an environmental risk.

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