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Heavy metal fluxes at the sediment–water interface of three coastal ecosystems from south-west of the Iberian Peninsula

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Abstract

Concentrations of the heavy metals Cr, Cu, Fe and Mn were measured in sediments and porewater samples collected in three coastal ecosystems southwest of the Iberian Peninsula: the Odiel and Barbate River Salt Marshes and the Bay of Cádiz. Both the sediment and the porewater metal concentrations in the Odiel River Salt Marshes are higher than the values found in the Bay of Cádiz and Barbate River Salt Marsh, particularly for copper, a metal associated with mining activity. In porewater, the profiles were not the same as those in the solid phase and reflect the different behaviours of the elements in relation to the redox conditions. The heavy metals Cr and Cu show a typical enrichment in the porewater of the oxic zone. The heavy metals Mn and Fe show an increase in the porewater at the depths where the maximum nitrate and phosphate concentrations occur, respectively. Significant differences between background levels for each heavy metal in the various studied zones exist. Iron and Cu showed larger background levels in the Odiel River Salt Marshes than those in the Cádiz Bay and the Barbate River Salt Marshes. In the Bay of Cádiz the background levels are also high, particularly for Cr. At the Odiel River Salt Marshes the diffusive flux of Cu is high (1.3–230.1 μg cm^{-2} year^{-1}), which suggests that the Odiel River Salt Marshes are subject to strong contamination by Cu, which is presumably introduced to the sediment in particulate form. In the Bay of Cádiz, Cr is the only metal with positive diffusive flux (2.15 μg cm^{-2} year^{-1}). It is higher than those obtained in other coastal ecosystems including the Odiel River Salt Marshes. The positive diffusive flux of Cr has been associated with the input of this metal by the naval industry and the manufacturing of car and aircraft components. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Heavy metals; Coastal ecosystems; Sediment; Porewater; Diffusive fluxes; Background levels

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1. Introduction

Sediments may act as sources as well as sinks for certain trace elements (Petersen et al., 1995; Riedel et al., 1997). Most of the contaminants are adsorbed on suspended particulate matter (SPM) which can be transported into the sediment by flocculation and sedimentation. In the sediment–water interface, particularly within the oxic zone, enhanced mineralisation processes occur. These microbially catalysed reactions may change both the minerals on which trace elements are bound and their speciation and therefore also the mobility of the trace elements. Thus, diagenetic reactions may redissolve a portion of deposited materials into the porewater, from where diffusive fluxes, resulting from the concentration gradient at the sediment–water interface, may transport these dissolved contaminants from the sediments to the overlying water (Lyons and Fitzgerald, 1980; Lyons et al., 1983; Ciceri et al., 1992). The organic matter and the manganese and iron oxide phases are the main factors that govern the transport process velocity of metals in the pore water (Ciceri et al., 1992).

In particular, heavy metal fluxes in the sediment–water interface are very important in coastal areas with high productivity. These ecosystems have a lot of organic matter in their sediments, which produces reduced zones close to surface. The aims of this work were to establish the sign and importance of the diffusive flux of metals (Cr, Cu, Fe and Mn) in three littoral ecosystems of the Iberian Peninsula, and the distribution and pattern of heavy metals in sediment and porewater phases.

2. Materials and methods

2.1. The study area

The Bay of Cádiz and the Odiel and Barbate River Salt Marshes are located on the southwest of the Iberian Peninsula (Fig. 1). The Odiel River Salt Marshes are affected by inputs of contaminants from the Huelva industrial area and the Odiel River, which flows through a well-known mining area called the ‘Cinturón Pirítico Ibérico’ (Iberian Pyrite Belt). The Bay of Cádiz suffers intense harbour traffic and has supported for decades an important industrial activity related to the naval construction. During recent years this activity has diversified by incorporation of other industries utilising metals for the manufacture of car and aircraft components. The Barbate River Salt Marsh is an area lacking domestic and industrial contaminants and its inputs could be related to agriculture activities.

2.2. Sampling and sample pre-treatment

Sediment samples were taken in June–July 1996 in five sampling stations: SC, DR and CI in the Odiel River Salt Marshes (zone 1); GA in the Bay of Cádiz (zone 2); and the other one (BA) in the Barbate River Salt Marshes (zone 3). Their locations are shown in Fig. 1. Sediments were collected using PVC sediment cores of 40-cm length and 4-cm diameter. Within 3 h, the sediment cores were transported to the laboratory into a refrigerator and were frozen at −30°C until their processing. Cores were placed in an anaerobic hood with a N_2 atmosphere and sectioned into samples of 1-cm thickness from the surface down to 30 cm in depth. After defrosting, the different core sections were packed into 15-cm Pyrex tubes and centrifuged at $37\,000 \times g$ for 60 min to separate porewater, which was divided into two parts, one for the heavy metal analysis and the other for the nutrient determinations. The porewater for the heavy metal analysis was acidified with HNO_3 to pH 1 and stored in a 20-ml polyethylene vial with a N_2 atmosphere at 4°C and in darkness. The porewater employed for the nutrient determinations was conserved in assay tubes with a N_2 atmosphere, until its analysis. Sediment obtained after centrifuging was dried at 70°C to a constant weight, homogenised and passed through a 1000-μm sieve.

2.3. Heavy metal and nutrient analysis

Metal concentrations in the sediment were de-

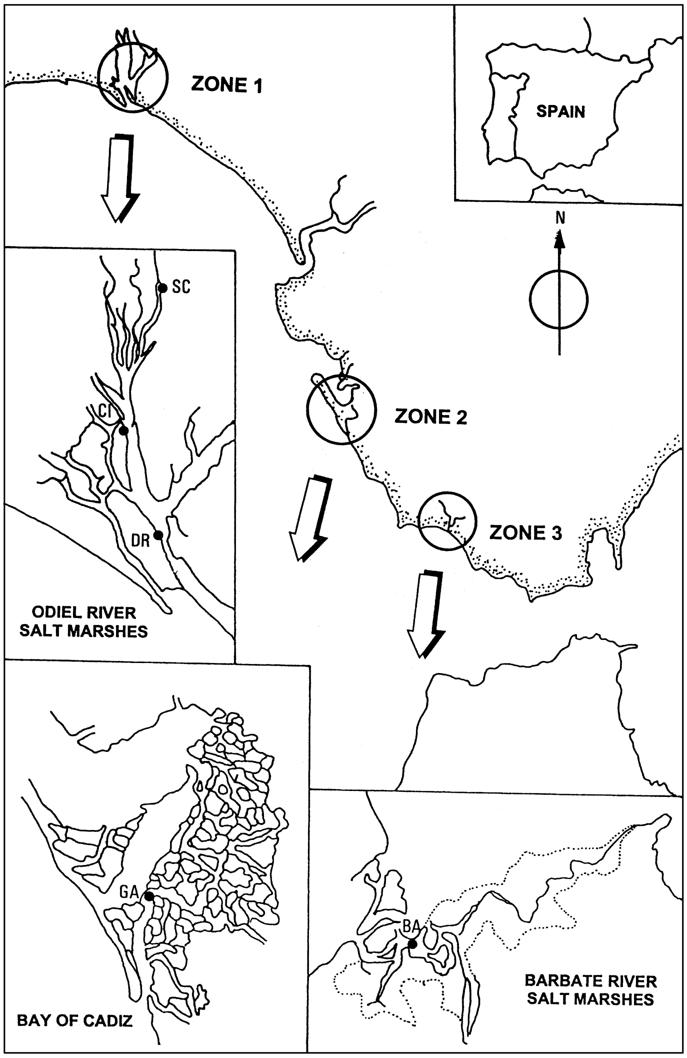

Fig. 1. Map of the Odiel River Salt Marshes, Bay of Cádiz and Barbate River Salt Marshes showing the sampling stations.

termined using the method described by Loring and Rantala (1992). This method consists of the treatment with a mixture of aqua regia (HNO_3/HCl, 1:3 v/v) and HF, which was added to the oven-dried sediment aliquot (approx. 0.1 g) in a 120-ml Teflon bomb. The mixture was heated in a 700-W microwave oven (Panasonic, mod. NN 6200) and then treated with boric acid (Bernas, 1968). This procedure was carried out in triplicate. Trace metal concentrations in the sediment were determined by flame atomic absorption spectrophotometry (AAS; Perkin-Elmer 3110). Sample blanks and reference sediment (Estuarine sediment 277 CRM certified by the Community Bureau of Reference, BCR) were used to ensure quality control in the quantification of the heavy metals in the sediments. The results obtained are shown in Table 1. Iron concentration in the porewater was determined by FAAS (Perkin-Elmer 3110) and Cr, Mn and Cu concentrations by GFAAS (Perkin-Elmer 4100 ZL). Nutrient determinations (NO_3^- and HPO_4^{2-}) in the porewa-

Table 1
Concentration and efficiency of the certified metals in the 277 CRM reference sediment from the Community Bureau of Reference, BCR, compared to those obtained in this study ($n = 3$)[a]

Heavy metal	CRM 277		Efficiency (%)
	This study	Certified	
Cr	155.3 ± 7	192.0 ± 7	80.9
Mn	1321.0 ± 22	1600.0	82.6
Fe	40700.0 ± 1222	45500.0	89.4
Cu	100.2 ± 1.3	101.7 ± 1.6	98.5

[a] The results are reported in $\mu g\ g^{-1}$ dry wt.

ter were performed in a Technicon Traacs 800 Autoanalyser using the procedure described by Forja (1991).

2.4. *Diffusive fluxes and background levels*

From the concentration gradients in the porewater, diffusive fluxes of trace elements from the sediment to the water column have been calculated by means of Fick's First Law of Diffusion:

$$J = -\phi D_s \left(\frac{\partial c}{\partial z} \right)_{z=0}$$

where J is the diffusive flux, ϕ is the porosity at the sediment–water interface, D_s is the molecular diffusion coefficient, and $(\partial c / \partial z)_{z=0}$ is the concentration gradient evaluated at the sediment–water interface. The molecular diffusion coefficient (D_s) is calculated from the empirical equation of Sweerts et al. (1991):

$$D_s = D_0 \cdot (-0.73\phi + 2.17)^{-1}$$

where D_0 is the diffusion coefficient in water (Li and Gregory, 1974).

Heavy metal background levels in the sediment have been calculated averaging the whole of available data from a depth greater than 15–20 cm.

3. Results

3.1. *Sediment and porewater metal concentration profiles — background levels*

The profiles of heavy metals in sediment showed an irregular pattern. In porewater, the profiles were not the same as in solid phase and reflect the different behaviours of the elements in relation to the redox conditions. Sediment and porewater profiles for analysed heavy metals in the three studied areas are shown in Figs. 2 and 3, respectively. Both the sediment and the porewater metal concentrations in the SC, DR and CI stations (Odiel River Salt Marshes) are higher than the values found in the GA and BA stations (Bay of Cádiz and Barbate River Salt Marshes, respectively), particularly for Cu, a metal associated with the mining activity. The heavy metals Cr and Cu show a typical enrichment in the porewater of the oxic zone. The heavy metals Fe and Mn show an increase in the porewater at depths ranging between 4 and 10 cm. Manganese showed its concentration maximum at a lesser depth than Fe.

The background levels for heavy metals analysed are shown in Table 2. The background levels for Fe and Cu are larger in the Odiel River Salt Marshes stations than those observed in the Bay of Cádiz and the Barbate River Salt Marshes stations, and the same in the three areas for Cr and Mn.

3.2. *Nutrient concentrations*

The nitrate and phosphate concentration data in the studied stations are shown in Tables 3 and 4, respectively. A nitrate concentration maximum that exceeds even the existing value at the surface is observed in the Odiel and Barbate River Salt Marshes at a depth ranging between 4 and 7 cm, depending on the station. A phosphate concentration maximum is produced in the Odiel and Barbate River Salt Marshes at a depth just below the depth where the nitrate concentration maximum is observed.

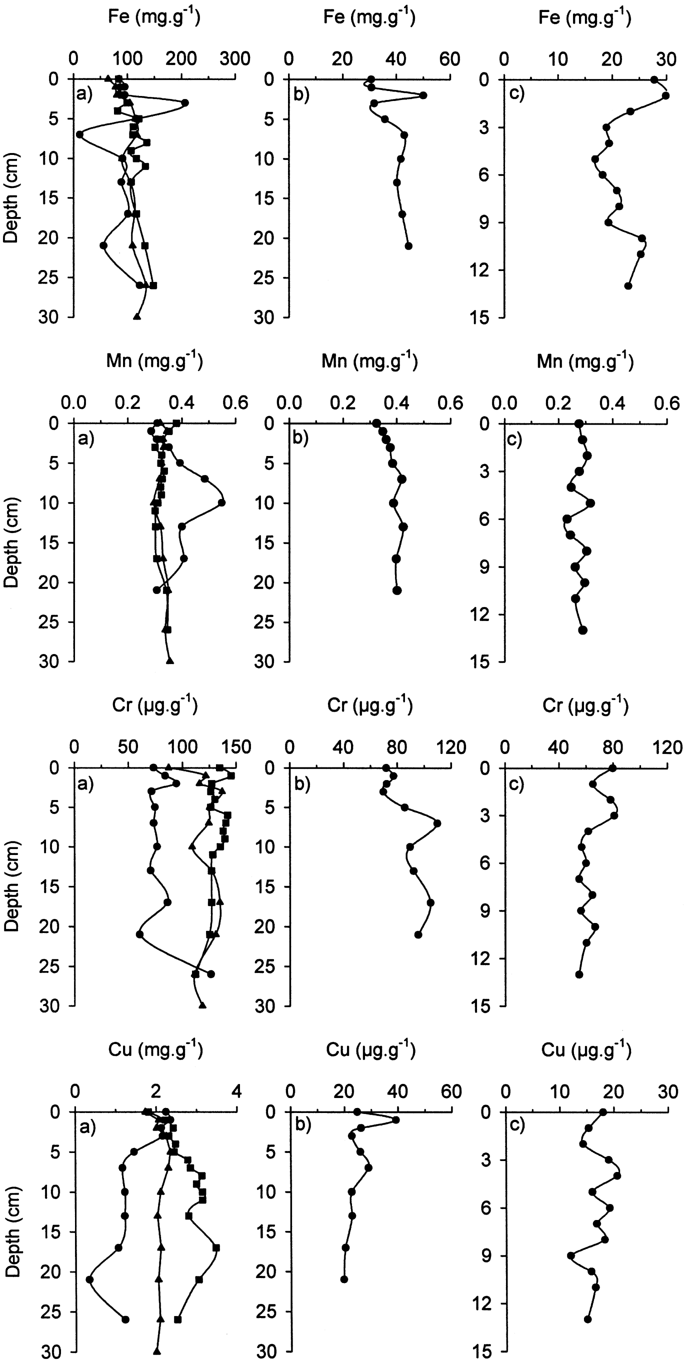

Fig. 2. Sediment heavy metal concentration profiles at the studied zones. (a) Odiel River Salt Marshes: ●, SC; ■, DR; ▲, CI. (b) Bay of Cádiz. (c) Barbate River Salt Marshes.

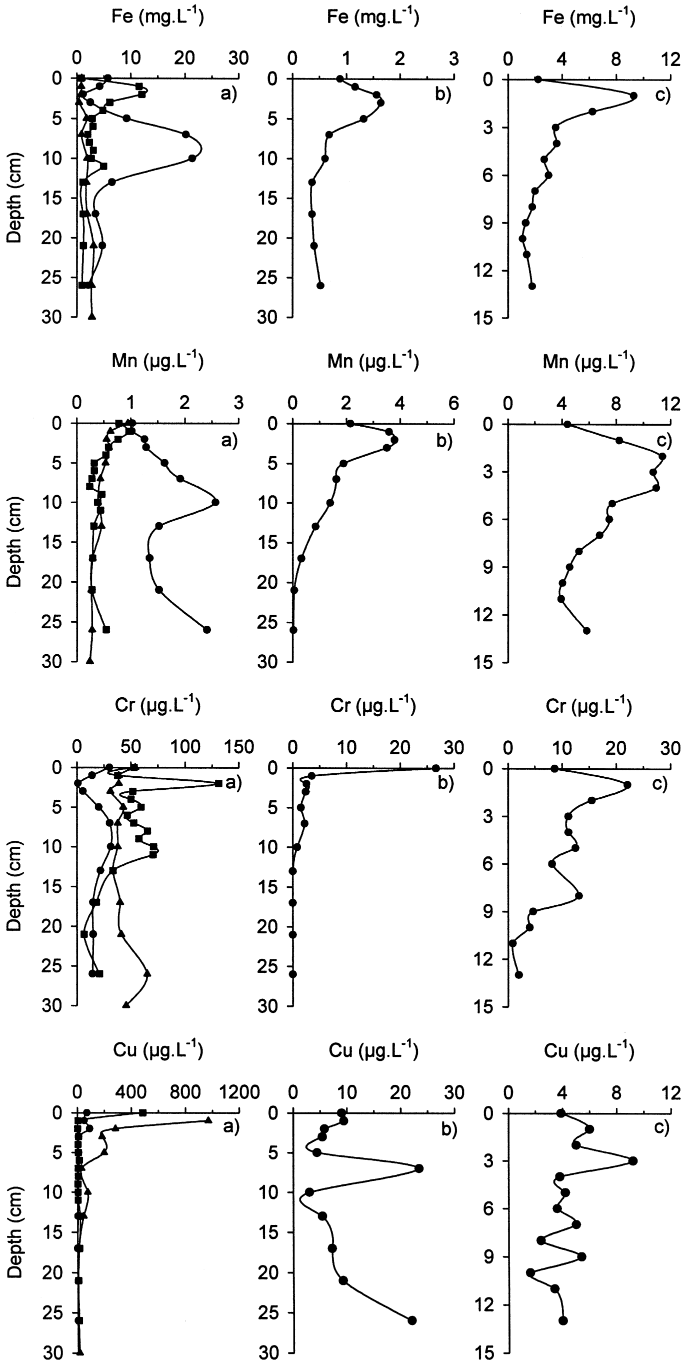

Fig. 3. Porewater heavy metal concentration profiles at the studied zones. (a) Odiel River Salt Marshes: ●, SC; ■, DR; ▲, CI. (b) Bay of Cádiz. (c) Barbate River Salt Marshes.

Table 2
Heavy metal background levels in the different sampling stations[a]

Heavy metal	Odiel River Salt Marshes			GA	BA
	SC	DR	CI		
Cr	90.9	121.3	123.7	97.4	60.4
Mn	371.3	324.0	343.0	402.8	278.0
Fe	91.7	131.9	118.5	42.2	22.5
Cu	870.6	3000.1	2054.7	21.3	14.8

[a] Concentration values are expressed in $\mu g\ g^{-1}$, except for Fe (given in $mg\ g^{-1}$).

3.3. Heavy metal diffusive fluxes

The diffusive fluxes of trace elements in the Odiel River Salt Marshes, the Bay of Cádiz Salt Marshes and the Barbate River Salt Marshes are shown in Table 5. The results are compared with others obtained by different authors in other coastal ecosystems. At the Odiel River Salt Marshes stations the diffusive fluxes of Cr and Cu are positive which implies a release of these trace elements to the water phase. Positive diffusive fluxes for Fe were observed at the SC and CI stations and at the CI station for Mn as well. In the salt marshes of Cádiz Bay (GA) only Cr showed a positive diffusive flux and in the Barbate River Salt Marshes the diffusive fluxes for all the analysed heavy metals were negative. In the Odiel River Salt Marshes the fluxes are higher than the values found in the Bay of Cádiz and Barbate River Salt Marshes.

4. Discussion

The heavy metals Cr and Cu show a typical enrichment in the porewater of the oxic zone (first 3 cm) because they are associated with particulate organic substances and can be remobilised due to the strong mineralisation of these compounds in this zone (Klinkhammer et al., 1982; Petersen et al., 1995). In the deeper anaerobic layers the degradation of organic material is limited by the supply of less effective oxidising agents.

Under anoxic conditions the evolution of trace elements in the water overlying the sediment is determined by the release of the reductively formed Fe(II) and Mn(II) species as well as the sulfide arising from the reduction of SO_4^{2-}. At a depth ranging between 4 and 7 cm, depending on the station, a maximum in the nitrate concentration was observed (Table 3), produced according to a nitrification process happening in the upper layer of sediment, in the transition zone in redox conditions, in the presence of oxygen (Henriksen et al., 1981; Lohse et al., 1993). At the same depth as the maximum nitrate concentration, Mn is released, followed by the liberation of Fe at a depth ranging between 4 and 10 cm, depending on the station. This depth coincides with the appearance of a maximum in the phosphate concentration (Table 4). In the oxic zone of the sediments, a decrease of the porewater phosphate concentration with the depth is produced connected with the strong adsorption capacity of the phosphate by the iron oxyhydroxide phases. In the anoxic sediments, at a depth higher than the transition zone, the iron oxyhydroxide phases are transformed into FeS and FeS_2, which are poorly efficient sulfide phases to adsorb the phosphate (Krom and Berner, 1980; Van Raaphorst and Kloosterhuis, 1994; Barbanti et al., 1995; Petersen et al., 1995). Consequently, at the depth of the maximum phosphate concentration, Fe is re-

Table 3
Nitrate concentration values (μM) at different depths and sampling stations[a]

	Depth (cm)	SC	Depth (cm)	DR	Depth (cm)	CI	Depth (cm)	BA
(1)	5	2.95	3	1.24	3	3.26	5	2.40
(2)	7	12.20	4	41.29	5	13.11	6	56.97
(3)	10	3.72	5	0.92	7	2.00	7	19.76

[a] The second line shows the depths of nitrate concentration maximums, lines 1 and 3 show nitrate concentrations above and below these depths, respectively.

Table 4
Phosphate concentration values (μM) at different depths and sampling stations[a]

	Depth (cm)	SC	Depth (cm)	DR	Depth (cm)	CI	Depth (cm)	BA
(1)	7	0.68	5	4.71	7	12.36	8	1.89
(2)	10	2.03	6	7.09	10	48.72	9	18.03
(3)	13	–	7	5.90	13	14.03	10	2.18

[a] The second line shows the depths of phosphate concentration maximums, lines 1 and 3 show phosphate concentrations above and below these depths, respectively. '–', below the equipment specific detection limit.

leased. This unusual tendency in the vertical evolution of the nitrate and phosphate concentration (decrease with the depth as far as the maximum appears) is found at all the stations except the Bay of Cádiz, where a diminution of the nitrate concentration and an increase of the phosphate concentration with the depth is observed.

In the anoxic sediments, iron and manganese oxyhydroxide phases are reduced leading to the release of trace elements which were coprecipitated or adsorbed by them. Release of heavy metals associated with the organic matter degradation contributes to the increase of the trace element concentration in the porewater. Desorption of trace elements associated with the sediment mineral phases, as a result of the pH decrease in the porewater because of the CO_2 concentration increase, contributes also to the increase of the trace element concentration in the porewater (Ciceri et al., 1992). A combination of these processes causes an increase of the Cr and Cu concentration at the depths of increase of Fe and Mn concentration. This effect is especially observed for Cr. Decreasing the Eh value results in sulfate reduction and, consequently, the heavy metal release is inhibited because of the formation of insoluble metallic sulfides (Petersen et al., 1995). This event is explained by the Cr, Cu, Fe and Mn concentration decrease at depths higher than 4–10 cm, depending on the station.

From a certain depth, where heavy metals mobilisation processes are less intense, their concentrations in the sediment tend to be constant. In consequence, heavy metal background levels

Table 5
Heavy metal diffusive fluxes expressed in μg cm^{-2} $year^{-1}$ in the different sampling stations of the Odiel River, Bay of Cádiz and Barbate River Salt Marshes, and in other coastal ecosystems[a]

Location	Cr	Mn	Fe	Cu	Reference
SC	0.47	−5.72	158.29	1.26	This study
DR	0.69	−16.24	−942.23	230.07	This study
CI	0.34	3.39	8.37	123.24	This study
GA	2.15	−106.09	−14.55	−0.03	This study
BA	−0.42	−210.51	−429.08	−0.13	This study
Ansedonia Bay, Italy	−0.004	696.38–1428.48	9.82–12.50	−0.05	Ciceri et al., 1992
The River Bang Pakong Estuary, Thailand	1.0–1.2	nd	nd	2.1–4.8	Cheevaporn et al., 1995
The River Elbe Estuary, Germany	nd	nd	nd	17.62	Petersen et al., 1995
The River Kalix Estuary, Sweden	nd	nd	nd	0.18–0.56	Winderlund, 1996
Bay of Cádiz, Spain	nd	nd	nd	0.46–15.3	Ponce, 1996

[a] nd, not determined.

can be established. Differences between background levels for each heavy metal in the various studied stations exist. Iron and Cu showed larger background levels in the Odiel River Salt Marshes than those observed in the Bay of Cádiz and the Barbate River Salt Marshes. The following order can be established according to the background levels: $\mathrm{DR} > \mathrm{CI} \gg \mathrm{SC} \gg > \mathrm{GA} > \mathrm{BA}$. Sedimentation rate data was available for none of the three studied zones and, therefore, it is not possible to carry out a dating (even an estimate) of the samples used to establish the background levels. High sedimentation rates can be expected in the three zones in any case, from which we can infer that the estimated heavy metal background levels cannot be considered free from the influence of previous contamination processes. This would justify the observed variations in the stations from the Odiel River Salt Marshes.

In the Odiel River Salt Marshes the background levels obtained in this study are high, particularly for Fe and Cu, in comparison with other data found in the bibliography for these and other coastal ecosystems (Table 6). If the results obtained in this study are compared with the background level data corresponding to a more than 3000-year-old sample of this area, obtained by Borrego and Pendón (1991) it can be observed that still at 20–30 cm in depth heavy metals concentrations have a partial anthropogenic origin for copper. Iron background levels are also higher in the Odiel River Salt Marshes than in Cádiz Bay (Establier et al., 1985) and in the Barbate River Salt Marshes (Cabrera et al., 1987).

In the Bay of Cádiz the background levels are also high, particularly for Cr, although the obtained data are not as high as those found in the Odiel River Salt Marshes. Gómez-Parra et al. (1990) have found a value of 50 $\mu g\ g^{-1}$ for the Cr background level in this zone at a different location from this work. A temporal evolution in Cr concentration over a large area was found, which may be closely related to successive modifications of industrial effluent outlets located in this zone. These authors have also found notable differences in heavy metal concentrations in certain zones of the bay, reaching the highest values in the flowing sounds from the bay. In the Barbate River Salt Marshes the background levels are characteristic of unpolluted sediments.

At the Odiel River Salt Marshes stations the diffusive fluxes of Cr and Cu are positive, which implies the releasing of these trace elements to the water phase. The flux of Cu is high in comparison with calculated flux by different authors in other coastal ecosystems, which suggests that the Odiel River Salt Marshes are subject to a strong contamination by Cu that is presumably introduced to the sediment in particulate form. The following order can be established for the sampling stations of this zone, according to the heavy

Table 6
Heavy metal background levels in the sediment of different zones[a]

Location	Cr	Mn	Fe	Cu	Observation	Reference
The Odiel Estuary, Spain	94.0	500	nd	15	More than 3000-year-old sample	Borrego and Pendón, 1991
The Tinto Estuary, Spain	58.0	214	nd	1389	30–40 cm deep	Conde, 1993
Bay of Cádiz, Spain	nd	350.9	29.8	22	50–55 cm deep	Establier et al., 1985
Bay of Cádiz, Spain	nd	nd	nd	60.6	20–30 cm deep	Ponce, 1996
The Barbate Estuary, Spain	nd	268.1	26.7	33.6	5–10 cm deep	Cabrera et al., 1987
Doñana, Spain	nd	478–661	nd	29.6–29.7	100 cm deep	Cabrera et al., 1987
The Severn Estuary, UK	nd	nd	nd	49.0	Pre-industrial	French, 1993
Average shale	90.0	850	46.7	45.0		Turekian and Wedepohl, 1961
The Odiel Estuary, Spain	112	346.1	114	1975	20–30 cm deep	This study
Bay of Cádiz, Spain	97.4	402.8	42.2	21.3	20–30 cm deep	This study
The Barbate Estuary, Spain	60.4	278.0	22.5	14.8	10–15 cm deep	This study

[a] Values are expressed in $\mu g\ g^{-1}$, except for Fe (given in $mg\ g^{-1}$); nd, not determined.

metal diffusive fluxes: for Cr, DR > SC > CI; and for Cu, DR > CI > SC. The diffusive flux for Fe is positive both in station SC and in station CI, which implies the release of this heavy metal to the water phase.

In the Bay of Cádiz, Cr is the only metal with positive diffusive flux. It is higher than those obtained in other coastal ecosystems (Ciceri et al., 1992; Cheevaporn et al., 1995) including the Odiel River Salt Marshes. This fact has been associated with the input of this heavy metal by the naval industry and the manufacturing of car and aircraft components (Gómez-Parra et al., 1990). In the Barbate River Salt Marshes the diffusive fluxes for the analysed heavy metals were negative.

The high diffusive fluxes observed for Fe and Cu in the Odiel River Salt Marshes are a consequence of the high concentrations of these trace elements in the sediment because of strong contamination of a mining and anthropogenic origin, respectively, and the existence of a 3-cm-thick layer of at the surface of the sediment with aerobic conditions.

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