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Contamination of heavy metals in the suspended and surface sediment of the Gulf of Cadiz (Spain): the role of sources, currents, pathways and sinks

Heavy metals
Gulf of Cadiz
Continental margin
Sediment
Contamination

Métaux Lourds
Golfe de Cadix
Marge continentale
Sédiments
Contamination

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ABSTRACT

The Gulf of Cádiz has been affected by contamination from terrestrial mining activities (copper and pyrites) since the times of the Tartesians and Romans. This activity has drastically increased during the past century. Industries implanted during recent decades have supplied another input of contaminants to the marine system. Most of the contaminants are discharged into rivers or in the littoral area, but some contaminated industrial waste was dumped on the continental slope from ships until 1990. Sediment from the continental margin has been sampled to study the heavy metal contamination on the sea bed.

The strongest heavy metal anomalies were detected on the continental shelf near the mouths of the Guadiana and Tinto-Odiel Rivers and on the continental slope near the head of some submarine canyons. Continental shelf anomalies are associated with flocculation processes in the marine water-freshwater interface. The contaminated river particles that remain suspended in the water column are transported by advective or diffusive processes, transferred to the slope, and reoriented by the Mediterranean outflow. They can accumulate in the slope mud patch, where bottom currents decrease, or can follow the Mediterranean outflow and reach deeper Atlantic areas.

RÉSUMÉ

Contamination en métaux lourds dans les sédiments superficiels et en suspension du golfe de Cadix (Espagne) : rôle des sources, des courants, des trajectoires et des dépôts.

Le Golfe de Cadix a été contaminé par les activités minières (cuivre et pyrites) dès l'époque des Tartésiens et des Romains. Cette activité a crû considérablement durant le siècle dernier. Les industries établies pendant les dernières décennies ont apporté de nouveaux contaminants au système marin. La plupart sont déchargés dans les fleuves et les rivières ou dans la zone littorale. Cependant, les déchets contaminés de certaines industries ont été déversés par des bateaux sur le talus continental jusqu'en 1990. Les sédiments de la marge continentale ont été échantillonnés afin d'étudier la contamination en métaux lourds du fond de la mer.

Les plus fortes anomalies en métaux lourds ont été détectées sur le plateau continental près de l'embouchure des fleuves Guadiana et Tinto-Odiel ainsi que sur le talus continental près de certains canyons sous-marins. Les anomalies du plateau continental sont associées aux processus de flocculation de l'interface eau de mer - eau douce. Les particules contaminées des fleuves qui restent en suspension dans la colonne d'eau sont transportées par advection et diffusion, puis transférées vers le talus et entraînées par le courant de sortie méditerranéen. Elles peuvent s'accumuler dans la zone vasière du talus, là où le courant de fond diminue, ou bien elle peuvent suivre le courant de sortie de la Méditerranée et atteindre des zones atlantiques plus profondes.

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INTRODUCTION

The Gulf of Cadiz receives heavy metal contamination from mining, cities and industries located in southwestern Spain (Fig. 1). Heavy metal pollution is mainly transported by rivers discharging in this area (Fig. 1). The most important rivers are the Guadalquivir, which has a drainage basin of 57,390 km^2 and a mean water discharge of 164 m^3/s, and the Guadiana, whose drainage basin has 67,500 km^2 and a mean water discharge of 78.8 m^3/s. The Tinto-Odiel River is smaller (its drainage basin is 3352 km^2 and its mean water discharge 0.7 m^3/s), but has a considerable environmental impact because most of the sulphide mines are located in its drainage basin. Pyrite production of all these mines during the last century has amounted to some 2.3 x 10^8 tons (Pinedo, 1963). The mouths of these rivers are estuaries where the contaminated terrigenous supplies can remain trapped. However, high amounts of polluted sediment from estuaries are discharged and dispersed at sea during river floods (Meade, 1969; Allen *et al.*, 1980). High heavy metal concentrations have been detected in the sediment from the Tinto Odiel estuary (Tomás *et al.*, 1983). In the Gulf of Cadiz, heavy metal inputs are also directly discharged from industries and cities located along the coast, and in the open sea by ocean dumping activities.

Heavy metals discharged in the aquatic environment have a high affinity with fine sediment particles (Salomon and Förstner, 1984). Therefore, the transport and fate of heavy metals are associated with fine sediment dynamics. Most of the fine sediment particles on the continental shelf are discharged by rivers and transported seaward as suspended particulate matter (SPM) (MCave, 1972). After being discharged at sea, heavy metals linked with suspended fine sediment particles are dispersed by mixing and advective processes (Drake, 1976). SPM tends to be more concentrated in surface and near-bottom turbid layers; although intermediate turbid layers also develop locally (Drake, 1976). The final sink is controlled by the prevailing short-term currents (Csanady, 1981), and is the result of a dynamic interaction between anthropogenic input and natural processes.

In the Gulf of Cadiz, the sediment dynamics is influenced by both the Atlantic and the Mediterranean water circulation. This circulation has been widely studied by several authors (Lacombe, 1961; Madelain, 1970; Zenk, 1974, 1975; Thorpe, 1976; Ambar and Howe, 1979; Fernandez and Ortega, 1984). The surface Atlantic water flows eastward and southward near the Strait of Gibraltar. The Mediterranean water flows northwestward along the slope between the 300 m and the 1200 m isobath and is reoriented towards the southwest by submarine canyons. The fine river sediment has accumulated on most of the continental shelf between about 30 and 100 m water depth, forming prodeltaic deposits that prograde towards the SE and the S (Díaz *et al.*, 1995; Maldonado and Nelson, 1988).

The objective of this paper is to study the heavy metal contamination in the suspended and surface sediment of the Gulf of Cadiz, analyzing its relationship with the modern sedimentary processes of this zone.

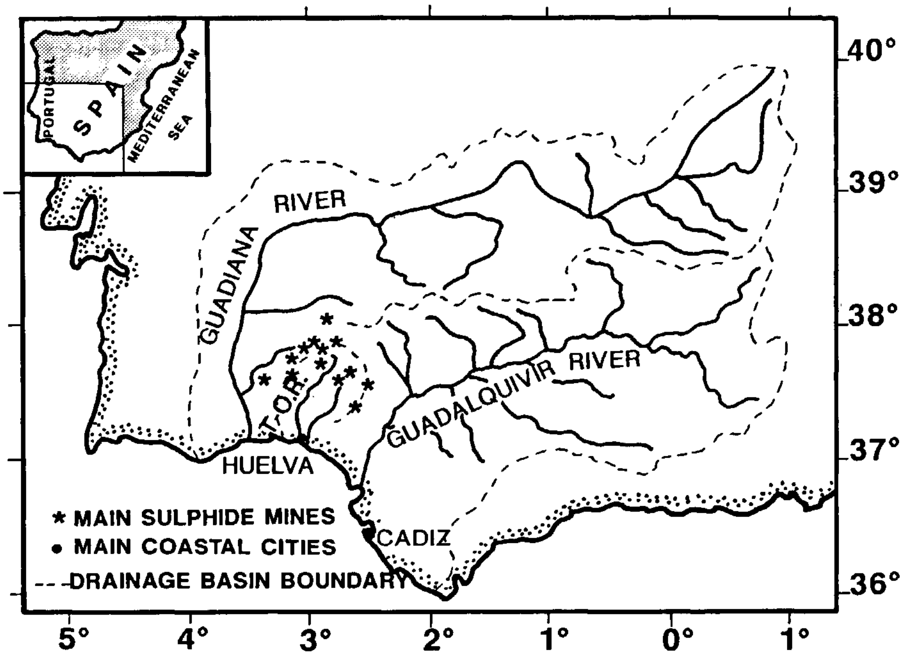


Figure 1

Drainage basin of the rivers discharging in the Gulf of Cadiz, indicating the main cities and the main mines affecting the marine system. T. O. R.: Tinto-Odiel River.

Bassin de drainage des fleuves qui déchargent dans le Golfe de Cadix. Les villes principales et les mines qui affectent le système marin son indiquées. T. O. R. : Fleuve Tinto-Odiel.

MATERIAL AND METHODS

105 surface sediment samples were taken by core sampling during three cruises carried out on board the *Nerva* in 1984 and the R.V. *García del Cid* in 1986 and 1988. Sample location is shown in Figure 2. Grain size analyses of the samples were performed using a 2 m recording settling tube for the fraction coarser than 50 mm and a Sedigraph for the fraction finer than 50 mm, following the method described by Giró and Maldonado (1985). Separation of coarse fraction and fine fraction was carried out by wet sieving. Sediment samples were digested with nitric acid which extracts weakly held metals including those originated from anthropogenically contaminated waters (Agemian and Chau, 1976). Analytical procedures were those described in Palanques and Díaz (1994). The concentration of Cu, Cr, Pb, Ti, Ni, Co, and Fe was determined by inductively coupled argon-plasma emission spectrometry (ICP). Five samples were chosen at random for triplicate analysis and the coefficient of variation (Kolthoff and Sandell, 1965) was lower than 10 % for all metals. Natural levels of metal leached by this method were determined by the analysis of uncontaminated sediments from the study area. As the silt + clay fraction is the principal carrier of metal contamination, an index of the extent of the anthropogenic metal input is provided by dividing the metal concentration of each sample by the fraction of silt+clay (Krom *et al.*, 1983). Samples with more than 80 % of sand were eliminated in order to avoid the magnification of small possible errors. The carbonate content was determined by HCl acid digestion.

Twenty-two water samples were taken with Niskin bottles at different depths of nine hydrographic stations (Tab. 1).

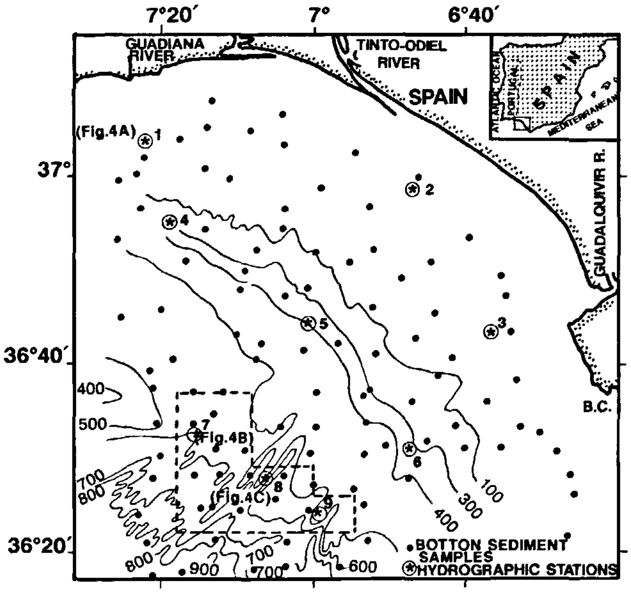


Figure 2

Map showing the location of the samples taken for this study. Bathymetry in metres. Dashed line limits the dumping slope area. B.C: Bay of Cadiz.

Plan indiquant la situation des points d'échantillonnage de cette étude. Bathymétrie en mètres. Les lignes discontinues limitent la zone de décharge du talus. B.C. : Baie de Cadix.

Table 1

Suspended particulate matter concentrations of the water samples taken in the Gulf of Cadiz (see location of hydrographic stations in Fig. 2).

Concentration de matériaux en suspension dans les échantillons prélevés dans le Golfe de Cadix (la position des stations hydrographiques est indiquée sur la Fig. 2).

Station number	Seabed depth (m)	water sample depth (m)	SPM (mg/l)
1	40	5	0.6
1	40	35	1.6
2	40	5	0.3
2	40	35	0.6
3	40	5	0.6
3	40	35	1.9
4	245	5	0.2
4	245	240	0.3
5	405	5	0.6
5	405	400	0.3
6	245	5	0.5
6	245	240	0.8
7	555	5	0.17
7	555	270	0.2
7	555	550	0.3
8	505	5	0.5
8	505	270	0.27
8	505	500	0.25
9	455	5	0.23
9	455	270	0.3
9	455	450	0.4

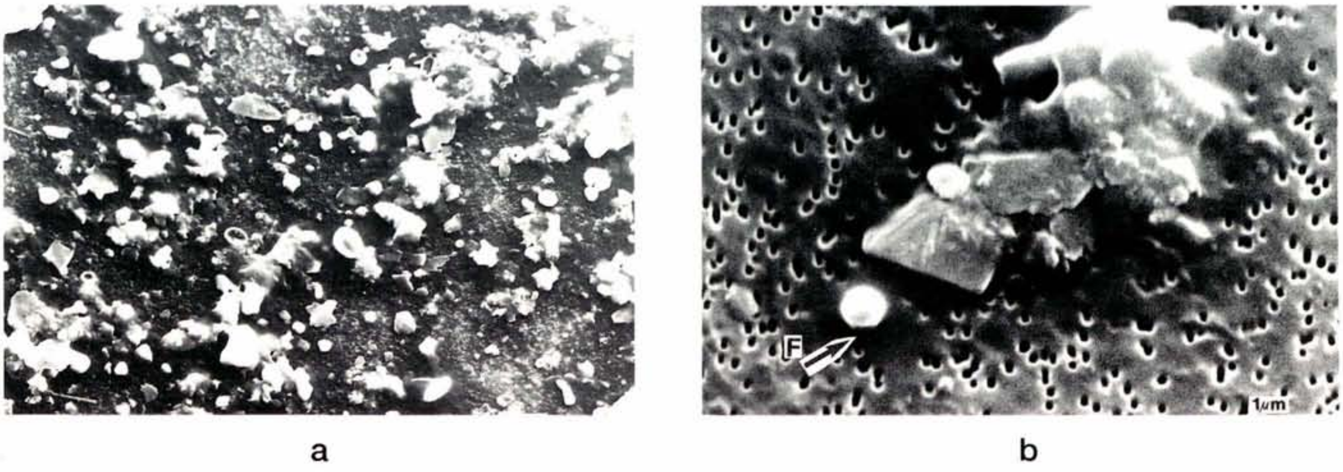
Suspended particulate matter (SPM) from these water samples was obtained by filtering them through Nuclepore membranes of 0.47 m pore diameter. Suspended particles were studied by Scanning Electronic Microscopy (PSEM-500). The elemental composition of single particles was analysed by EDAX. SPM samples were digested in hot nitric acid. Analytical procedures of heavy metal analysis in SPM are described in Palanques *et al.* (1989). Cd, Co, Cr and Ti contents of SPM were analysed by ICP, Pb and Ni by graphite furnace and Fe by flame atomic absorption.

Correlation and R-Mode factor analysis were run with the resulting data. These analyses show relations among metals. Significative correlations are those higher than 0.45 (Carruesco, 1978). In the factor analysis, active variables have a contribution > 0.5 in absolute value (Olade *et al.*, 1975).

RESULTS

Transport and fate of fine sediment

Fine sediment discharged into the sea is transported as suspended particulate matter (SPM) before reaching the sea bed. The concentration of SPM in the water samples taken in the Gulf of Cadiz ranged between 0.2 and 1.9 mg/l (Tab. 1).



a

b

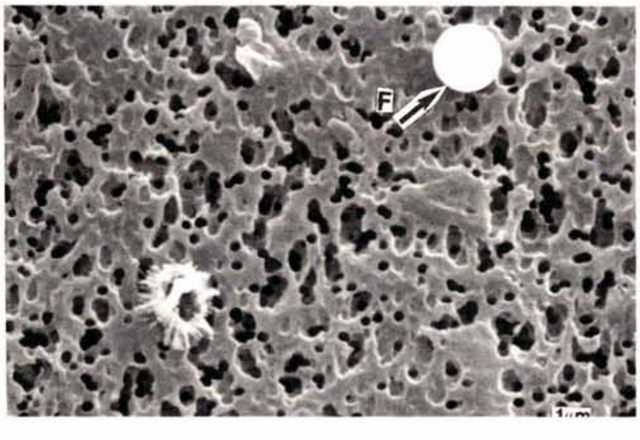


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Figure 3

SEM photomicrographs of : A) clay aggregates, single clay laminae, single particles of quartz and carbonate and coccoliths from shelf near-bottom SPM (location indicated in Fig. 2); B) iron spheric floc (F) beside a clay aggregate in near-bottom SPM from the upper slope in the dumping area over the mud patch (location indicated in Fig. 2); C) iron spheric floc (F) sampled in surface water (location indicated in Fig. 2)

Photomicographies A) des agrégats d'argile, d'une lamelle d'argile, de particules de quartz, de carbonate et de coccolithes de la matière en suspension de près du fond du plateau (situation indiquée dans la Fig. 2). B) flocons sphériques de fer (F) dans un agrégat d'argile de la matière en suspension près du fond dans la partie supérieure du talus de la zone de décharge au-dessus de la zone de boue (situation indiquée dans la Fig. 2). C) Flocon sphérique de fer (F) échantillonné à la surface de l'eau (situation indiquée dans la Fig. 2).

The higher SPM concentrations were detected in the near-bottom water samples taken over the 40 m isobath at the stations closer to the mouths of the Guadiana and the Guadalquivir Rivers, which are the major rivers discharging in the study area (Fig. 2). In the station closer to the Tinto-Odiel River mouth, the near-bottom SPM concentration over the 40 m isobath was lower, due to the lower discharge of this river. SPM concentrations decreased around the river mouths because of the deposition of aggregated fine particles (Fig. 3a) on the shelf and the dispersion of the lighter ones by currents. On the continental slope, the higher SPM concentration were near the bottom in the eastern stations over the 300 and the 450 m isobaths as a consequence of the input of particles escaping from the shelf after being transported by the southeastward Atlantic flow. These particles are reoriented and dispersed by the Mediterranean outflow towards the northwestern slope (Palanques *et al.*, 1989). In surface water SPM concentrations ranged between 0.2 and 0.5 mg/l, and in intermediate water between 0.2 and 0.3 mg/l.

The fate of the fine sediment particles is shown by the distribution of the clay + silt content (< 63 mm fraction) in the surface sediment (Fig. 4). A large proportion of the fine particles supplied by rivers form aggregates when they enter into the marine environment (Beck *et al.*, 1974; Rashid, 1974; Monaco, 1977; Hawley, 1982; Gibbs, 1986). These aggregates are mainly generated by flocculation processes and biological activity, and have higher settling velocities than those of their single component particles.

The aggregates of fine particles with a high settling velocity (> 5.5 cm/min) are quickly deposited in the shelf (Gibbs, 1986). The distribution of this deposit indicates a dominant

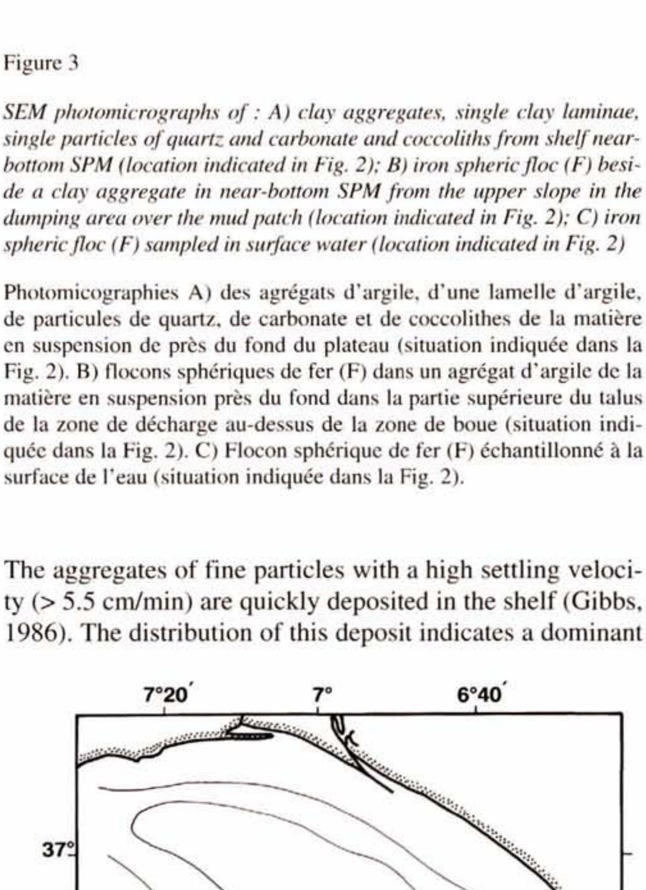

Figure 4

Distribution of percentage of silt + clay fraction (< 63 mm) in the bottom sediment of the Gulf of Cadiz.

Répartition limon + argile (< 63 mm) des sédiments du fond du Golfe de Cadix.

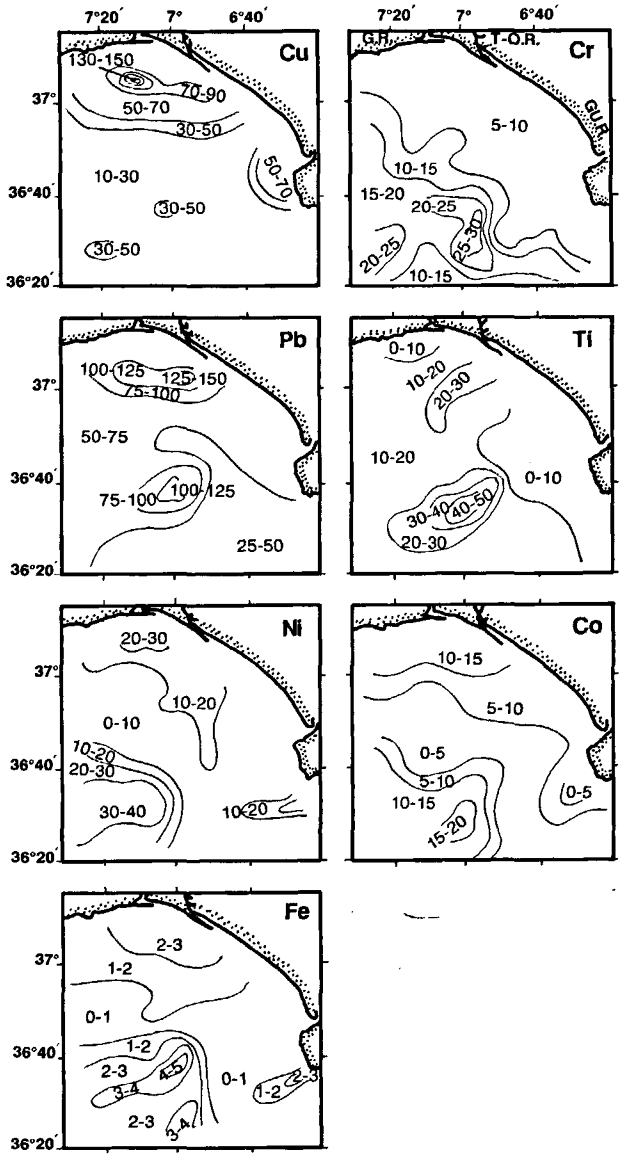

Figure 5

Maps showing the surface distribution of the most important heavy metal contaminants in the fine fraction of the bottom sediment. All metal concentrations are given in ppm, except Fe which is expressed in %. G.R.: Guadiana River; Gu.R.: Guadalquivir River; T. O. R.: Tinto-Odiel River.

Cartes montrant la répartition superficielle des métaux lourds contaminants les plus importants dans la fraction fine du sédiment. Toutes les valeurs de concentrations sont données en ppm, excepté pour celles du Fe qui sont données en %. G.R. : Fleuve Guadiana; Gu.R. : Fleuve Guadalquivir; T. O. R. : Fleuve Tinto-Odiel.

alongshelf transport controlled by the eastward mean flow (Fig. 4) forming a cohesive prodeltaic mud deposit. The mud of this deposit contains more than 90 % of clay + silt, and stretches from the 30 m to the 100 m isobath. On the continental slope, the silt + clay content of the bottom sediment decreases seaward, probably due to the winnowing action of the westward Mediterranean flow, which in this area is in contact with the bottom and attains velocities higher than 80 cm/s (Boyum, 1963; Madelain, 1970; Zenk, 1975). This trend is interrupted in a continental slope area incised by submarine canyons where the clay + silt content increases. The slope sediment with a higher silt + clay content (> 90 %) accumulates where currents decrease just northwestward from the canyons. Mud escaping from the shelf settles in this calmer area, which is sheltered from strong currents due to the southwestward reorientation of the Mediterranean flow through the canyons. This area is named the "slope mud patch".

Anthropogenic heavy metal contamination in sediment

The extent of anthropogenic contamination on the sea bed is shown by the distribution of the heavy metal content in the fine grain fraction of the sediment. This distribution is shown in maps that indicate the dispersion and sink for each metal (Fig. 5). Natural levels and maximum values of heavy metal content in different zones of the study area are shown in Table 2. The matrix shows that Cr, Ti, Ni, Co and Fe are mutually correlated, Cu is only correlated with Pb and both are correlated with the fine fraction. None of the metals are correlated with the $CaCO_3$ content which is inversely correlated with the fine fraction (Tab. 3).

Table 2

Natural levels and maximum concentrations (MC) of heavy metals detected in the fine fraction of bottom sediment from different zones of the study area. Ratios of maximum concentrations in relation to natural background levels (F) are also shown. All the values of heavy metal concentrations are given in ppm, except Fe which is given in % (*). C. S: continental shelf.

Niveaux maximaux et naturels de la concentration (MC) en métaux lourds détectée dans la fraction fine des sédiments du fond à différents endroits de la zone d'étude. Le rapport des concentrations maximales par rapport aux niveaux naturels de base est également indiqué (F). Toutes les valeurs de concentrations sont données en ppm, excepté pour celles du Fe qui sont données en %. (*). C.S. plateau continental.

Metal	Natural level	Guadiana C.S.		Tinto-Odiel. C.S.		Guadalquivir. C.S.		Continental slope	
		MC	F	MC	F	MC	F	MC	F
Cu	12.8	158.0	12.3	90.2	7.0	44.5	3.4	30.2	2.3
Cr	5.6	12.5	2.2	11.8	2.1	6.1	1.1	30.0	5.3
Pb	37.2	128.0	3.4	154.0	4.1	61.0	1.6	113.0	3.0
Ti	3.2	22.5	7.0	19.5	5.4	5.3	1.6	41.5	12.9
Ni	5.2	26.0	5.0	17.3	3.2	24.0	4.6	36.6	7.0
Co	3.1	13.3	4.3	11.9	3.8	4.9	1.6	19.0	6.1
Fe*	0,5	2.3	4.6	2.2	4.4	2.2	4.4	4.3	8.6

Table 3

Correlation matrix showing the coefficients of correlation between different pairs of variables measured in 105 bottom sediment samples. S + C: silt + clay.

Matrice de corrélation montrant les coefficients de corrélation entre différentes paires de variables mesurées dans 105 echantillons de sédiments du fond. S + C : limon et argile.

	Cu	**Cr**	**Pb**	**Ti**	**Ni**	**Co**	**Fe**	**S+C**	**$CaCO_3$**
Cu	1								
Cr	.17	1							
Pb	.53	.40	1						
Ti	.01	.45	.26	1					
Ni	-.03	.58	.09	.52	1				
Co	.10	.61	.46	.62	.78	1			
Fe	.23	.82	.55	.51	.59	.73	1		
S + C	.43	.28	.50	-.12	-.06	-.05	.26	1	
$CaCO_3$	-.30	-.11	-.30	.03	.25	.17	-.18	-.42	1

Table 4

Contribution of the variables to the first two factors defined in the factor analysis. S + C: silt + clay.

Contribution des variables des deux premiers facteurs définis dans l'analyse factorielle. S + C : limon et argile.

	Factor 1	**Factor 2**
Cu	.324	.649
Cr	.844	-.002
Pb	.645	.526
Ti	.662	-.342
Ni	.721	-.497
Co	.860	-.341
Fe	.915	-.037
S + C	.287	-.756
$CaCO_3$	.113	-.706

In the sediment of the continental shelf the highest heavy metal levels are located in the shallow prodelta near the Guadiana and the Tinto-Odiel River mouths. This area shows the highest ratios of Cu and Pb in relation to the natural levels of the Gulf of Cadiz (Tab. 2). An offshore decreasing gradient of heavy metal concentrations takes place around these maximum contamination areas. This gradient occurs across sediment of a similar texture (more than 90 % silt + clay) and composition, and is attributed to the diffusion of anthropogenic contamination. Near the Guadalquivir River mouth, only Cu, shows concentrations significantly higher than the natural levels. Anomalous levels of Fe and Ni are also detected near the Bay of Cadiz. The shelf contamination is represented by the second factor of the factor analysis which is statistically defined by the highest Cu, Pb and the clay + silt fraction. (Tab. 4).

Maximum heavy metal values and decreasing gradients in the sediment accumulated around the Guadiana and Tinto-Odiel River mouths suggest that metal anomalies have been caused by the rapid settling of highly contaminated flocs. This process is due to the scavenging of metals that takes place when flocculation occurs in the freshwater-saltwater transition area. Aggregates and flocs formed by this process have higher metal concentrations and a higher settling velocity than discrete single suspended particles (Gibbs, 1986). These mechanisms generate maximum heavy metal levels where aggregates and flocs are deposited, and decreasing heavy metal gradients around these maximum areas.

The SPM sampled on the continental shelf (Fig. 2) exhibits high heavy metal levels (Tab. 5). Despite deposition of the contaminated flocs with a higher settling velocity, heavy metal concentrations of the remaining SPM are higher than those of the bottom sediment (Tab. 5). This is due to: 1) the higher content of organic matter in SPM than in bottom sediment; 2) flocs with a lower settling

Table 5

Heavy metal concentrations detected in the suspended particulate matter (from Palanques et al., 1989) and ranges of heavy metal concentration in bottom sediment (this study) from different areas of the Gulf of Cadiz. Waste: Heavy metals measured in the suspended particulate matter sampled from the waste trail five minutes after being dumped in the slope waters. All the values of heavy metal concentrations are given in ppm, except Fe which is given in % (*). ud: undetectable. SPM: suspended particulate matter; B.S.: bottom sediment; Sf: surface; Nb: near-bottom; C. Shelf: continental shelf.

Concentrations en métaux lourds détectés dans la matière en suspension (Palanques *et al.*, 1989). Gamme des concentrations en métaux lourds dans les sédiments du fond (cette étude) dans différentes zones du Golfe de Cadix. Déchets : métaux lourds mesurés dans la matière en suspension échantillonnée dans les déchets cinq minutes après que ceux-ci aient été déchargés dans les eaux du talus. Toutes les valeurs de concentrations sont données en ppm, excepté pour celles du Fe qui sont données en %. (*). ud : non détectables. SPM : matière en suspension; B.S. : sédiments du fond ; Sf : surface; Nb : près du fond; C. Shelf : plateau continental.

Metal	**Guadiana C. Shelf**			**Tinto Odiel C. Shelf**			**Guadalquivir C. Shelf**			**Continental slope**			**Waste**
	SPM		**B.S.**	**SPM**		**B.S.**	**SPM**		**B.S.**	**SPM**		**B.S.**	
	Sf	**Nb**		**Sf**	**Nb**		**Sf**	**Nb**		**Sf**	**Nb**		
Cu	190	260	38-158	620	470	36-90.2	340	120	19-44.5	200-380	ud-300	9.6-30.2	570
Cr	160	90	7.6-12.5	250	300	7.6-11.8	130	170	4.6-6.1	ud-260	ud-380	5.6-30.0	4280
Pb	210	180	68-128	910	1050	70-154	340	360	38-61	ud-600	ud-500	27-113	390
Ti	5	100	8.4-22.5	100	280	6.4-19.5	ud	ud	3.7-5.3	ud-240	ud-90	5.4-41.5	1770
Ni	510	60	7.6-26	20	280	13-17	20	20	4.3-24	100-250	40-520	7.1-36.6	500
Co	27	30	3.6-13.3	78	45	5.6-11.9	23	13	4.0-4.9	ud-33	ud-71	2.9-19.0	107
Fe	2.4	3.8	0.7-2.3	4.8	4.6	0.7-2.2	2.9	2.6	0.5-2.2	2.3-4.2	1.1-4.0	0.6-4.3	12.6

velocity which remain as SPM for longer periods of time and have higher metal concentrations (Gibbs, 1986); 3) the diagenetic mobilization of trace metals in bottom sediment; 4) recycling of heavy metals from bottom sediment to the water column by physical or biological reworking; and 5) biodegradation of heavy metals in the sediment column.

On the shelf, the higher metal concentrations are around the Tinto-Odiel River mouth, both for SPM and for bottom sediment; the lower ones are around the Guadalquivir river mouth for bottom sediment but not for SPM (Tab. 5; Fig. 5). The high heavy metal levels in the SPM near the Guadalquivir river mouth could be probably due not only to the Guadalquivir River inputs but also to the southeastward alongshelf transport of highly contaminated SPM from the Guadiana and Tinto-Odiel Rivers. The anomaly of Cu and Fe southward from the Guadalquivir River mouth could be related to contamination from the Bay of Cadiz, together with contamination of particles from northern rivers. This anomaly suggests a westward transfer of contaminated particles towards the continental slope. This is in concordance with the higher SPM concentrations measured in the near-bottom samples of the eastern hydrographic stations of the continental slope (station numbers 6 and 9).

On the continental slope, the higher metal levels are in the slope mud patch both in bottom sediment and in SPM. In the bottom sediment of the Gulf of Cadiz, the higher ratios of Cr, Ti, Ni, Co and Fe concentrations in relation to natural levels are in the slope mud patch (Tab. 2). The contamination of the continental slope is represented by the first factor of the factor analysis, which is statistically defined by Cr, Pb, Ti, Ni Co and Fe. This contamination can have been generated by dumping activities and by advective and diffusive transport of shelf SPM.

The fact that the maximum Cr, Ti, Ni, Co, and Fe levels of the slope sediment are higher than those of the shelf could be due to ocean dumping activities. About 1000 tons of industrial waste have been discharged almost daily since 1977 to 1990, which represents a discharge of about 3.5×10^5 tons of waste per year. The waste was discharged from ships at an average of 0.1 m^3/s and at a speed of 8-11 knots (Ambio, 1984). This waste flocculated in the slope waters because Fe in the waste precipitated as hydrous iron flocs when it was mixed with sea water. The new particles were efficient scavengers of waste metals (Kester *et al.*, 1980). Table 5 shows the heavy metal levels measured in the SPM sampled from the waste trail five minutes after being dumped in the slope waters in 1987. These SPM show high levels of the same metals that define statistically the continental slope contamination by the second factor of the factor analysis. The flocs were dispersed with time and could be identified as components of the SPM in the study area. Spherical flocs of 2-3 mm diameter were found in surface and near-bottom water samples taken in the dumping area (Fig. 4b and 4c). EDAX microanalysis show that the composition of these spherical flocs is mainly iron. The flocs with a higher settling velocity accumulated in the canyons and slope mud patch area, whereas the finer contaminated SPM was probably transported to deeper areas by the Mediterranean outflow.

DISCUSSION

The metal contamination in the Gulf of Cadiz is related to mining, industry and big cities. Contamination from mining has occurred at least since Tartesic ages, but has become really intense during the last century (Tab. 6). The main sources of mining contamination are located some 40 to 80 km upstream from the mouths of the Guadiana and Tinto-Odiel Rivers (Fig. 1) - two rivers of a low water and sediment discharge that also receive industrial and domestic waste. This contributes to producing high contamination levels in the river sediment particles that are transported downstream and discharged into the Gulf of Cadiz (Nelson and Lamothe, 1993).

Table 6

Amounts of pyrite extracted during different periods (Pinedo, 1963).

Quantités de pyrite extraites pendant différentes périodes (Pinedo, 1963).

Tartesic age	5.400.000 tons
Roman age	25.000.000 tons
Up to XVIII century	221.000 tons
XIX and XX centuries	207.230.000 tons

In addition to the waste dumped into the rivers, the Gulf of Cadiz also receives waste directly discharged from coastal cities, such as Huelva and Cadiz, and industries. The contamination on the shelf of the Gulf of Cadiz is essentially controlled by industrial and domestic activities on land. The dispersion and accumulation of waste depends mainly on the energy of marine processes. In the Gulf of Cadiz, fine sediment and associated metal contamination are not usually deposited in areas shallower than about 30 m, whereas in some Mediterranean areas, such as the Ebro Delta, where currents are weaker, this limit has been observed at about 15-20 m (Díaz *et al.*, 1994).

Although a significant amount of fine sediment is accumulated in the shelf of the Gulf of Cadiz, the transfer of fine contaminated particles to the slope can be important, especially towards the southeast. Recent experiments show that, in some areas, more than 50 % of the suspended particulate matter supplied from the continent can be transferred to the slope diluted with autogenic biogenous particles (Biscaye *et al.*, 1988; Monaco *et al.*, 1990). Furthermore, the suspended particulate matter that reaches the slope may be an important carrier of contaminants because its small grain size allows it to have a high content of adsorbed material, as was observed, for example, in the suspended matter of the Ebro continental slope (Palanques *et al.*, 1990).

In the Gulf of Cadiz, the contaminated SPM discharged by rivers that is not deposited on the shelf is transported southeastward by the shelf mean flow. SPM transported by this mechanism is transferred to the slope near the Gibraltar Strait and when it sinks deeper than 300 m it must be reoriented and transported northwestward along the slope by the Mediterranean outflow, the speed of which can range from 12 to more than 80 cm/s (Boyum, 1963; Madelain, 1970; Howe, 1984). During high-energy events such

Table 7

Maximum heavy metal contamination from different systems worldwide compared with those measured in the Gulf of Cadiz. C. S.: continental shelf, slu.: sludge, du.: dumpsite, G.of C. dum. a: Gulf of Cadiz dumping area.

Contamination maximale en métaux lourds dans différents systèmes du monde, comparés à ceux qui ont été mesurés dans le Golfe de Cadix. C.S. : plateau continental, slu. : Boues, du. : Point de décharge, G.of C. dum. a : Point de décharge du Golfe de Cadix.

	Cu	Cr	Pb	Fe	Ni	Ti	Co	
Besos C.S.	406	889	1490	3.4	110	–	44	Palanques and Diaz, 1994
Hudson C.S.	590	570	610	–	160	–	–	Krom *et al.*, 1993
Pop C.S.	63	86	92	–	63	99	13	Friganani *et al.*, 1978
Ebro Delta C.S.	22	24	64	2.4	44	–	17	Palanques *et al.*, 1990
Mississippi C.S.	56	84	49	4.6	56	–	21	Trefry and Shokes, 1981
Gulf of Cadiz C.S.	158	12	154	2.3	26	22	13	This paper
Clyde slu. du.	270	120	360	–	77	–	–	Halcrow *et al.*, 1973
G. of C. dum. a.	30	30	113	4.3	36	41	19	This paper

as storms, the contaminated SPM supplied by rivers could be transported southward across the shelf and transferred directly to the slope by diffusive processes. However, the most important supply of highly contaminated particles to the slope probably came from ocean dumping activities untill 1990. In addition, significant amounts of polluted particles can also be transported offshore from near-coastal industrial centres to the continental slope by aeolic processes. The slope mud patch could be a sink of at least part of this contaminated SPM. Metal anomalies detected in deeper areas southward from Portugal suggest that significant amounts of heavy metal contamination from the Gulf of Cadiz could be transported far away towards the deep Atlantic by the action of the Mediterranean underflow.

Table 7 show heavy metal anomalies of some continental shelves. The maximum heavy metal anomalies caused by the Guadiana and Tinto-Odiel Rivers in the sediment of the continental shelf are stronger than those caused by other rivers, such as those of the Mississippi, Po, and Ebro Rivers in their respective continental shelves. However, values on the continental shelf of the Gulf of Cadiz are lower than those caused by rivers discharging near big cities such as the Hudson River (New York) and the Besós River (Barcelona). Table 7 also compares the heavy metal anomalies of the sediment from the dumping area of the Gulf of Cadiz with those from the Clyde sludge dumpsite.

CONCLUSIONS

Anthropogenic heavy metal contamination discharged in the Gulf of Cadiz is not efficiently diluted by the processes affecting the area, and produces significant anomalies in the bottom sediment of the continental shelf and slope. The most important anomalies of heavy metals in the continental shelf are located near the mouths of the Tinto-Odiel and Guadiana Rivers, and are related with the scavenging of metals associated with flocculation near the river mouths and with the deposition of the denser contaminated flocs. The anomaly of the continental slope is generated by the contaminated suspended particles dumped from ships and by an additional input of contaminated particles transferred from the shelf to the slope and transported from land by aeolic processes. These particles are affected by the Mediterranean outflow before reaching the sea bed. At least part of these particles accumulate in a slope area westward from several submarine canyons, which was called "the slope mud patch". Fine sediment particles and associated heavy metals can be deposited in this calmer area, because it is less affected by the alongslope Mediterranean outflow, which is reoriented basinward through the submarine canyons.

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