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Copper, zinc and lead impact in SW Iberian shelf sediments: An assessment of recent historical changes in Guadiana river basin

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In the present study, lithogenic/biogenic and anthropogenic elements were determined in five sediment cores collected at the SW Iberian Continental Shelf in order to investigate the spatial and temporal heavy metal distribution and to associate them with specific continental influences/events.

Elemental concentrations suggest a heavy metal (Cu, Zn and Pb) enrichment at the upper sections of all the cores. This enrichment is larger for cores localised closer to the coastline and probably exposed to a stronger continental influence. The geochemical regional background values for the studied elements are reached at ~25–30 cm for all the studied cores with one exception (core 8), which showed to be metal-enriched down to ~80 cm. It is worthnoting that core 8 is located closer to the coastal area, in a different fine sedimentary deposit, in which the deposition rates seem to be considerably higher. Enrichment factors (EF) calculated by using the natural background value determined at the deeper layers show that the EF values vary at the upper sections of cores, between 1.0 and 4.5 and the spatial distribution of the sediment cores show a similar behaviour in the heavy metal distribution patterns along this area of the continental shelf. Cu, Zn and Pb are heavy metals associated with mining exploitation along the Iberian Pyrite Belt, one of the most important mining areas of southwestern Europe, with massive orebodies of these metals. The combination of enrichment factors downcore profiles with sedimentation rate values signifies the beginning of heavy metal pollution in shelf sediments (~200–250 years ago) and is coincident with the mining exploitation reactivation during the XIX century.

Keywords: SW Iberian Continental Shelf, sediment core, mining exploitation, geochronology, heavy metal, enrichment factor

INTRODUCTION

Marine sediments are the ultimate sink for particulate material supplied by rivers and atmosphere to the oceans. Sediments act as records of environmental changes and their general characteristics are a combination of drainage areas lithology, temporal evolution, human impacts and diagenetical processes (Zwolsman *et al.*, 1993). Thus, these sediments can provide us with a historical pollution record and are well suited to study anthropogenic influences on the marine environment.

The Guadiana River basin is one of the largest on the Iberian Peninsula, and together with the Guadalquivir, the most important sediment supplier to the Gulf of Cádiz (Gonzalez *et al.*, 2001). Sediment load transported by River Guadiana to the continental shelf is very irregular and has been severely modified due to a wide range of anthropogenic activities responsible for important environmental alterations, including damming, mining and urbanisation. The River Guadiana drains the Iberian Pyrite Belt, one of the most important mining areas of southwestern Europe, with giant orebodies of Cu and Zn which are also very rich in Fe, As, Pb, Ag and Au. These mineral resources have been extracted during the last 5000 years, with two main periods of extraction: the Roman Age (2000–1900 years BP) (Craddock, 1995) and the past two centuries. In this latter period, the intensive exploitation along the area has caused an important environmental impact, with the presence of vast surfaces covered by mining residues (Alvarenga *et al.*, 2004) subjected to erosion with significant impacts in the coastal marine environment (Sainz and Ruiz, 2006).

During the Roman period, the River Guadiana became an important transport route for the exploited minerals from S. Domingos mine, which caused some significant environmental impact on both local and regional scales (Craddock, 1995). However, environmental impacts seem not to be very relevant until the XIX century, when large-scale mining operations began.

During the XIX century, mining exploitation was reactivated, mainly after the construction of the Pomarão fluvial mining port (~50 km upstream mouth) and the railway construction connecting mines to the port. By the

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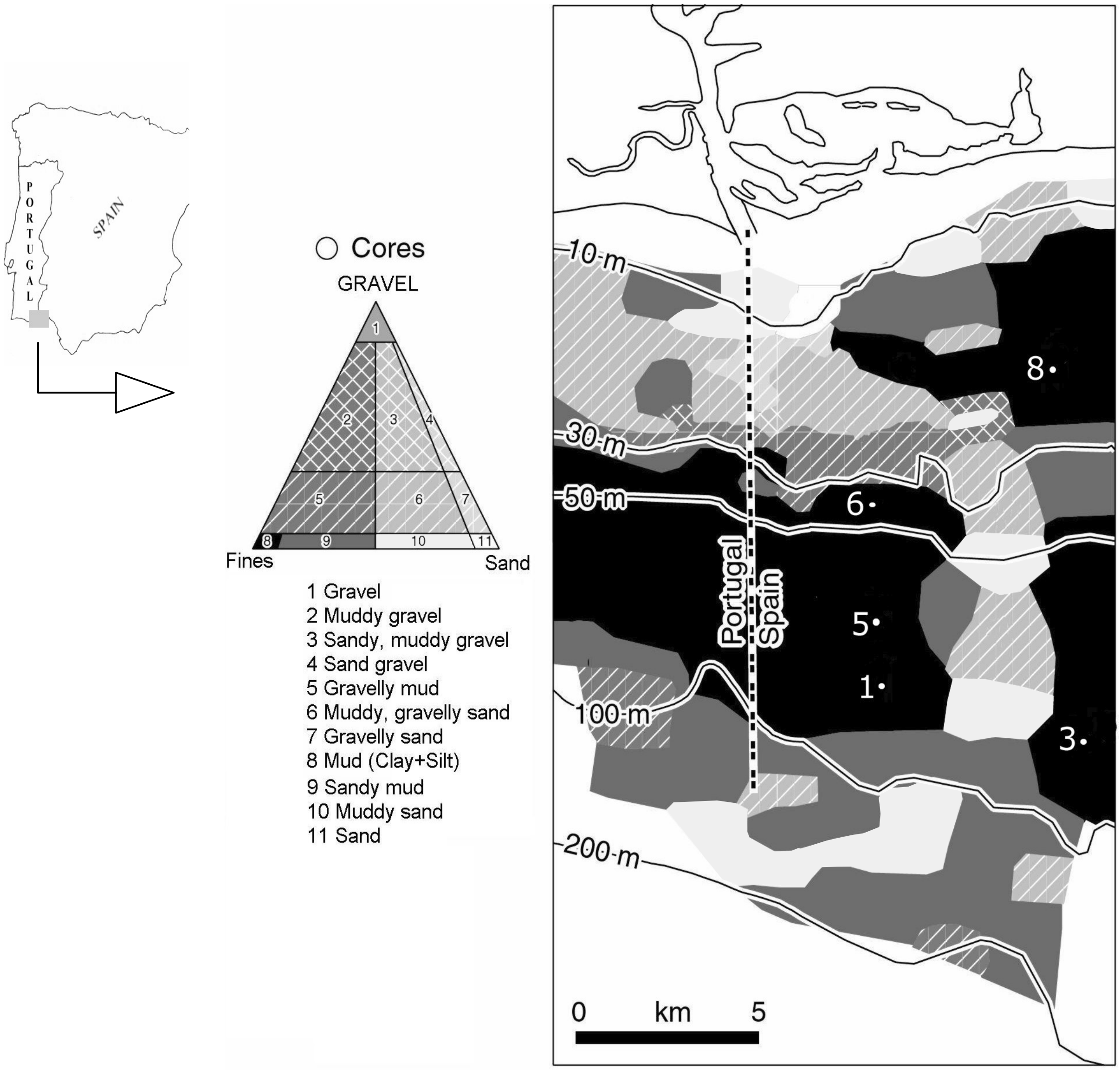

Fig. 1. Sediment cores (1, 3, 5, 6 and 8) location (adapted from Gonzalez et al., 2007).

end of 1880, the Pomarão mining port was used by approximately 400 ships per year, with a transport of 1500–2000 tons of ore per day. Within the Guadiana estuary, many boats have been sunk due to flooding. A remarkable flood occured at January 1876, sinking several ships which contain the majority of ore stocks at Pomarão and La Laja mining ports.

These accidents and the pollution of the watercourses caused by the discharges derived from ore washing, were responsible for the delivery of heavy metals towards coastal and shelf zones (Cossa *et al*., 2001).

Recently, studies have been published evaluating the consequences of changes that occurred in some main rivers' sediment loading during the last centuries in SW Iberia and the adjacent continental shelf (Gonzalez *et al*., 2007; Machado *et al*., 2005; Morillo *et al*., 2004). However, geochemical studies have focused mainly on surface sediments rather than assessing historical trends. A recent geochemical study of the Guadiana estuary (Caetano *et al*., 2006) reported results of one core collected at the coastal area. However, this paper considered just one core and no geochronological study was performed which could have attributed chemical composition variations to specific events.

In the present study, lithogenic/biogenic (Al, Si, Ca and Sr) and anthropogenic elements (Cu, Zn and Pb) were determined in selected fractions of sediment cores (~3–4 m long) collected at the SW Iberian Continental Shelf off

Guadiana River mouth. Sedimentation rates will also be discussed. The aim of this study is to investigate the spatial and temporal Cu, Zn and Pb distribution on the continental shelf and to associate them with specific continental influences/events. The Cu, Zn and Pb downcore variation profiles and accumulation rates give relevant information about the start and extent of the impact of anthropogenic activities on the shelf sediments during the last centuries. Other elements, such as As and Cd, are also important in old mining pollution events, particularly in this study area, once the Iberian Pyrite Belt is characterized by massive sulfides ore bodies, containing arsenopyrite and sphalerite. In the present work these elements were not determined due to some limitations of the analytical technique related to strong spectral interferences.

MATERIAL AND METHODS

Sampling

Five cores, approximately 3 m long (vibro-corer) were collected during the CRIDA0702 campaign (July 2002). Cores were taken at different depths in the SW Iberian Continental Shelf (core 1–92 m; core 3–85 m; core 5–72 m; core 6–40 m and core 8–22 m) and at varying distances off the Guadiana River mouth (Fig. 1).

After collection, cores were opened, described and subsampled for different studies. Sediment fractions were carefully sampled for chemical analysis, avoiding any metal contamination, stored in plastic bags and deep-frozen for later use.

Analyses

Sedimentation rate (^{210}Pb) Radioisotopic measurements were made by gamma-spectrometry, using a high resolution, low background, semi-planar hyperpure germanium detector (EGSP 2200-25-R from EURYSIS Mesures) coupled to a multichannel (8000 channels) analyser. Dry homogenized samples were packed and sealed in 9.5 ml Petri dishes.

^{210}Pb activity was determined by direct measurement of its gamma decay energy (46.5 keV). Excess ^{210}Pb was calculated from the total ^{210}Pb activity of which is subtracted ^{226}Ra, the supported ^{210}Pb. ^{226}Ra is estimated as the average of two ^{214}Pb peaks (295.2 keV and 351.9 keV) and a ^{214}Bi peak at 609.3 keV (Reyss *et al.*, 1995; Simpson and Grün, 1998).

The use of the natural radionuclide ^{210}Pb (half-life = 22.3 yr) is a well established technique to determine marine sedimentation rates during, at least, the last century (Nittrouer *et al.*, 1979). Excess ^{210}Pb apparent sedimentation rates were estimated based on a one-dimensional, two-layers model (Radakovitch, 1995).

Energy-Dispersive X-Ray Fluorescence Spectrometry (EDXRF) Some grams of sediment sample were freeze-dried and ground. The samples were dried at 110°C for 24 hours and then stored in a silica gel desiccator prior to weighing. About 2 g of the ground sediment were mixed with an organic binder (*Chemplex-Liquid Binder*®) and pressed by hydraulic manual press (15 ton) into a pellet for 20 minutes. The elemental composition was determined by EDXRF analysis using a Kevex EDX-771 Analyst System, with a rotating 16-position sample tray. A computer running the WinXRF/ToolBox applications software, which commands the X-ray generator, the detection system and the multichannel analyser, controls the spectrometer. A 200 W rhodium anode X-ray tube equipped with six secondary targets (Gd, Ag, Zr, Ge, Ti, Al) and filters produces the primary photon beam. All the samples and standards pellets were irradiated using three different operating conditions, under low vacuum conditions during 500 seconds: direct excitation emitted by the anode (4 kV, 0.15 mA); the Ge secondary target radiation (15 kV, 3.0 mA) and the Ag secondary target (35 kV, 1.0 mA). Elemental concentrations were determined using the EXACT (Energy-dispersive X-ray Analysis Computation Technique) computer program that uses a minimum set of standards and is based on a fundamental parameter method to correct for both absorption and secondary fluorescence effects. Samples of certified reference materials were also analysed to determine the accuracy and precision of the analytical procedure: GSD9 Stream Sediment from the Institute of Geophysical and Geochemical Exploration (IGGE - China) and SRM2704 River Sediment from the National Institute of Standards and Technology (NIST - USA). The accuracy is usually better than 5% except for the elements that present strong spectral interference. The precision is better than 10% for most of the elements. A detailed description of the sample preparation, quantitative analysis as well as the accuracy and precision of the overall procedure has been previously published (Araújo *et al.*, 2003).

Enrichment factors (EF)

Enrichment factors are useful indicators reflecting the status and the degree of environmental contamination. In the present study the EF values are applied to evaluate the dominant source of the sediments, as well as indicators for pollution effects, being mathematically expressed by

$$EF = \frac{\left(\frac{\text{Me}}{\text{Al}}\right)\text{sample}}{\left(\frac{\text{Me}}{\text{Al}}\right)\text{background}},$$

where (Me/Al)sample is the metal to Al ratio in the sample of interest; (Me/Al)background is the natural background value of metal to Al ratio. The regional geochemical background was calculated by the average composition of non-contaminated sediment, determined in the deeper layers of the cores. Downcore profiles exhibit a decrease in metal content that becomes nearly constant at specific depths of the cores. As previously stated, the EF is a useful indicator reflecting the status of environmental contamination. Thus, if an EF value is between 0.5 and 1.5, it indicates that the trace metals may be entirely from crustal materials or natural weathering processes. However, if a value of EF is greater than 1.5, it indicates that a significant portion of the trace metal is derived from non-crustal materials, or non-natural weathering processes, i.e., the trace metals are probably provided by anthropogenic sources (Feng *et al.*, 2004).

Geochemical normalisation

Since particulate metals from natural and anthropogenic sources accumulate together, it can be difficult to determine what proportion of the sedimentary load is natural and what proportion is anthropogenic. Normalisation of the data is an attempt to compensate for the natural variability of trace metals in sediments, so that any anthropogenic metal contributions may be detected and quantified (Loring, 1991).

Two principal different approaches are widely used to correct for variable sediment composition. The first uses a normalisation method by relating the contaminant concentration in sediments with the abundance of compounds of high affinity or high binding capacity for contaminants. Parameters representing this binding capacity are called normalisers. Normalisation can also be performed by simple contaminant/normaliser ratios or linear regression. The second approach uses sieving as a physical normalisation to reduce the contaminant variability due to grain size variation in sediments. By sieving, the fine fraction is separated from the total sample for subsequent analysis. This has the advantage that the contaminant is pre-concentrated because coarse particles, which usually do not contribute to the contaminant-binding capacity, are removed from the sample before analysis. Geochemical normalisation of trace metal data is superior to granulometric methods because it compensates for natural mineralogical as well as granular variability (Loring, 1991). In the present work Al content was used as a means of geochemically normalising the anthropogenic component. Al is a conservative element, as it is not significantly affected by, for instance, early diagenetic processes and strong redox effects frequently observed in sediments, and it is a major constituent of fine-grained aluminosilicates with which the bulk of the trace metals are associated.

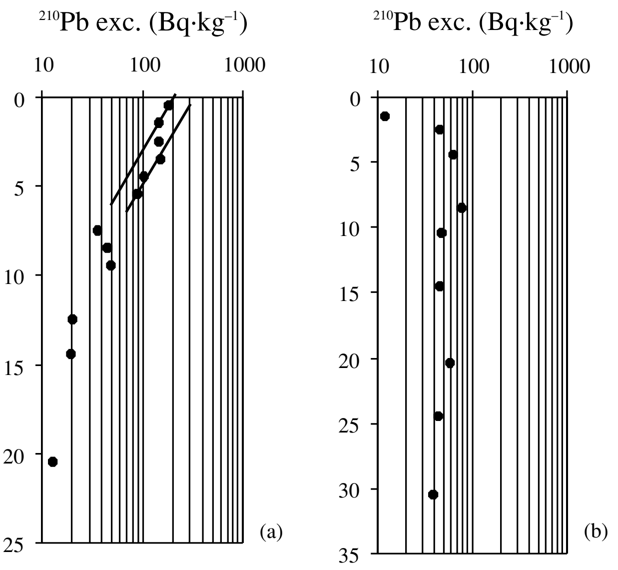

Fig. 2. ^{210}Pb excess activity profiles of cores 5 (a) and 8 (b).

RESULTS AND DISCUSSION

Sedimentation rate

The ^{210}Pb excess vertical distribution of cores 5 and 8 is represented in Fig. 2. Core 5 shows a decrease in the ^{210}Pb activity, from nearly 200 Bq·kg^{-1} at the surface to values close to 10 Bq·kg^{-1} at about 20 cm depth. Based on the ^{210}Pb excess value the maximum sedimentation rate is 0.12 cm·yr^{-1}. This low deposition rate and the absence of subsurface peaks may be an indicator that bioturbation is not very significant.

However, for core 8, sedimentation rate could not be estimated because of a significant excess of ^{210}Pb is present down to 30 cm depth, (~40 Bq·kg^{-1}), which indicates the presence of a thick mixing layer as a result of a high bioturbation. In spite of this, the ^{210}Pb excess present in the top layers is systematically lower than in core 5, probably due to the prevalence of coarser grain size particles in these core sections. The enrichment in coarser particles is related to the occurrence of a littoral drift (Gonzalez *et al.*, 2001), which favours the removal of the sediment particles especially the finer grain size fractions.

Lithogenic/biogenic elements downcore profiles

In Table 1 the Al, Si, Ca and Sr minimum, maximum and average concentrations and standard deviation values for each core are presented. The downcore profiles of Al and Si determined in the analysed fractions of the cores are given in Fig. 3.

Core 1 presents a homogeneous Al and Si downcore profile, with average concentrations of 6.2% and 23.0%,

Table 1. Al, Si, Ca and Sr minimum and maximum concentrations, average and standard deviation values

	Al (%)					Si (%)				
	min	–	max	average	std	min	–	max	average	std
Core 1	4.6	–	7.3	6.2	0.5	19.6	–	28.6	23.0	2.9
Core 3	3.1	–	7.6	6.3	1.5	20.6	–	30.6	24.5	2.8
Core 5	5.5	–	7.6	7.0	0.5	21.9	–	27.8	23.7	1.6
Core 6	4.6	–	9.0	6.2	1.1	17.8	–	25.4	22.1	1.9
Core 8	4.0	–	8.9	6.3	1.5	22.0	–	34.3	26.2	2.1

	Ca (%)					Sr (mg/kg)				
	min	–	max	average	std	min	–	max	average	std
Core 1	2.6	–	11.8	7.3	1.9	160	–	489	251	48
Core 3	2.2	–	9.8	7.3	1.5	137	–	503	286	71
Core 5	4.3	–	9.6	6.7	1.1	181	–	286	228	23
Core 6	0.5	–	11.0	6.2	2.7	107	–	499	272	88
Core 8	1.2	–	11.6	4.5	3.0	90	–	532	235	105

respectively. Core 3 displays Al and Si content variations above ~60 cm, after which the Si values show a slight increase while Al concentrations decrease (minimum of 3.1%). The sediments of the deeper layers of core 3 are coarser and these Al oscillations are probably dependent on the grain-size distribution. Core 5 shows a homogeneous downcore profile for Al and Si and average concentrations of 7.0% and 23.7%, respectively. Core 6 and core 8 reveal a very similar behaviour and the small variations seem to be related with the granulometric pattern.

Downcore profiles of Ca and Sr are given in Fig. 4. Distribution patterns follow the same trend, for both alkaline earth metals, due to their similar chemical behaviour. Sediment cores present different Ca vertical profiles. For core 1 high Ca contents are observed above 200 cm of core depth, oscillating between 7.1% and 11.8%. Below 200 cm an accentuated decrease is observed and the Ca values reduced to ~4.2%. An average concentration value of 7.3% is observed for core 1. The same value is found for core 3 which presents a homogeneous Ca downcore profile till 200 cm with values ranging between 6.4% and 9.8%. At greater than 200 cm, Ca contents decreases to ~4.4%. Core 5 also shows a more homogeneous profile with a Ca increase (~8.9%) between 50 cm and 130 cm of core depth. The average Ca concentrations determined in core 5 is 6.7%, and presents the lowest variation range. Core 6 presents a very irregular downcore profile for Ca content with much higher variation ranges (0.5% and 11.0%, respectively) and an average value of 6.2%. Core 8 presents a uniform Ca profile with low concentrations (~2.2%) down to 160 cm depth; after that an accentuated increase is observed with a maximum of 11.6% at 272 cm. In this core the average Ca concentration is 4.5%. Higher averages values for Ca are obtained in sediment cores collected at greater depths (Fig. 4), which are more enriched in carbonate biogenic particles.

The observed oscillations coincident with a Ca content increase are always due to a granulometric increase and/or to the presence of marine biogenic particles. In other studies along the Portuguese continental shelf adjacent to Tagus and Douro estuaries, rather high Ca concentrations were found at the outer shelf where benthic activities are prominent (Paiva *et al*., 1997; Araújo *et al*., 2002), even though Douro river sediment load is depleted in Ca due to the granitic lithology of the northern Portugal (Araújo *et al*., 2002).

High Ca concentrations can cause a heavy metal depletion attributed to a dilution by biogenic coarse particles (carbonated enriched sediments). Since high Ca variations are observed for all the analysed sediment cores, a calcium carbonate correction is made. The calcium carbonate concentration is calculated from the Ca content of each sample. An increase of 20–25% of heavy metal concentrations is observed with the exception of top layers of core 8, located in the coastal area, which is less Ca enriched presenting an increase of only about 4%.

Copper, zinc and lead downcore profiles

Depth profiles of Cu, Zn and Pb are given in Fig. 5 and are expressed on a calcium carbonate free basis due to the high Ca variation ranges among all the analysed samples. Looking at Fig. 5, heavy metal enrichment is observed at the upper sections of all cores. This enrichment is more visible for cores 5, 6 and 8, which are lo-

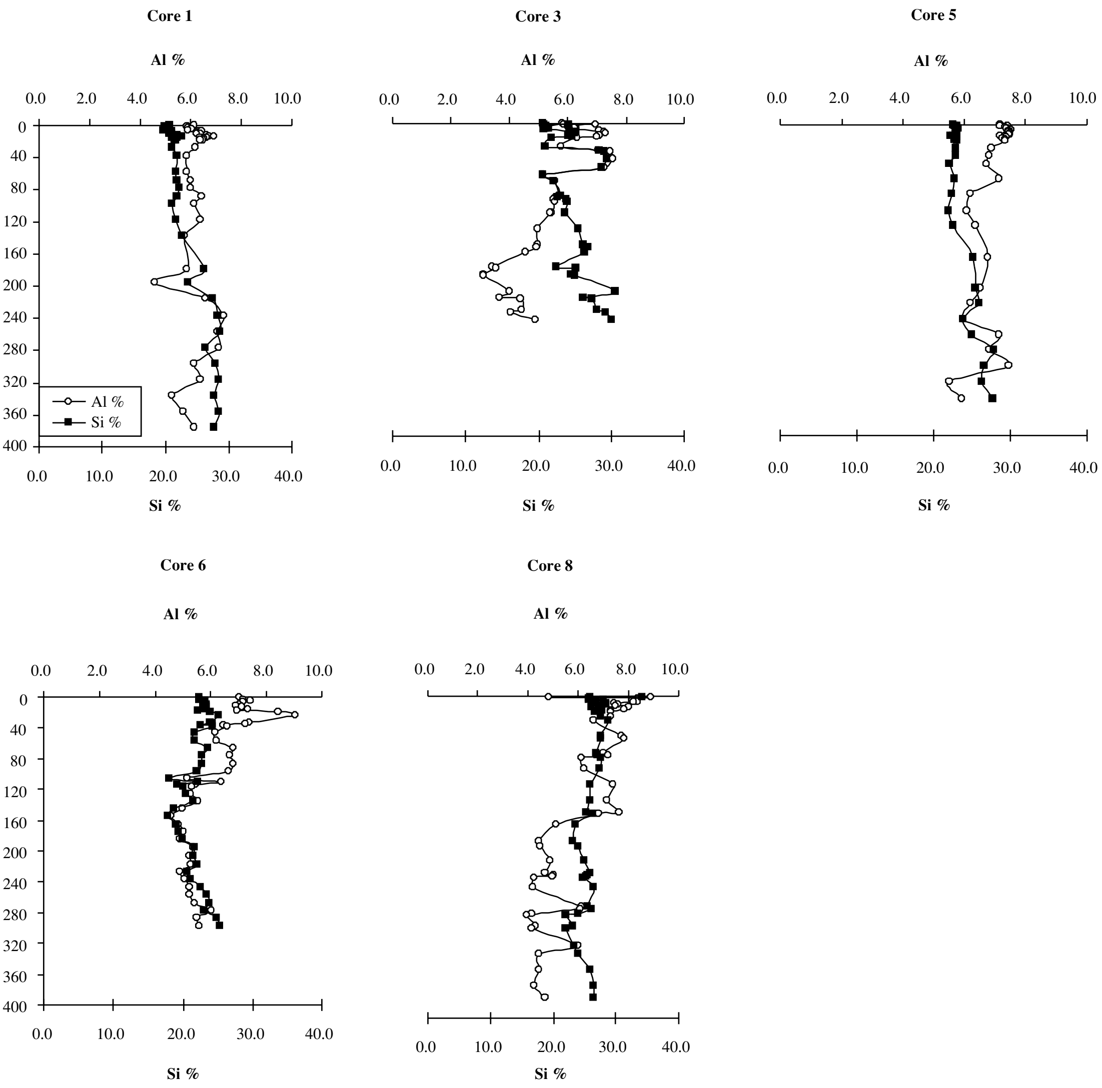

Fig. 3. Al and Si downcore profiles.

cated closer to the coastline (Fig. 1) and probably exposed to a stronger continental influence. Cu concentrations are very similar for all the studied cores, although highest Cu contents (Table 2) are observed in core 8 (127 mg/kg maximum). The Pb downcore profiles exhibit a similar pattern and the higher concentrations are observed in core 6 (144 mg/kg maximum) (Table 2). In the study by Paiva *et al.* (1997) carried out on the geochemistry of surface sediments at Tagus River adjacent shelf, Pb and Zn concentrations reach values up to 120 mg/kg and 300 mg/kg, respectively, due to anthropogenic activities (industrial and domestic wastes). However, no Cu enrichment was detected on shelf sediments. Furthermore, at the northwestern continental shelf none of the anthropogenic heavy metals enrichment measured within the Douro estuary were detected on the adjacent sedimentary deposits (Araújo *et al.*, 2002). In the present work, Cu and Pb enrichments at the surface layers of the sediment cores are followed by a slight decrease which becomes nearly constant at ~25–30 cm of depth cores. Core 8 is an exception and the Cu and Pb concentrations become nearly constant only at ~80 cm. A distinct pattern is observed for Zn, which shows an increase in the concentration values from the top layer until around 10 cm depth (except for core 8, for which enrichment is visible until around 25 cm depth). A maximum Zn concentration of 415 mg/kg is obtained in core 5 which also presents the higher average value (190 mg/kg), see Table 2. Below these levels an accentuated decrease is observed reaching nearly constant values at the same depths observed for Cu and Pb. This is not necessarily an indication for an episodic increase of anthropogenic input. It could be a phenom-

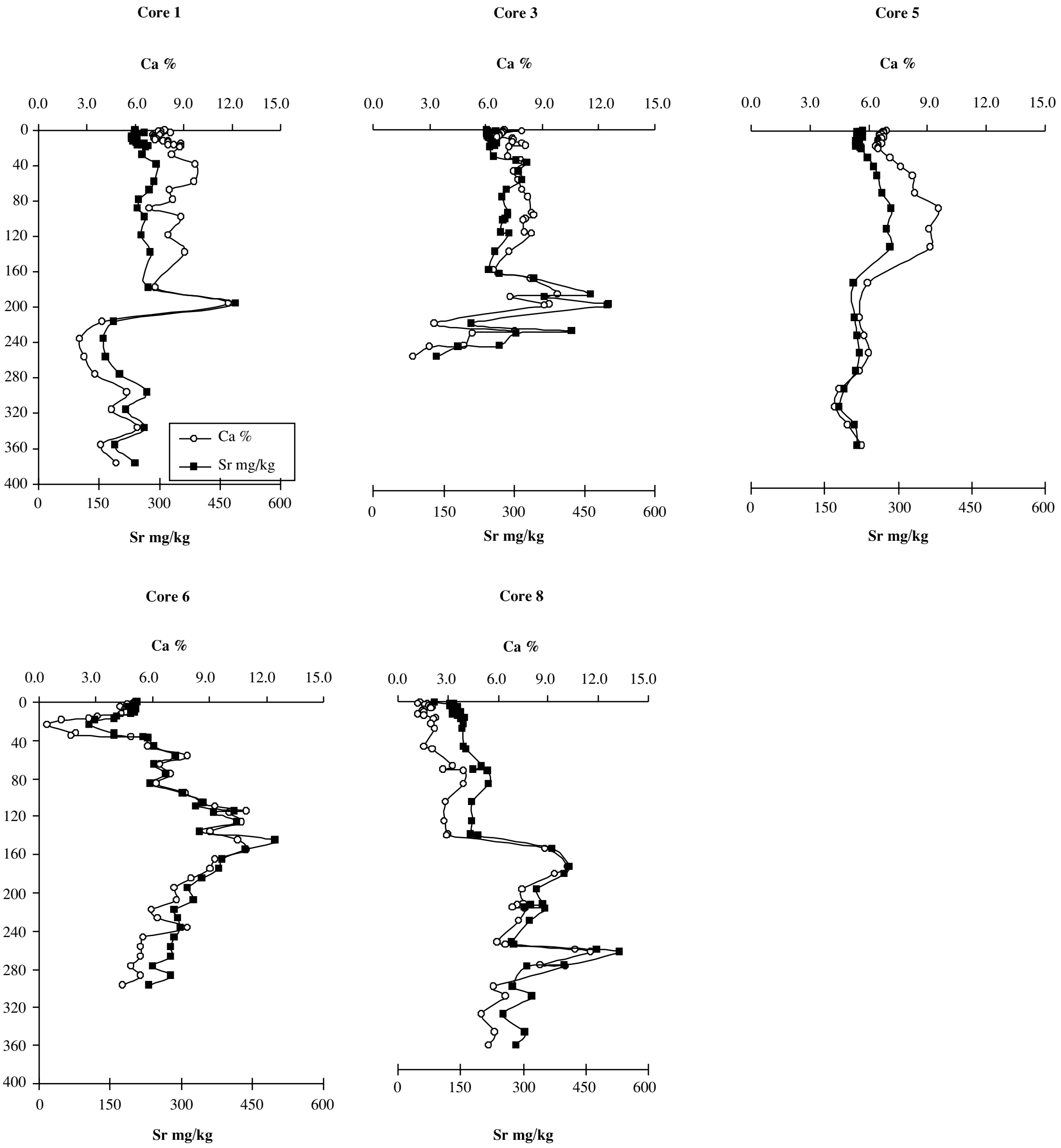

Fig. 4. Ca and Sr downcore profiles.

enon caused by the remobilization of these metals associated with the diagenetic recycling of Fe and Mn. As a matter of fact, these metals formely associated with Fe/Mn oxides are diagenetically reactive, especially Zn followed by Cu and to a lesser extent Pb, often showing some enrichment at depth. Therefore, their vertical profiles (mainly Zn) may be modified whenever they have undergone some remobilization (Spencer *et al.*, 2003).

As previously mentioned, Cu, Zn and Pb concentrations become nearly constant at ~25–30 cm for cores 1, 3, 5 and 6, and at ~80 cm for core 8. Thus, at these depths, the heavy metal regional background values for Guadiana adjacent continental shelf are found. It is worth to note, that core 8 is located closer to the coastal area, in a different fine sedimentary deposit, in which the deposition conditions seem to be rather distinct.

The heavy metal regional background values are very similar for all the analysed cores. Thus, an average of the values obtained for the different cores is made leading to the results of 21 mg/kg for Cu, 65 mg/kg for Zn and 27 mg/kg for Pb.

Enrichment factors (EF)

Cu, Zn and Pb concentrations are normalised to Al, since the grain-size distribution exercises a decisive influence on metal concents. Only in the 1st and 3rd centi-

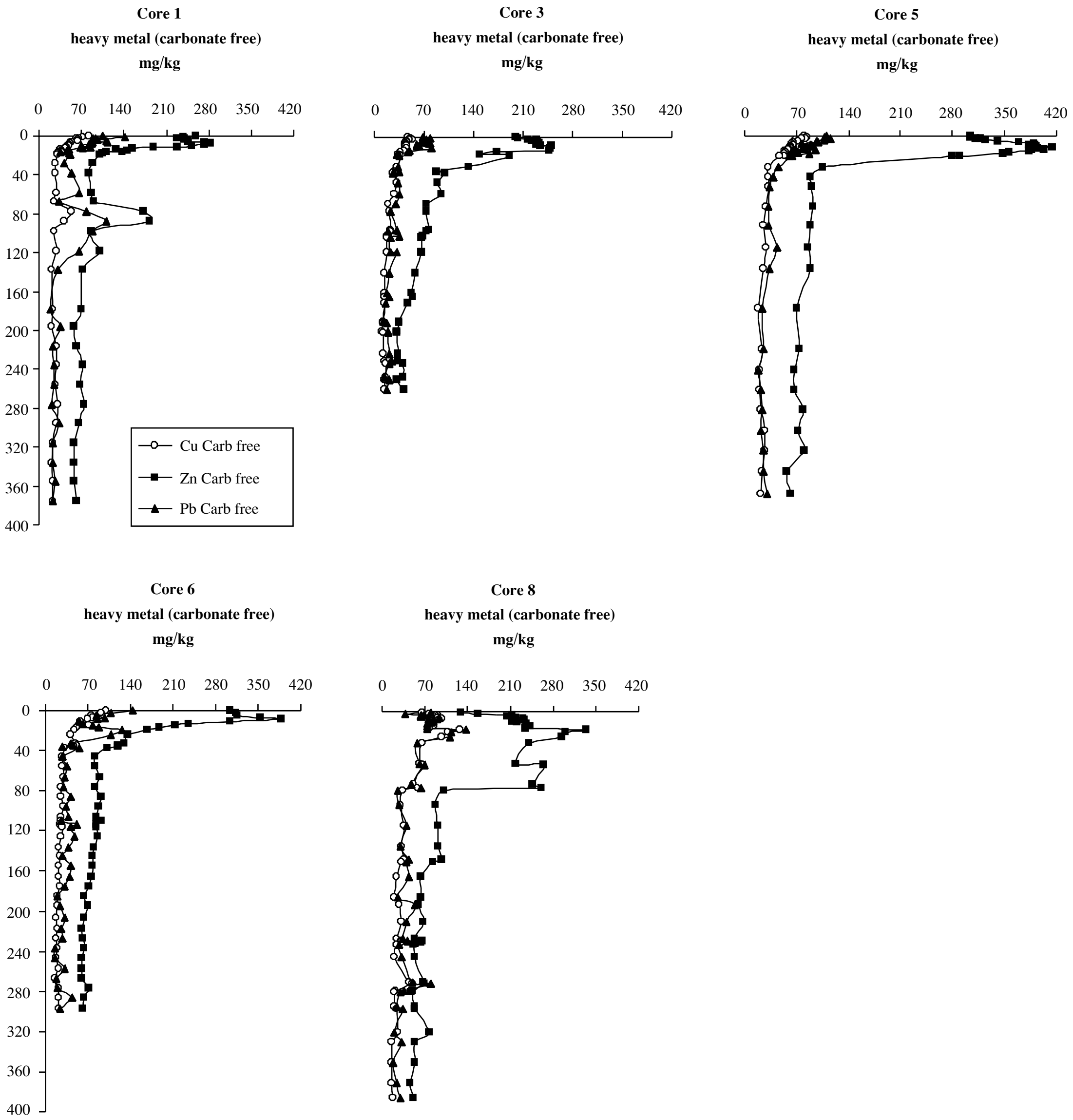

Fig. 5. Heavy metal concentrations (Cu, Zn and Pb) downcore profiles on a calcium carbonate free basis.

metres of the upper part of core 8 is detected a metal enrichment in a coarser grain-size fraction. However, as already mentioned and based on the ^{210}Pb excess downcore profiles, core 8 seems to present some specificities, due to its location closer to the coastline. It is probable that these enriched levels are a consequence of the aforementioned specific hydrodynamic conditions at the area. In Fig. 6 are plotted the EF profiles for Cu, Zn and Pb for the five studied sediment cores. Once the heavy metal enrichment is visible only at the surface layers of the cores, the graphics only show the top (100 cm) of the cores to give us an easier interpretation of the EF distribution patterns.

At the upper sections of sediment cores collected at the shelf the EF values vary between 1.0 and 4.5. Most of the values are greater than 1.5, suggesting Cu, Zn and Pb contamination. Sediment cores show a similar behaviour in the heavy metal distribution patterns along this area of the continental shelf. Only in core 8 it is possible to observe a more irregular metal distribution patterns at the surface layers. This core is localised closer to the coastline (Fig. 1) at a depth of 22 m and these irregularities on the heavy metal composition can be associated to the particular hydrodynamic conditions in the coastal area.

In general, EF values (cores 1, 3, 5 and 6) for Cu and Pb are lower than for Zn, possibly because Zn is a more

Table 2. Heavy metals minimum and maximum concentrations, average and standard deviation values (expressed on a calcium carbonate free basis)

	Cu (mg/kg)					Zn (mg/kg)				
	min	–	max	average	std	min	–	max	average	std
Core 1	20	–	81	31	13	57	–	282	114	63
Core 3	11	–	54	23	11	31	–	251	98	66
Core 5	19	–	84	39	17	57	–	415	190	116
Core 6	16	–	100	32	20	59	–	388	110	85
Core 8	15	–	127	47	31	46	–	334	130	88

	Pb (mg/kg)				
	min	–	max	average	std
Core 1	18	–	141	47	26
Core 3	13	–	80	40	43
Core 5	18	–	116	50	26
Core 6	15	–	144	42	30
Core 8	19	–	138	51	30

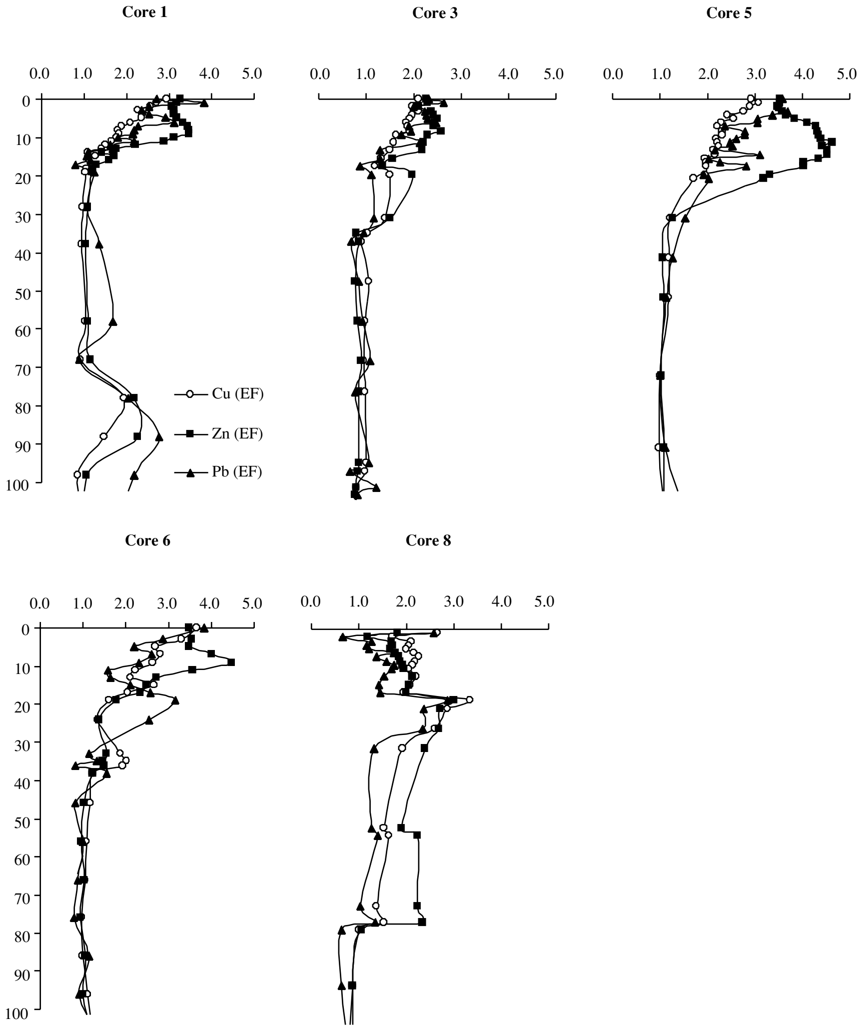

Fig. 6. Enrichment factors (Cu, Zn and Pb) downcore profiles.

stable element with less capacity to form soluble complexes (Silva and Williams, 1994).

Cu, Zn and Pb are sulphide-associated heavy metals and the combination of EF downcore distribution values and sedimentation rate determined by the excess ^{210}Pb on the upper levels of core 5 (0.12 cm/year) points to a register of the beginning of pollution in shelf sediments. These pollutants are coincident with the mining exploitation reactivation during XIX century (namely S. Domingos, in Portugal, and Las Herrerías, Cabezas del Pasto, Santa Catalina, La Isabel, Lagunazo and El Toro, in Spain), especially after the construction of the Pomarão fluvial mining port (~50 km upstream mouth) and the railway construction connecting mines to the port.

CONCLUSIONS

Geochemical and geochronological studies have obtained important information concerning to spatial and temporal heavy metal distribution at SW Iberian continental shelf (adjacent to Guadiana River).

The Al and Si contents reflect the sediment texture and the observed variations of sediment downcore profiles were dependent on the grain-size distribution. Ca distribution was related to either granulometric variation and/or to the presence of marine biogenic particles.

All the upper sections sediment cores showed an enrichment of Cu, Zn and Pb. This enrichment was more evident for cores localised closer to the coastline, which are exposed to a stronger continental influence. Heavy metal concentrations became nearly constant at ~25–30 cm for most of the cores and at ~80 cm for the core closely located to the coastal area (core 8). At these depths, the Cu, Zn and Pb regional background values for Guadiana adjacent continental shelf could be established as they are nearly constant and very similar for all the analysed cores: 21 mg/kg for Cu, 65 mg/kg for Zn and 27 mg/kg for Pb. The downcore profiles of the metal contents and the ^{210}Pb excess at the top 30–40 cm levels in core 8 indicated that in the coastal area, close to River Guadiana mouth, sediments undergo particular high energy hydrodynamic conditions.

The combination of EF downcore distribution and sedimentation rate values pointed to a register of the beginning of pollution in shelf sediments coincident with mining exploitation reactivation during XIX century.

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