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ORIGINAL PAPER

Distribution of heavy metals and pollution pathways in a shallow marine shelf: assessment for a future management

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Abstract The spatial distribution and geoaccumulation indices of four heavy metals were investigated in very shallow marine sediments of southwestern Spain. Surface sediments were collected from 43 sites with water depth ranging from 3 to 20 m. High to very high pollution levels ($I_{geo} > 4$ for zinc, lead and copper) were detected near the end of the Huelva bank, whereas chromium shows a more hazardous distribution in the southwestern Spanish littoral. Low to moderate heavy metal contents (mainly zinc and lead) were also observed in other two areas at different water depths (Isla Cristina-Piedras River: 10–18 m water depth; Mazagón–Matalascañas: <10 m water depth), whereas unpolluted to moderately polluted sediments were detected in the very shallow zones (<8 m water depth) located between the mouths of the Guadiana and the Piedras Rivers. A regional scenario indicates a strong pollution of the adjacent marine areas by polluted inputs derived from the Tinto–Odiel rivers, with a partial transport of heavy metals by W–E littoral currents even 40 km eastward. The Guadiana River is an additional source of zinc–lead contamination near the Spanish–Portuguese border, mainly at water depths up to 10 m. All these rivers are affected by acid mine drainage processes, derived from millennial mining activities. This pollution affects the sediment quality even 40 km eastward.

Keywords Environmental pollution · Trace metals · Geoaccumulation indices · Future assessment · Inner shelf

Introduction

In the last century, environmental impacts derived from anthropogenic inputs have increased in littoral areas, with remarkable effects in water quality, sediments or fauna. An environmental indicator of these impacts is the measurement of heavy metal concentrations in sediments (Yang et al. 2012), because some fluxes from different effluents, urban sewage, acid mine drainage processes or intensive agriculture may cause a remarkable increase in pollution that greatly exceed the natural background levels (Förstner and Wittmann 1979; Sekabira et al. 2010; Zhong et al. 2012).

Some elements (e.g., Cr, Cu, Pb, Ni) have been used to test the sediment degree of contamination and the original pollution sources. For example, high concentrations of Cu or Pb are related to recent or historical mining activities in some estuaries and shelves (Irabien et al. 2012; Duman et al. 2012), whereas Zn concentrations are markedly enhanced due to industrial wastewaters (Xia et al. 2012) and high Cr contents are derived from coal/oil combustion, acid mine drainage or urban wastes (Martins et al. 2012). In all cases, the sediment grain size plays an important role in controlling the distribution of these metals (Gao and Li 2012). In these investigations, it is important to use a previous background obtained from unpolluted sediments collected in sediment cores (Ruiz et al. 1998) or to characterize a regional or local background from surface

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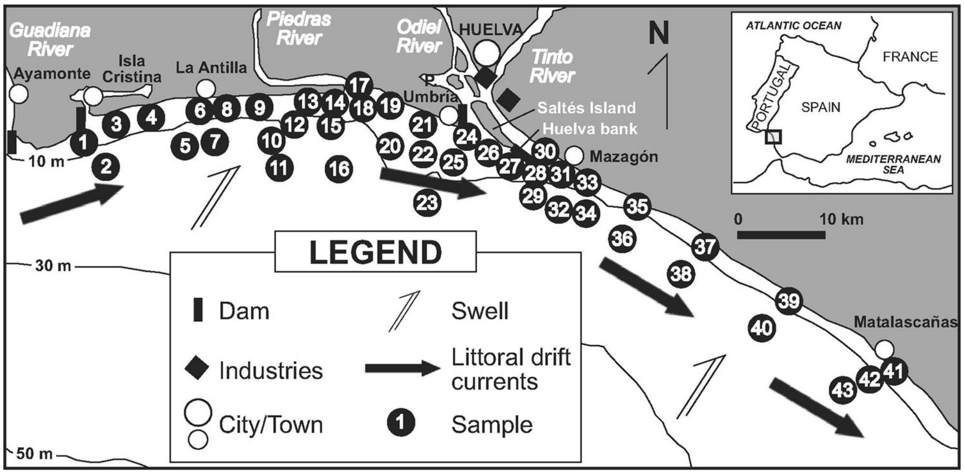

Fig. 1 Location map of the studied area, with inclusion of the main hydrodynamic features and sampling points

samples (Delgado et al. 2010) in order to delimitate the extent of pollution and to assess the contamination levels.

In addition, the analysis of enrichment factors and the application of bivariate or multivariate statistics are helpful to draw the areal extent of contamination and the factors contributing to its spread (Salomons et al. 1995; Prudencio et al. 2007). Moreover, these methods can discriminate the effects of specific pollution sources, such as populated urban areas, industrial establishments or vehicular emissions (Mohiuddin et al. 2010; Qi et al. 2010).

In southwestern Spain, there is a confluence of several factors (historical mining, industrial effluents and farm inputs) that have led to major environmental problems in the catchment areas of the Guadiana, Tinto and Odiel rivers (Fig. 1). At present, high pollution levels have been detected in estuarine sediments (Ruiz 2001; Borrego et al. 2002; Sainz et al. 2003; Delgado et al. 2010) and soils or plants are negatively affected (Madejón et al. 2009; Pérez-Lòpez et al. 2010). In highly polluted sites, the animals show a high frequency of histopathological lesions and bioaccumulation of metals (Riba et al. 2004). Consequently, this contamination represents a serious risk for the food chain in this area.

The aims of this paper are as follows: (a) to determine the pollution levels of bottom sediments in the adjacent shallow shelf of southwestern Spain; (b) to apply a geochemical background to draw the current state of pollution; (c) to delineate the coastal zone affected by possible pollution sources; and (d) to propose some guidelines for the future environmental management of this area.

Materials and methods

Description of the study area

The regional oceanography of the southwestern Spanish coast is controlled by the North Atlantic geostrophic current, which flows to the east within this study zone (Fig. 1). Littoral drift currents transport sand-size sediments from the Portugal coast to the Spanish nearshore zone (300×10^3 m^3/year; Cuena 1991).

Tidal regime, wave action and fluvial discharge control the hydrodynamic processes. The tidal regime is mesotidal (mean range 2.15 m; Borrego et al. 1993). Dominant waves associated with Atlantic circulation come from the southwest. Fluvial sediment runoff from the nearby land is important during December and January when rainfall is highest. Medium-grade, saltation-transported sand dominates the sediment input of the Guadiana, Tinto and Odiel rivers. Sediment supply by the Piedras River is restricted due to a dam upstream.

Fine and very fine sands are the most abundant sediments on the southwestern Spanish coast from Ayamonte to Matalascañas (Fig. 1). Coarser grain sizes are dominant in samples from down to 11 m water depth, which starts from La Antilla to Punta Umbría and near the mouths of the Guadiana, Tinto and Odiel rivers. Clay and silt deposits were found at the junction of the Tinto and Odiel rivers. The highest content of bioclastic material (mainly Mollusca) is associated with high percentages of medium-grained sands in the inner part of the Huelva bank and the deeper samples (>10 m) in front of the Piedras River mouth (Ruiz et al. 1997).

Environmental framework

The Guadiana, Tinto and Odiel rivers discharge into the Atlantic Ocean after flowing through the Iberian Pyrite Belt, in which large deposits of polymetallic massive sulfide are interbedded. Since prehistoric times, large scale mining and smelting operations have occurred on the river banks, and waters are extremely polluted by sulfide-associated heavy metals. Therefore, the Tinto and Odiel rivers transport very high quantities of these pollutants (Nieto et al. 2007), which represent 60 % of the global flux of dissolved Zn transported by rivers to the ocean and 17 % of the global flux of dissolved Cu (Olías et al. 2006). Moreover, the Guadiana River receives important polluted inputs from Spanish and Portuguese mines (Company et al. 2008).

In addition, large amounts of wastes and pollutant effluents have been discharged from a variety of chemical factories (phosphate fertilizer plants, chloro-alkali industries) and petroleum refineries located around the Tinto–Odiel estuary since the 1960s. The final consequence of these anthropogenic inputs is the presence of highly contaminated sediments in the Tinto–Odiel estuary. This area has been classified among the most polluted zones in the world, with extremely high concentrations of Cu (1,000–3,000 μg/g), Zn (400–3,400 μg/g) or Pb (150–4,900 μg/g) (Ruiz 2001; Borrego et al. 2002).

Impact of this pollution on the adjacent shelf is comparatively poorly known. Several investigations were focussed on very shallow areas (<5 water depth; Sainz and Ruiz 2006; Usero et al. 2008), whereas others are limited to a restricted zone of the shelf (Sánchez García et al. 2010) or the analysis of some isolated cores (Guerra et al. 2010). This paper attempts to delimitate the effects of these inputs on deeper areas of this littoral.

Sediment sampling

Surface sediment samples were collected from 43 stations located off the North Cádiz Gulf at depths ranging from 2.5 to 20 m (Fig. 1). Each sample was obtained by collecting the upper 5 cm of sediment with a Van Veen modified sediment-grab. The grain-size distribution was determined by sieving for particles greater than 63 μm, owing to the very high proportions of sand-size particles in all samples.

Analysis of sediments

Chemical analysis for heavy metals in sediment (Cr, Cu, Pb and Zn) was conducted by X-Ray Assay Laboratories, Toronto (Canada). These metals are used as tracers of anthropogenic inputs in numerous environmental studies (López-González et al. 2006; Harikumar et al. 2009).

Metal concentrations were determined on the bulk samples by X-Ray fluorescence spectrometry, with a previous nitric aqua regia digestion. Calibration is based on the analysis of over 40 international standard reference materials. Ten replicated were realized with very close results (error <7 %) in relation to the initial data. Analytical errors for each element were included in Table 1.

Determination of geoaccumulation index: pollution assessment

Metal pollution assessment from sediment analysis was based on the geoaccumulation index (Muller 1981):

$$I_{\text{geo}} = \frac{\mathrm{B}_n}{1.5 \times \mathrm{C}_n}$$

where B_n is the measured concentration of the element B in the n sample and C_n is the regional background of this element in unpolluted sediments. The factor 1.5 is used because of the possible variations of the background data due to lithogenic effects. This regional background was obtained for the different heavy metals and sediment grain sizes by Ruiz et al. (1998) in Holocene (>5,000 cal year BP), unpolluted marine sediments of the Tinto–Odiel estuary (Table 1).

Samples were divided into seven groups: unpolluted (Class 0: $I_{\text{geo}} \leq 0$); unpolluted to moderately polluted; (Class 1: $0 < I_{\text{geo}} \leq 1$); moderately polluted (Class 2: $1 < I_{\text{geo}} \leq 2$); moderately to heavily polluted (Class 3: $2 < I_{\text{geo}} \leq 3$); heavily polluted (Class 4: $3 < I_{\text{geo}} \leq 4$); heavily to extremely polluted (Class 5: $4 < I_{\text{geo}} \leq 5$); and extremely polluted (Class 6: $I_{\text{geo}} > 5$). This index has been utilized to assess metal enrichment of sediments (e.g. Mohiuddin et al. 2010).

Statistical procedures

A statistical study of the geoaccumulation index set was accomplished by multivariate analysis. The variables were row-normalized scaling the raw analytical data of each element to zero mean and unit variance in order to eliminate the effect of differences in magnitude and variance of the data. The next step was to calculate the Pearson's linear correlation coefficient matrix between the different heavy metals and the partial correlation between them, indicating the probability level for each pair. This coefficient is expressed as:

$$r = \frac{\sum_{i=1}^{n} (x_i - \bar{x})(y_i - \bar{y})}{\sqrt{\sum_{i=1}^{n} (x_i - \bar{x})^2 \sum_{i=1}^{n} (x_i - \bar{x})^2}}$$

Values range from (−1) to 1, indicating a direct (positive values) or an inverse (negative values) relation between two variables (x,y). In this study ($n = 43$), this coefficient is significant ($p > 95$ %) if $|r| > 0.3$ (Table 2).

A cluster analysis was applied using the Statistical Package for the Social Sciences (SPSS$^{\text{TM}}$). This analysis permits to establish different groups of samples with similar geochemical concentrations or to detect outliers with very high or very low contents. The clustering method was the Ward's method, with a former elaboration of the agglomeration distance plot to decide the adequate distance

Table 1 Grain size, heavy metal concentrations (in mg kg^{-1}) and geoaccumulation indices of samples

Sample	Grain size	Cr		Cu		Pb		Zn	
		µg/g	I_{geo}	µg/g	I_{geo}	µg/g	I_{geo}	µg/g	I_{geo}
1	MS	12	0.42	4	<0	4	0	41	2.19
2	FS-VFS	62	2.2	72	1.88	54	3.17	226	3.24
3	MS	20	1.15	6	<0	6	0.58	55	2.61
4	MS	19	1.08	6	<0	4	0	57	2.66
5	FS-VFS	10	<0	31	0.67	126	4.39	86	1.84
6	MS	21	1.22	9.5	0.08	9	1.17	76	3.08
7	FS-VFS	51	1.92	56	1.52	60	3.32	189	2.98
8	FS-VFS	58	2.1	21	0.11	22	1.87	146	2.61
9	FS-VFS	60	2.15	20	0.03	27	2.17	137	2.51
10	FS-VFS	67	2.31	48	1.3	69	3.52	155	2.69
11	MS	10	0.15	26	1.53	23	2.52	72	3
12	FS-VFS	27	1	40	1.04	32	2.42	154	2.68
13	FS-VFS	43	1.67	20	0.04	15	1.32	141	2.55
14	FS-VFS	59	2.13	20	0.04	24	2	135	2.49
15	FS-VFS	42	1.63	69.5	1.83	42	2.81	245	3.35
16	FS-VFS	7	<0	17.5	<0	14	1.22	52	1.11
17	FS-VFS	61	2.18	24	0.3	30	2.32	178	2.89
18	FS-VFS	56	2.05	18	<0	22	1.87	161	2.75
19	FS-VFS	81	2.58	22	0.17	20	1.74	161	2.75
20	FS-VFS	33	1.29	52	1.42	29	2.27	252	3.39
21	FS-VFS	77	2.51	40	1.04	30	2.32	203	3.08
22	MS	5	<0	26	1.53	6	0.58	75	3.05
23	FS-VFS	8	<0	23	0.24	20	1.74	74	1.62
24	FS-VFS	25	0.89	35	0.84	23	1.94	186	2.95
25	FS-VFS	16	0.24	26	0.42	15	1.32	144	2.58
26	MS	16	0.83	9	0	7	0.81	62	2.78
27	MS	3	<0	17	0.92	12	1.58	61	2.76
28	FS-VFS	53	1.97	421	4.43	295	5.62	611	4.67
29	FS-VFS	51	1.92	305	3.97	135	4.49	592	4.62
30	FS-VFS	10	<0	85.5	2.13	517	6.43	177	2.88
31	FS-VFS	45	1.74	77	1.98	90	3.91	278	3.53
32	FS-VFS	33	1.29	177	3.18	105	4.13	375	3.97
33	FS-VFS	46	1.77	79	2.02	63	3.39	354	3.88
34	FS-VFS	39	1.53	400	4.36	100	4.06	77	1.68
35	FS-VFS	48	1.83	63	1.69	50	3.06	249	3.38
36	FS-VFS	40	1.57	108	2.47	90	3.91	272	3.5
37	FS-VFS	56	2.05	59	1.6	58	3.27	335	3.8
38	MS	16	0.83	8	<0	9	1.17	36	2
39	FS-VFS	50	1.89	46	1.24	54	3.17	299	3.64
40	FS-VFS	32	1.24	55	1.5	53	3.14	188	2.97
41	FS-VFS	47	1.8	45	1.21	49	3.03	308	3.68
42	FS-VFS	36	1.42	53	1.44	53	3.14	252	3.39
43	FS-VFS	31	1.2	20	0.04	23	1.94	112	2.22
Background	MS	6		6		2		6	
	FS-VFS	9		13		4		16	
Analytical error (µg/g)		1		0.5		2		0.5	

MS medium sand, *FS* fine sand, *VFS* very fine sand. Background from Ruiz et al. (1998)

for the division between clusters. A rescaled distance of five units was used to separate the different clusters (Fig. 3).

Results and discussion

Spatial distribution of heavy metal concentrations and geoaccumulation indices

The chromium content varies between 3 (sample 27) and 81 µg/g (sample 19). The majority of samples (~70 %) are moderately or moderately to heavy polluted (Table 1: $1 < I_{geo} < 3$), whereas some unpolluted sediments occur near between Isla Cristina and Punta Umbría, and for a water depth between 4.5 and 18 m (Fig. 2). A moderate pollution was located mainly near the Piedras River mouth ($2.05 < I_{geo} < 2.58$).

High to very high levels of Cu were only found in four samples collected near the end of the Huelva bank (177–421 µg/g; $3.18 < I_{geo} < 4.43$), whereas other twenty-nine samples (67.4 %) fall in a range of 20–100 µg/g and an associate I_{geo} between 0 and 2. Most of unpolluted sediments (5 samples) were located in the shallow areas (<8 m water depth) between Isla Cristina and Punta Umbría.

Significant anomalies of Pb (>100 µg/g; $I_{geo} > 4$) were detected in front of Isla Antilla and near Mazagón. Heavily polluted sediments are found between Mazagón and Matalascañas (<8 m water depth in most cases) and between Isla Cristina and Isla Antilla (12–20 m water depth). Unpolluted areas are located in the Carreras River mouth and near Punta Umbría, to the east of Saltés Island, at water depths between 4 and 8 m.

High concentrations of Zn (354–611 µg/g; $3.88 < I_{geo} < 4.67$) were measured near the end of the Huelva spit. These values decrease significantly toward the east, with higher mean values at depths down to 10 between Mazgón and Matalascañas). Moderate to high I_{geo} values of this metal (2.1–3.4) characterize the Isla Cristina-Punta Umbría littoral stretch (4–18 m water depth).

Correlation analysis

The Pearson's product moment correlation coefficients are significant (probability up to 99 %) except for two element pairs studied (Table 2a: Cr–Cu and Cr–Pb). The high degree of correlation is very evident between Cu and Pb ($r = 0.805$), whereas Zn was correlated, to a lesser extent, with the three remaining metals ($0.449 \leq r \leq 0.606$).

An additional analysis of partial correlation confirms these high correlations but shows an interesting change for the Pb–Zn pair (Table 2). The partial coefficient ($r = -0.065$) indicates that the initial connection of Pb and Zn (Table 2; $r = 0.485$; $p > 99$ %) was linked to the common correlation with Cu and not between them.

Cluster analysis

On the basis of the geoaccumulation indices (Cr, Cu, Zn, Pb), five statistical significant sample groups can be determined (Fig. 3a), which are depicted on the Huelva littoral map (Fig. 3b). Samples included in each sample present similar geochemical features in most of cases. Table 3 summarizes the metal pollution assessment for each cluster.

Cluster 1 (15 samples) includes the majority of shallow samples (<10 m water depth) collected between Isla Cristina and Punta Umbría and two isolated, deeper samples (14–18 m water depth) located between Mazagón and Matalascañas. These medium and fine sands present very low concentrations of Cu and moderate to high pollution levels for Cr, Pb and Zn. Cluster 2 (three samples) differs from Cluster 1 in the presence of highly polluted sediments by Pb and lower concentrations of Cr. These samples are adjacent to Cluster 5.

Cluster 3 (7 samples) spreads over a zone located between the Piedras River mouth and Punta Umbría (Fig. 3b). This group presents the lowest heavy metal contents of the area studied, except for Zn. These low values contrast with those detected in Cluster 4 (2 samples), with very high I_{geo} values for Cu, Pb and Zn. These samples are confined to the end of the Huelva bank.

Finally, Cluster 5 (16 samples) is dominant in the Mazagón–Matalascañas stretch and includes additional samples collected between Isla Cristina and Punta Umbría (8–20 m water depth in most cases). In these two areas, sediments are heavily polluted by Pb and Zn.

Heavy metal concentrations measured in shallow marine sediments of southwestern Spain can be explained by different hydrodynamic and physical–chemical processes. In the western sector, moderate contents of some pollutants (mainly Pb and Zn) are deposited mainly at water depths up to 10 m between Isla Cristina and the Piedras River mouth (Fig. 3b: Cluster 5), although Zn presents an additional, diffuse pollution in shallower areas (Fig. 2).

It is likely that this pollution comes from the contributions of the Guadiana River, which also drains a significant part of the Iberian Pyrite Belt with a remarkable mining activity since the 19th century. These inputs have caused the contamination by heavy metals (mainly Zn and Pb) in the river mouth and the adjacent zones (Corredeira et al. 2008). Littoral drift currents will lead this pollutant flow toward the east in a direction nearly parallel to the coast, mainly between 10 and 18 m water depth (Fig. 3b). Part of this flow could reach shallower areas ranging from Isla

Table 2 (A) Pearson correlation matrix and (B) partial correlation matrix

	Cr	Cu	Pb	Zn
A				
Cr	1			
Cu	0.179	1		
Pb	0.213	**0.805**	1	
Zn	**0.449**	**0.606**	**0.485**	1
B				
Cr	1			
Cu		1		
Pb		**0.740**	1	
Zn	**0.439**	**0.449**	0.065	1

Bold numbers: $p > 99\ \%$

Antilla to Punta Umbria, with moderate to high geoaccumulation indices of Zn and low levels of Cr (Fig. 2).

In contrast, the Isla Cristina-Isla Antilla stretch includes unpolluted to moderately polluted sediments (Fig. 3b: Cluster 1). This area is partially protected from the Guadiana inputs by salt marshes and sandy spits that surround Isla Cristina. Pollution levels of these sedimentary beds are very low (Ruiz 2001).

This pollution decreases near Punta Umbría, despite the proximity of the Tinto and Odiel rivers. This area is partially protected from the highly polluted inputs of these rivers by salt marshes bodies (Fig. 1, e.g., Saltés Island) and the Huelva bank, which directs them to the east. These barriers cause a significant hydrodynamic and sedimentary isolation of this area in relation to the main channels of both rivers (Borrego 1992).

The highest polluted sediments of this littoral are located very close to the end of the Huelva bank (Fig. 3b: Cluster 4), clearly related to the Tinto–Odiel river inputs. In this area, metal deposition was linked to the partial removal of metals from solution through adsorption, coagulation and flocculation processes, according to Braungardt et al. (2003). This deposition caused a strong environmental impact in the 1990s, with the presence of bivalves with very polluted soft tissues by heavy metals, not suitable for human consumption (Usero et al. 1996). The presence of isolated samples with lower pollutant concentrations (Fig. 3b: Cluster 2) may be due to the periodical dredging of the main estuarine channel.

In the eastern sector (Mazagón–Matalascañas), pollutant flows are directed mainly near the coast (<10 m water depth) by littoral drift currents (Fig. 3b: Cluster 5). Moderate levels of Zn or Pb were measured even at 40 km to the east of the Tinto–Odiel pollution source, whereas lower contents are obtained in deeper sediments. This pollution pathway controlled by the littoral drift currents is also observed in water models and carry the metals discharged from the Tinto–Odiel system to the Strait of Gibraltar (Elbaz-Poulichet et al. 2001). In addition, these data confirm those reported by González et al. (2007), which found no evidence of such heavy metal contamination in the middle shelf sediments of the Cádiz Gulf.

Implications for fluvial and coastal management

Different implications are deduced from this study for a future development and the integral management of the fluvial catchment zones and the adjacent littoral:

(a) At present, large amounts of mining residues and industrial by-products (phosphogypsum, pyrite cinders) are stockpiled on the banks of the main rivers. As a consequence of the derived acid mine drainage processes (AMD), some tributaries of the Guadiana, Tinto and Odiel rivers have very acid waters, with an extremely high pollution by toxic metals that are discharged into the main channels (Fernández Caliani et al. 1997; Grande et al. 2010). So, these AMD processes need to be eliminated or diminished, at least, to improve the quality of estuarine and marine waters and sediments.

(b) The Huelva bank causes an artificial interruption of the natural dynamics and promotes the transport of this pollution parallel to the coastline between Mazagón and Matalascañas. These effects must be take into account if new groynes are developed in this area to arrest the sediments transported by the littoral drift currents, with a possible increase in pollution in the western side of future protective structures.

(c) This littoral is an important tourist area, being visited by more than one million people between May and September. Consequently, it is necessary to test frequently the sediment and water quality of the most polluted areas, such as the end of the Huelva bank, the shallowest zones between Mazagón–Matalascañas or the deepest areas (10–18 m water depth) between Isla Cristina and the Piedras River mouth.

(d) During the last decades, periodic pollution of commercial bivalves has been detected in the Tinto–Odiel estuary and the end of the Huelva bank, with high contents of heavy metals in soft tissues (Cu: 25–45 µg/g; Usero et al. 1996), which caused a temporary closure of collection and sale of these organisms. According to this study, it is important to include the Mazagón–Matalascañas area in any future environmental analysis, due to the moderate concentrations of heavy metals observed (Fig. 3: Cluster 5).

(e) All these data will be a part of the baseline for a long-term coastal model of geochemical evolution of this

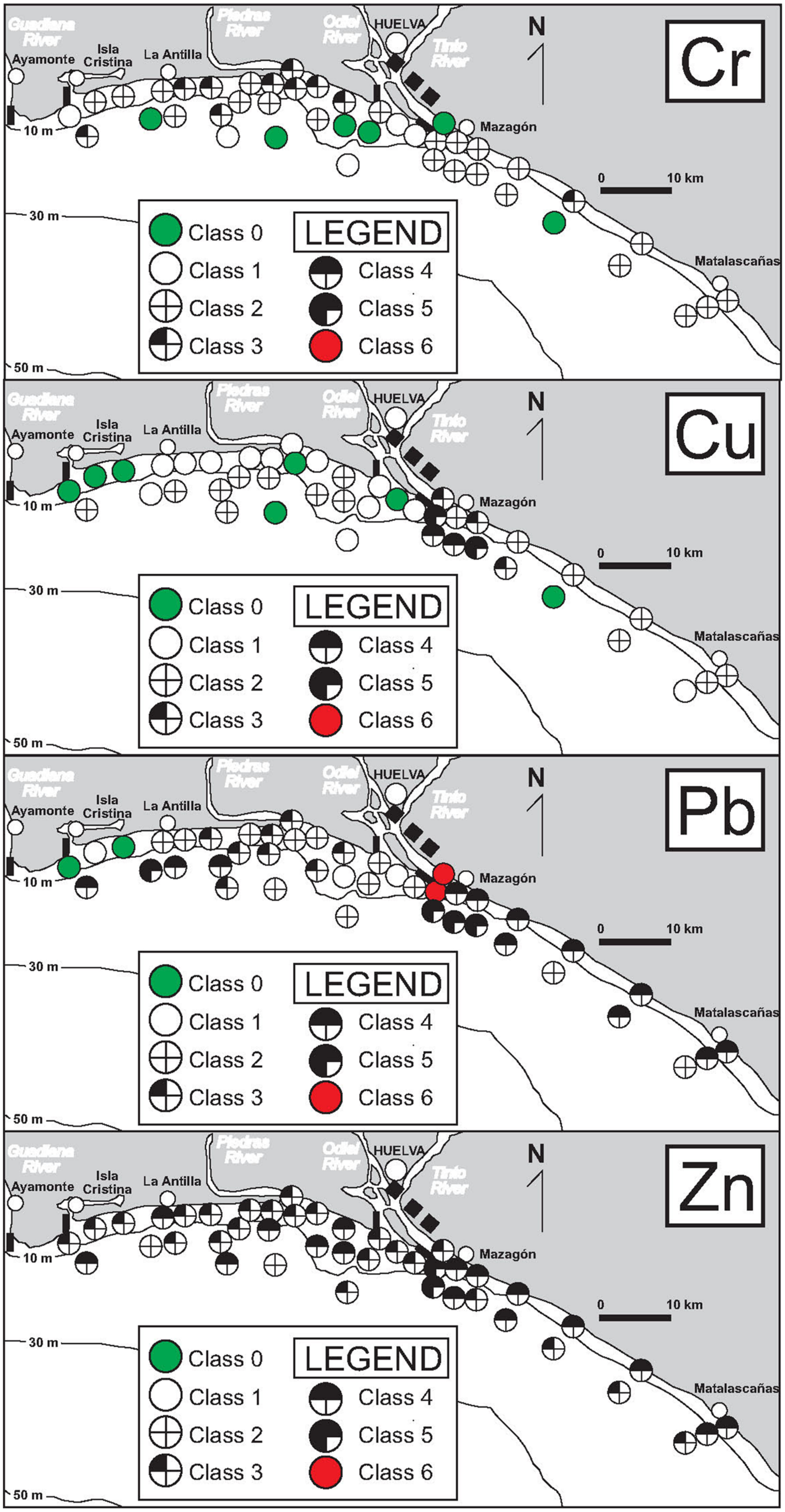

Fig. 2 Pollution levels of the southwestern Spanish littoral, according to the geoaccumulation indices obtained

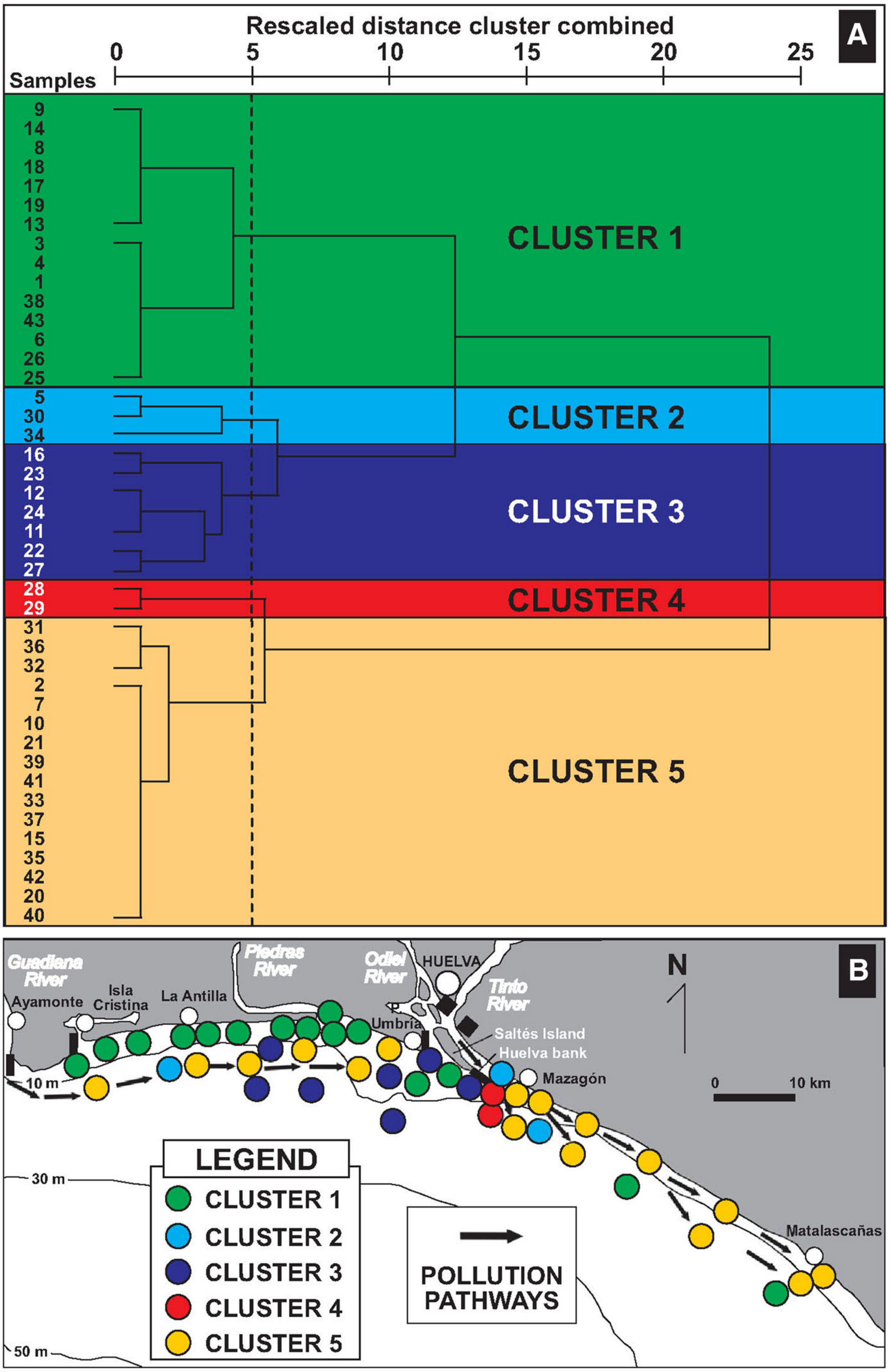

Fig. 3 **a** Cluster analysis (Ward method); **b** Geographical distribution of the different clusters

area, in examining the roles of rivers, waves, tides and sediments in coastal pollution. Nowadays, the Huelva estuary and the adjacent shallow shelf are subjected to a corrective plan for control of anthropogenic inputs, with the purpose of improvement of environmental quality in this coastal zone.

Conclusion

In this paper, the application of geoaccumulation indices as tracers of quality sediment was used to obtain a general scenario of pollution pathways in shallow marine sediments of southwestern Spain. The Tinto–Odiel system

Table 3 Geochemical characterization of the different clusters

Cluster	Samples	Cr			I_{geo} Cr			Cu			I_{geo} Cu		
		Mean	Max.	Min.	Mean	Max.	Min.	Mean	Max.	Min.	Mean	Max.	Min.
1	1-3-4-6-8-9-13-14-17-18-19-25-26-38-43	37.93	81	12	C2	2.6	0.24	14.93	26	4	C1	0.42	<0
2	5-30-34	19.67	39	10	C0	1.53	<0	172.17	400	31	C2	4.36	0.67
3	11-12-16-22-23-24-27	12.14	27	3	C0	0.89	<0	23.86	40	17	C1	1.53	<0
4	28-29	52	53	51	C2	1.97	1.92	363	421	305	C5	4.43	3.97
5	2-7-10-15-20-21-31-32-33-35-36-37-39-40-41-42	47.81	77	33	C2	2.51	1.24	68.72	177	40	C2	3.18	1.04

Cluster	Samples	Pb			I_{geo} Pb			Zn			I_{geo} Pb		
		Mean	Max.	Min.	Mean	Max.	Min.	Mean	Max.	Min.	Mean	Max.	Min.
1	1-3-4-6-8-9-13-14-17-18-19-25-26-38-43	15.8	30	4	C2	2.32	0	109.47	178	36	C3	3.08	2
2	5-30-34	247.67	517	100	C5	6.43	4.06	113.33	177	86	C3	2.88	1.68
3	11-12-16-22-23-24-27	18.57	32	6	C3	2.52	0.56	96.29	186	52	C3	3	1.11
4	28-29	215	295	135	C6	5.62	4.49	601.5	611	592	C5	4.67	4.62
5	2-7-10-15-20-21-31 -32-33-35-36-37-39-40-41-42	59.31	105	29	C4	4.13	2.27	261.25	375	155	C4	4	2.69

C0 Class 0, *C1* Class 1, *C2* Class 2, *C3* Class 3, *C4* Class 4, *C5* Class 5, *C6* Class 6

reveals as the most important pollution source of this area, with high concentrations of Cu, Pb or Zn near the end of the Huelva bank. The continuous inputs due to acid mine drainage processes and industrial wastes cause the presence of moderate levels of Pb and Zn in a wide coastal area (40 km long) located eastward between Mazagón and Matalascañas.

These elements are also provided, to a lesser extent, by the Guadiana River, with an additional redistribution to the east by the W–E littoral drift currents. The main consequence is the presence of moderate geoaccumulation indices for Zn and Pb between Isla Cristina and the Piedras River mouth, at 10–18 m water depths.

This study permits to obtain a baseline for future environmental strategies of this area and a first approach to a possible long-term integral management of the sediment geochemical quality.

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