

Sediment geochemistry and accumulation rates on the northeastern shelf of the Gulf of Cádiz (SW Iberian Peninsula)

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SUMMARY: Geochemistry, total organic carbon and total nitrogen of three sediment cores collected in the Gulf of Cádiz and the Guadalquivir prodelta areas in Spain were investigated. The C/N ratio, mostly around 10, seems to indicate a predominantly marine origin for the sedimentary organic matter. Major and minor elements (Si, Ti, Al, Fe, Mg, Ca, K, Na, P, S) and trace elements (Mn, Sc, V, Cr, Ni, Cu, Zn, Rb, Sr, Y, Zr, Ba, Ce, Pb, Hg) showed significant differences in bulk chemical composition between the two areas. Despite the effects of bioturbation, vertical changes in downcore profiles of heavy metals occur only in the cores of the Cádiz area, although the concentrations keep to low levels. The relatively high concentrations of Zr and Y, elements commonly associated with the heavy minerals fraction, at the top of cores from the Cádiz area are attributed to an enrichment of heavy minerals related to selective transport that concentrates this fraction. ¹³⁷Cs and ²¹⁰Pb activities in one of the two sediment cores collected in the Gulf of Cádiz were also measured. The distribution of excess ²¹⁰Pb was used to determine the modern (last 100 yr) mass accumulation rate and the depth of sediment mixing on the continental shelf of the gulf. Estimated sediment accumulation rate was 0.1 g cm⁻² yr⁻¹. The uppermost 4 cm had uniform excess ²¹⁰Pb activity profiles above a region of steadily decreasing ²¹⁰Pb activity, and this phenomenon was attributed to sediment mixing (bioturbation). ¹³⁷Cs activity was lower than 3 Bq kg⁻¹ and the profile does not show evidence of fallout peaks.

Keywords: radioactive tracers, ²¹⁰Pb, ¹³⁷Cs, γ -spectrometry, mass accumulation rates, bioturbation, geochemistry, Gulf of Cádiz.

RESUMEN: GEOQUÍMICA SEDIMENTARIA Y TASAS DE ACUMULACIÓN EN LA PLATAFORMA NORORIENTAL DEL GOLFO DE CÁDIZ (SO DE LA PENÍNSULA IBÉRICA). – Se ha estudiado la geoquímica, el carbono orgánico total y el nitrógeno total de tres testigos de sedimento tomados en el área del Golfo de Cádiz así como en el área del prodelta del río Guadalquivir (España). El cociente C/N, con un valor alrededor de 10, parece indicar un origen predominantemente marino para la materia orgánica sedimentaria. Elementos mayoritarios y minoritarios (Si, Ti, Al, Fe, Mg, Ca, K, Na, P, S) y oligoelementos (Mn, Sc, V, Cr, Ni, Cu, Zn, Rb, Sr, Y, Zr, Ba, Ce, Pb, Hg) muestran diferencias significativas en el grueso de la composición química entre las dos áreas. A pesar de los efectos de la bioturbación, sólo aparecen cambios verticales en los perfiles de metales traza de los testigos del área de Cádiz, si bien las concentraciones se mantuvieron en niveles bajos. Las concentraciones relativamente altas de Zr y Y, elementos generalmente asociados a fracciones de minerales pesados, en la parte superior de los testigos del área de Cádiz se atribuyen a un enriquecimiento de minerales pesados relacionado con el transporte selectivo que ayuda a concentrar esta fracción. También se han medido las actividades de ¹³⁷Cs y ²¹⁰Pb en uno de los dos testigos de sedimento tomados en el Golfo de Cádiz. Se ha empleado la distribución de exceso de ²¹⁰Pb para determinar la tasa reciente de acumulación de masa (para los últimos 100 años), así como la profundidad de mezcla de sedimentos en la plataforma continental del golfo. La tasa de acumulación de sedimentos estimada fue de 0.1 g cm⁻² yr⁻¹. Los 4 cm superiores mostraron unos perfiles de exceso de actividad de ²¹⁰Pb uniformes, por encima de una región de firme actividad decreciente en actividad de ²¹⁰Pb y este fenómeno se atribuyó a mezcla del sedimento (bioturbación). La actividad de ¹³⁷Cs fue inferior a 3 Bq kg⁻¹ sin presentar los perfiles evidencias de picos debidos a lluvia radiactiva.

Palabras clave: trazadores radiactivos, ²¹⁰Pb, ¹³⁷Cs, γ -espectrometría, tasas de acumulación de masa, bioturbación, geoquímica, golfo de Cádiz.

INTRODUCTION

The importance of the Gulf of Cadiz continental margin (SW Spain) lies in its proximity to the Strait of Gibraltar, a point of singular geographic interest because it is the place where the Atlantic Ocean and the Mediterranean Sea interchange their water masses (Gutiérrez-Mas *et al.*, 2003). The configuration of the study area in this study is the result of a natural evolution determined by geological agents, principally the littoral dynamics, the mouth of the river Guadalquivir and the aeolian regime of the zone (Ligero *et al.*, 2005). Continental shelves (defined as 30-200 m areas) represent <10% of the global oceanic area (Berelson *et al.*, 2003) and are considered as the transition zone between the continents and the open ocean. They receive large amounts of terrestrial organic matter and nutrients, mainly through river systems. Because the mean water depth of continental shelves is significantly less than in the open ocean, the seafloor sediments play a significantly more important role in the biogeochemistry and ecology of these systems (MacKenzie *et al.*, 2005).

Other major topics that geochemical studies can face in these areas are those of sediment provenance, which is useful to define sediment sources and their dispersion patterns, and to assess local human impacts (Carranza-Edwards *et al.*, 2005; Spagnoli *et al.*, 2008).

Natural and artificial radionuclides such as ^{210}Pb and ^{137}Cs can provide useful information as tracers to determine time scales for various sedimentary processes affecting continental shelves (Sánchez-Cabeza *et al.*, 1999; Palinkas and Nittrouer, 2007; Jouanneau *et al.*, 2008). ^{210}Pb (half life: 22.3 years) is a naturally occurring radionuclide belonging to the ^{238}U series whereas ^{137}Cs (half life: 30.2 years) is produced artificially as a result of anthropogenic activities.

Two cruises were carried out in two periods of the year 2006 on the northeastern shelf of the Gulf of Cádiz. This paper presents the results obtained from the study of sediment cores that were sampled on these cruises in order to characterize in this area the geochemistry of sediments and the accumulation rates by means of ^{210}Pb and ^{137}Cs radioisotopes.

MATERIALS AND METHODS

Study site

The study was carried out on the northeastern shelf of the Gulf of Cádiz (southwestern coast of the Iberian Peninsula; Fig. 1). The Gulf of Cádiz is the meeting place for the North Atlantic Ocean and the Mediterranean Sea through the Strait of Gibraltar. This gulf is a wide basin influenced by: a) the dense plume of Mediterranean water that penetrates through the strait, and b) the freshwater inputs from several adjacent rivers, such as the Guadiana, the Guadalquivir, the Tinto and the Odiel.

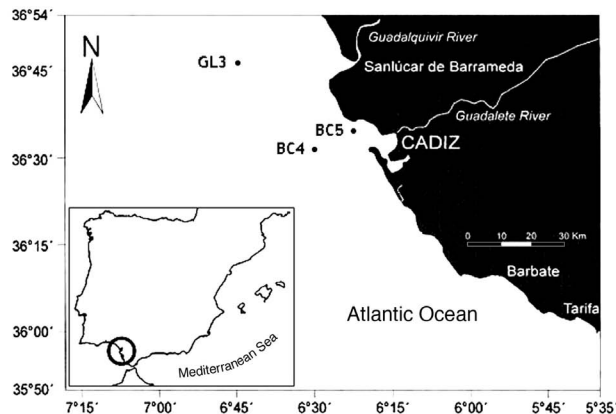


FIG. 1. – Location of the study area and sampling area on the northern shelf of the Gulf of Cádiz (SW Spain). Sediment cores BC4 and BC5 were obtained from the outer Bay of Cádiz, whereas core GL3 was obtained from the submarine prodelta of the River Guadalquivir.

The River Guadalquivir is the main fluvial source draining into the Gulf of Cádiz margin, with a mean annual water discharge of $160 \text{ m}^3 \text{ s}^{-1}$ (Van Geen *et al.*, 1997). The circulation on the northeastern shelf of the Gulf of Cádiz is mainly controlled by: a) North Atlantic Surface Water (NASW), which flows towards the east and southeast to the Strait of Gibraltar, and b) an intermittent counter-current system which seems to be considerably induced by wind forcing (Lobo *et al.*, 2004). The Cádiz area has a regime of semidiurnal tides and is characterized by predominant winds from the west and the east.

The data reported in this paper belong to two cruises on board the R/V *Mytilus* covering two seasonal periods: June 2006 and November 2006 (summer and autumn, respectively). Three sampling stations were selected for the study, and sediment cores were sampled by scuba divers. Two stations were located in the Bay of Cádiz and its neighbouring outer region (BC4 and BC5) and the other one off the mouth of the River Guadalquivir (GL3) (Fig. 1). Station GL3 is located on the Guadalquivir submarine prodelta, which is characterized by high fluvial supply and a moderate hydrodynamic regime (Lobo *et al.*, 2004), whereas the BC stations are located in a more energetic area affected by the tidal currents between the Bay of Cádiz and the outer shelf. Sediments in the study area are mainly siliclastic, with 25% of bioclastic carbonates, predominantly calcite (Gutiérrez-Mas *et al.*, 2003).

Specifically, in this research work three cores were analyzed: GL3 (from station GL3), which was extracted in June 2006, and BC4 and BC5 (from stations BC4 and BC5), which were extracted in June 2006 and November 2006, respectively.

Cores were extracted without alteration to the structure of the sediment. In order to ensure the immobilization of the core, the pipes were cooled at -10°C . Afterwards, the sediment profiles were cut into 1-cm thick slices up to a depth of 14–15 cm for GL3, 9–10 cm for BC4 and 13–14 cm for BC5.

Organic carbon and total nitrogen analysis

Sediment samples were ground to a fine powder with an agate pestle and mortar. Total carbon (TC) and nitrogen (TN) contents were determined using elemental analysis of combusted aliquots (30 mg) with a TCM 480 Carlo Erba Elemental Analyzer. Total organic carbon (TOC) was measured on decarbonated samples (1.5 N HCl) following the method of Hedges and Stern (1984). The precision of this method based on replicate measurements (n=30) of a standard reference sediments BCSS-1 is 2.0% for TOC and 1.2% for TN.

Sediment geochemistry

Bulk chemical composition for major and minor elements (Si, Ti, Al, Fe, Mg, Ca, K, Na, P, S) and trace elements (Mn, Sc, V, Cr, Ni, Cu, Zn, Rb, Sr, Y, Zr, Ba, Ce, Pb) were determined by X-ray fluorescence spectrometry using a Philips PW 1480 spectrometer equipped with an Rh tube on pressed powder pellets following the matrix correction methods of Franzini *et al.* (1972) and Leoni *et al.* (1982). About 30 international reference materials were used for the calibration, and PACS-2 (marine sediment, National Research Council, Canada), NBS1646a (estuarine sediment, National Institute of Standards and Technology, USA) as external monitors. Precision and accuracy were better than 5% for trace-element determinations.

Total mercury was determined by cold vapour atomic absorption spectrometry (CVAAS) after hot digestion of 0.5-1 g dry sediment with concentrated HNO₃ + H₂SO₄ for 3 h at 90°C (Fabbri *et al.*, 2001). The analytical precision of the Hg data, estimated as relative percent difference among replicates, was 5.0% (n=10), and analytical accuracy estimated as the mean% recovery in PACS-2 reference sediment (National Research Council, Canada) was 95% (n=10).

Radioactive tracer analyses

Water content and wet and dry bulk densities were calculated from samples that were weighed before and after drying at 60°C until constant weight. Dry homogenized samples were packed in 9.5-mL sealed Petri dishes and 'aged' at least four weeks to allow the equilibrium between ²²²Rn and its descendants, ²¹⁴Bi and ²¹⁴Pb, to be established for the determination of ²²⁶Ra. Radioactive tracers (²¹⁰Pb, ²²⁶Ra, and ¹³⁷Cs) were measured on sediment core BC4 using HPGe coaxial detector with an energy resolution (full-width at half-maximum) of 1.9 keV at 1.33 MeV (⁶⁰Co), and a 22.6% efficiency. Efficiency calibration was performed using a Standard U-Th Ore (Canada Centre for Mineral and Energy Technology). Reference sediments IAEA 315 and IAEA 368 from the International Atomic and Energy Agency (IAEA) were used to check the accu-

racy of the results. Samples and background were counted for nominally 172800 s (corresponding to two days). ²¹⁰Pb activity was determined by direct measurements of its gamma decay energy at 46.5 keV. Activity concentrations of ²¹⁴Pb and ²¹⁴Bi were quantified using the 351.9 keV and 609.3 keV photopeaks, respectively. ¹³⁷Cs (half life: 30.2 years) was measured by its emissions at 662 keV. Excess ²¹⁰Pb (²¹⁰Pb_{xs}) activity was calculated by subtracting the ²²⁶Ra activity from the total ²¹⁰Pb.

Sediment accumulation rate

Sediment reworking due to physical or biological agents may affect the excess ²¹⁰Pb distribution along the sediment. Goldberg and Koide (1962) pointed out that the main processes governing excess ²¹⁰Pb profiles in the seabed are sediment accumulation rates, radioactive decay and particle mixing. They proposed a one-dimensional advection-diffusion model to calculate the sedimentation rate (S, in cm yr⁻¹) and the mixing coefficient (D_b; in cm² yr⁻¹) that describes the intensity of particle reworking (D_b, in cm² yr⁻¹):

$$\frac{\partial A}{\partial t} = D_b \left(\frac{\partial^2 A}{\partial x^2} \right) - S \left(\frac{\partial A}{\partial x} \right) - \lambda A \quad (1)$$

where A is the excess ²¹⁰Pb activity (Bq kg⁻¹) at a depth x (cm), λ is the ²¹⁰Pb decay constant (0.0311 yr⁻¹), and S and D_b are assumed to be constant. As D_b and S cannot be determined independently, a solution for D_b can be obtained if S is known or assumed to be negligible. When the latter is not the case or no evidence supporting this is available, S can be determined from the ²¹⁰Pb profile of the non-mixed layer, where D_B is assumed negligible. Assuming steady state conditions and no mixing, Equation (1) can be solved under the boundary conditions of A = A₀ (x = 0) and A → 0 (x → ∞) by means of the equation:

$$A = A_0 \exp \left(-\frac{\lambda}{S} x \right) \quad (2)$$

This is usually done by least-squares fitting of the logarithm of excess ²¹⁰Pb versus depth for the strata below the sediment mixed layer (SML). Then, the sedimentation rate calculated by using Equation (2) can be introduced as a constant in Equation (1) to determine D_B, also using least-square fitting for the SML:

$$A = A_0 e^{\left(\frac{s - \sqrt{(s^2 + 4\lambda D_b)}}{2D_b} x \right)} \quad (3)$$

In this study, we consider the ²¹⁰Pb profile of core BC4 from the outer Bay of Cádiz as a two-layer system with an upper mixed layer extending to a distance L below the water-sediment interface (SML) and a second layer below L where no mixing takes place (Fig. 5).

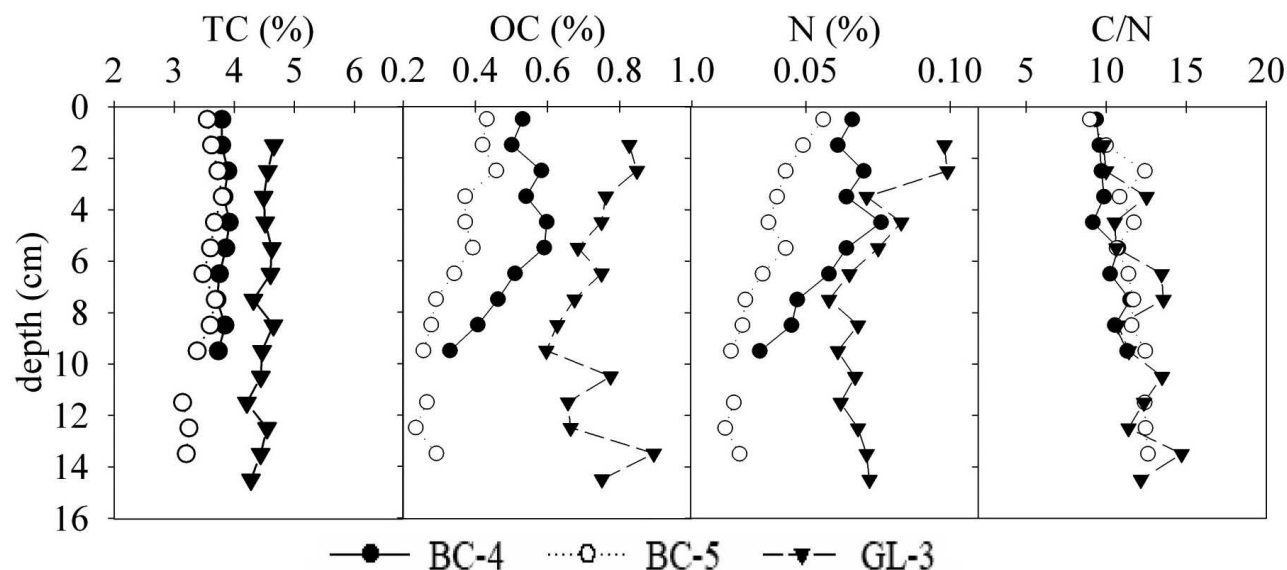


FIG. 2. – Depth profiles of TC, OC, TN, and OC:TN molar ratios of sediment cores from the Gulf of Cádiz. The origin of the cores is shown in Figure 1. Sediment cores BC4 and BC5 were obtained from the outer Bay of Cádiz, whereas core GL3 was obtained from the submarine prodelta of the River Guadalquivir.

RESULTS

Total organic carbon (TOC) and total nitrogen (TN) distribution and ratios

Data of TC (%), TOC (%), TN (%), and TOC:TN ratios are displayed in Figure 2. The TOC content varied from 0.24 to 0.90 wt% (of total weight), with mean values of 0.51 ± 0.09 , 0.34 ± 0.07 and 0.73 ± 0.09 in cores from the outer Bay of Cádiz (BC4 and BC5) and the Guadalquivir submarine prodelta (GL3), respectively; the TN content ranged from 0.02 to 0.10 wt%, with mean values of 0.06 ± 0.01 , 0.04 ± 0.01 and 0.07 ± 0.01 in cores BC4, BC5 and GL3, respectively; the TOC:TN ratio varied from 9.0 to 14.7, and mean values of 10.2 ± 0.8 , 11.5 ± 1.1 and 11.9 ± 1.5 were found in cores BC4, BC5 and GL3, respectively.

Sediment geochemistry

The vertical profiles of major and minor elements (Si, Ti, Al, Fe, Mg, Ca, K, Na, P, S) and selected trace elements (Mn, Sc, V, Cr, Ni, Cu, Zn, Rb, Sr, Y, Zr, Ba, Ce, Pb, Hg) are reported in Figures 3 and 4 respectively. The profiles of the three cores are reported in the same diagram to facilitate comparison and discussion of the most relevant features.

CaO concentrations (Fig. 3) are directly related to carbonate content, which can be calculated from TC data (27.0-28.7 wt% CaCO_3 in BC4; 24.0-28.6 wt% CaCO_3 in BC5; 29.4-33.5 wt% CaCO_3 in GL3) that are consistent with the maps shown by López-Galindo *et al.* (1999). The profile of CaO is constant in BC4 (14.5-15.9 wt% CaO) but displays wider dispersion in BC5 (14.6-19.3 wt% CaO), with maxima between 1 and 3

TABLE 1. – Concentrations of metals measured in each core. Results for V, Cr, Ni, Cu, Zn and Pb are expressed in $\mu\text{g}\cdot\text{g}^{-1}$, whereas results for Hg are expressed in $\text{ng}\cdot\text{g}^{-1}$. Sediment cores BC4 and BC5 were obtained from the outer Bay of Cádiz, whereas core GL3 was obtained from the submarine prodelta of the River Guadalquivir.

	BC4	BC5	GL3
V	69	68	92
Cr	58	46	64
Ni	27	23	48
Cu	34	34	54
Zn	87	81	143
Pb	38	33	64
Hg	168	148	335

cm and minima between 11 and 13 cm; on average core GL3 from the Guadalquivir submarine prodelta had a higher concentration and a lower dispersion (16.3-18.0 wt% CaO).

Trace metals of environmental interest (Fig. 4 and Table 1) did not reach a high maximum concentration (Table 1) and displayed rather constant downcore profiles both in the outer Bay of Cádiz and in the Guadalquivir submarine prodelta area (Fig. 4), except for Hg in core BC4 and BC5, where an enrichment at the top was observed. The concentrations of trace metals in core GL3 were higher than those in the two cores of the Bay of Cádiz.

^{210}Pb and ^{137}Cs profiles and sediment accumulation rates

Data of bulk density and excess ^{210}Pb activity measured in the outer Bay of Cádiz (core BC4) are reported in Table 2; the ^{210}Pb profile is shown in Figure 5. The excess ^{210}Pb activity varied from about 40-50 $\text{Bq}\cdot\text{kg}^{-1}$ in the upper layers to 5 $\text{Bq}\cdot\text{kg}^{-1}$ in the deeper layer. On the basis of the excess ^{210}Pb activity profile,

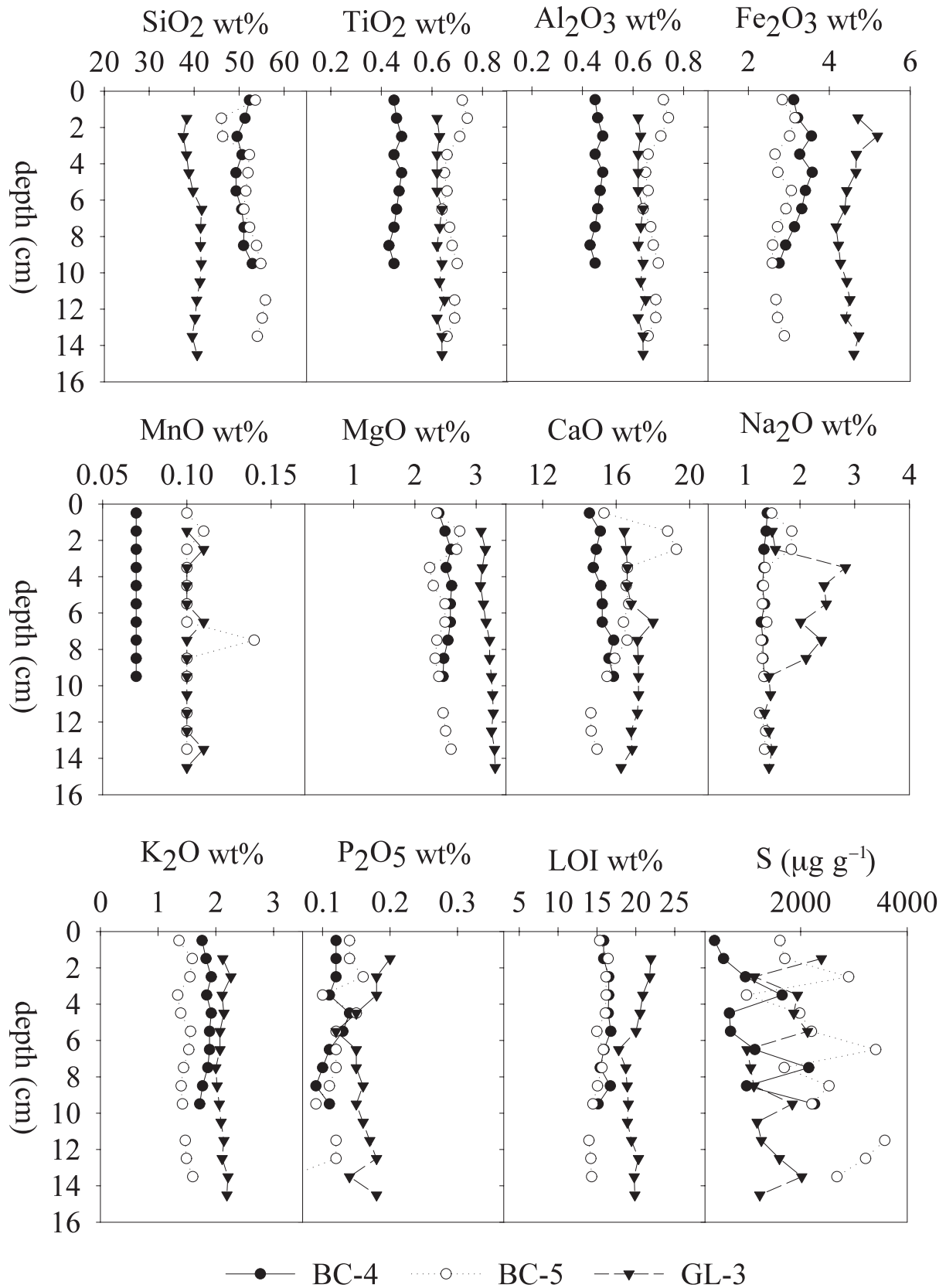


FIG. 3. – Depth profiles of major elements in the sediment cores from the Gulf of Cádiz. The origin of the cores is shown in Figure 1. Sediment cores BC4 and BC5 were obtained from the outer Bay of Cádiz, whereas core GL3 was obtained from the submarine prodelta of the River Guadalquivir.

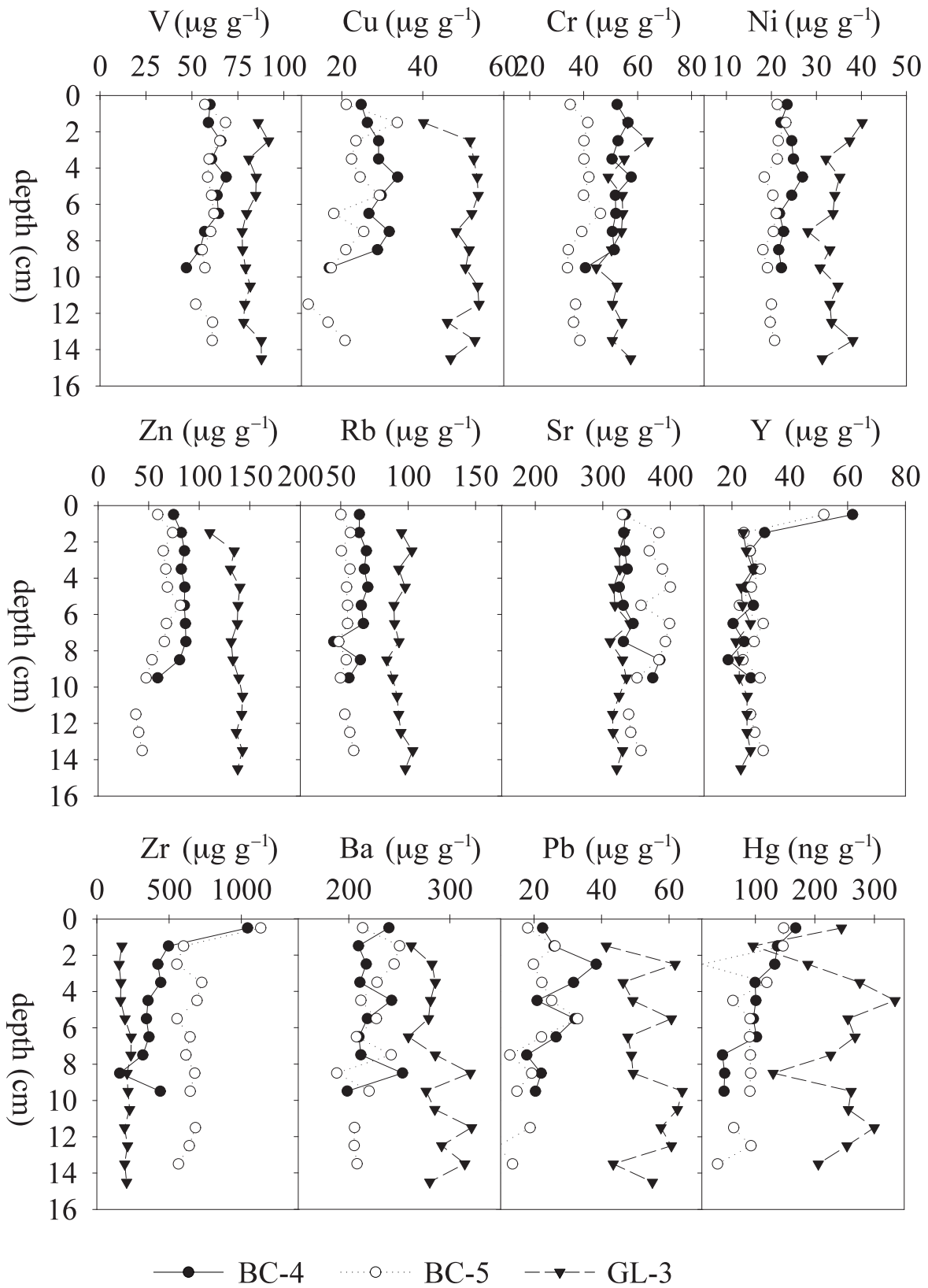


FIG. 4. – Depth profiles of trace elements in the sediment cores from the Gulf of Cádiz. The origin of the cores is shown in Figure 1. Sediment cores BC4 and BC5 were obtained from the outer Bay of Cádiz, whereas core GL3 was obtained from the submarine prodelta of the River Guadalquivir.

TABLE 2. – Bulk density and $^{210}\text{Pb}_{\text{xs}}$ profiles in sediment core BC4 from the outer Bay of Cádiz.

Section (cm)	Bulk density (g cm^{-3})	$^{210}\text{Pb}_{\text{xs}}$ (Bq kg^{-1})
0-1	0.9	44 ± 4
1-2	1.1	37 ± 4
2-3	1.0	45 ± 4
3-4	1.1	39 ± 4
4-5	1.1	51 ± 5
5-6	1.1	38 ± 4
6-7	1.1	29 ± 4
7-8	1.2	21 ± 3
8-9	1.3	17 ± 3
9-10	1.3	5 ± 3

we considered the surface mixed layer (SML) to be the slice from 0 to 5 cm and the non-mixed layer to be the slice from 5 to 10 cm. When applying Equation 2 to the non-mixed layer of core BC4, a sedimentation rate S of $0.10 \pm 0.01 \text{ cm yr}^{-1}$ ($r = 0.9847$, $p = 0.0007$) and an apparent sediment accumulation rate (SAR) of $0.11 \pm 0.01 \text{ g cm}^{-2} \text{ yr}^{-1}$ ($r = 0.9867$, $p = 0.0005$) were obtained. The ^{210}Pb mixing-coefficient (D_b) calculated with Equation 3 was $1.07 \pm 0.13 \text{ cm}^2 \text{ yr}^{-1}$ ($r = 0.77$, $p = 0.00003$).

^{137}Cs vertical profile remained quite constant in the upper layers (2-3 Bq kg^{-1}), declining downward to about 1 Bq kg^{-1} , with no evidence of fallout peaks (Fig. 5).

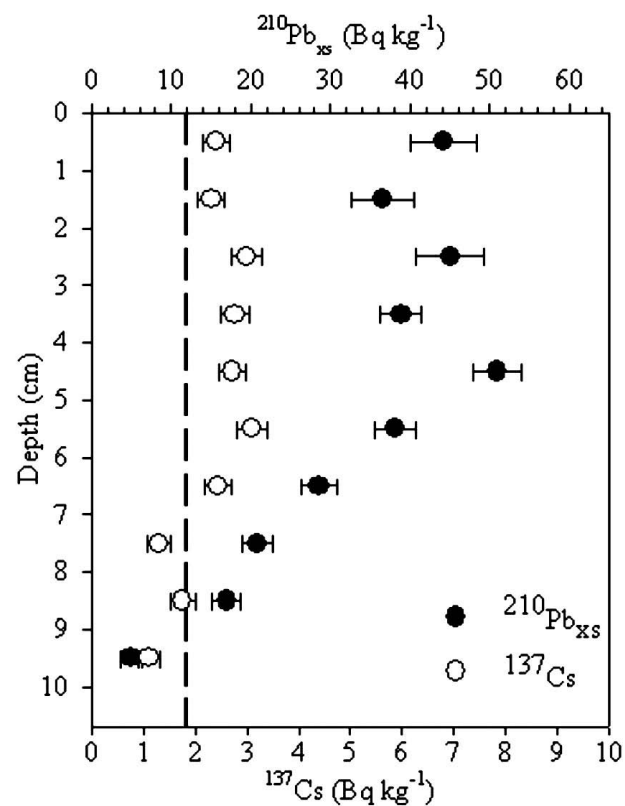


FIG. 5. – $^{210}\text{Pb}_{\text{xs}}$ (filled circles) and ^{137}Cs (open circles) activities in core BC4 from the outer Bay of Cádiz. Dashed line indicates average supported ^{210}Pb ($=^{226}\text{Ra}$).

DISCUSSION

Total organic carbon (TOC) and total nitrogen (TN) distribution and ratios

TOC values found in the sediments under the influence of the River Guadalquivir (core GL3) and those from the Bay of Cádiz (core BC4 and BC5) fall within the typical low range for coastal sediments (Dickens *et al.*, 2004), and are close to those reported for marine sediments from the inner continental shelf of the southwest Atlantic coast of Spain (López-Capel *et al.*, 2006; Sánchez-García *et al.*, 2008).

The most diagnostic point is the C/N index (atomic TOC/TN ratio), which can be used to distinguish among potential organic matter origins (e.g. marine phytoplankton $C/N = 7.4 \pm 1.3$, and cellulose rich vascular land plants $C/N \geq 20$; Meyers, 1994, 1997; Anderson and Sarmiento, 1994). Thus, the C/N values found here (Fig. 2), mostly around 10 with the exception of few layers in core GL3, seem to be attributable to a predominantly marine origin for the sedimentary organic matter (OM). However, one should be cautious with such an interpretation, since the observed $\delta^{15}\text{N}$ values in the top 20 cm from the Gulf of Cádiz (2.9-6.1‰, Sánchez-García *et al.*, 2008) are likely to indicate a mixed contribution of both marine and terrestrial organic matter.

Sediment geochemistry

Core GL3 from the area under the influence of the River Guadalquivir has a completely different composition to that of the other two cores. It has higher concentrations of Al_2O_3 and other elements such as Fe_2O_3 , MgO , K_2O , V, Ni, Cu, Zn, Rb, Pb (Figs. 3 and 4) that can be related to a clay mineral fraction, which is dominant in the sediments of this area (López-Galindo *et al.*, 1999). The profiles of these elements in core GL3 are rather regular, with a minimum in concentration for almost all elements at 7 cm depth within the core. These elements have lower concentrations and generally comparable downcore profiles in the two cores (BC4 and BC5) from the outer Bay of Cádiz (Figs. 3 and 4). Some difference is evident for K_2O , and in general, core BC5 displays a greater variation in the topmost 5 cm, with an increase between 2 and 3 centimetre followed by a more or less regular trend.

SiO_2 concentrations are high in cores from the outer Bay of Cádiz, and display profiles that are generally opposite to the clay mineral fraction described above (Fig. 3). The $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio shows a strong positive correlation with grain-size in several cases (Viscosi-Shirley *et al.*, 2003; Dinelli *et al.*, 2007) and in the cores of the Bay of Cádiz the values are typical of a sandy sediment (5.5-7.2 $\text{SiO}_2/\text{Al}_2\text{O}_3$ in BC4, 5.5-8.4 $\text{SiO}_2/\text{Al}_2\text{O}_3$ in BC5), whereas in core GL3 the lower values (3.4-4.2) point to a consistently finer mean grain-size, in accordance with the grain-size data pub-

lished by López-Galindo *et al.* (1999) and Gutiérrez-Mas *et al.* (2003). The significant enrichment of Y and Zr in both cores from the outer Bay of Cádiz can be related to sorting effects on trace minerals (e.g. zircon) (Fig. 4). A similar effect is common in sedimentary environments (Fralick and Kronberg, 1997; Dypvik and Harris, 2001; García *et al.*, 2004), and is related to the action of bottom currents that selectively remove the fine grain size fraction and concentrate the heavy minerals. In general, trace metals do not reach very high concentrations, except Pb in core GL3, which reaches maximum concentrations of 65 $\mu\text{g kg}^{-1}$ (Fig. 4), three times the average shale composition (20 $\mu\text{g kg}^{-1}$, Turekian and Wedephol, 1961). However, this result is consistent with data reported for the Guadalquivir estuary (Riba *et al.*, 2004).

The vertical profiles of the trace metals do not indicate surface enrichment in sediments from the outer Bay of Cádiz; however, a slight increase in Cr, Cu, Zn and Pb concentrations in core BC5 can be observed in the topmost 8 cm (Fig. 4), and the same feature can also be observed in BC4, though only one sample shows reduced values at the bottom of the core. No significant downcore changes can be observed in core GL3.

Cores collected in the outer Bay of Cádiz show similar mercury profiles (Fig. 4), with higher concentrations at the top decreasing to nearly constant levels with depth. Mercury levels found in the upper sections (133-168 ng g^{-1} and 119-148 ng g^{-1} , respectively) are consistently lower than those found in the inner Bay and littoral ecosystems in the Gulf of Cádiz (DeValles *et al.*, 2002; Ligeró *et al.*, 2002). The lowest levels were found in deeper layers of cores BC4 and BC5 (45-49 ng g^{-1} and 37-64 ng g^{-1} , respectively), showing values comparable to those detected in mud volcano cores collected from the Gulf of Cádiz (Mieiro *et al.*, 2007). Mercury concentrations of about 50 ng g^{-1} were also observed at the base of 2-m cores collected in the Gulf of Cádiz, and resulted from transport by the Rivers Tinto and Odiel (Cossa *et al.*, 2001). Conversely, core GL3 from the Guadalquivir area exhibited the highest concentrations, with mercury peaks observed at different depths (Fig. 4). These results are consistent with the fact that this core was collected in an area located in the submarine prodelta of the River Guadalquivir, which is the main fluvial input of the Gulf of Cádiz. Hg levels found in this core fall within the range detected in sediments from the River Guadiamar, a tributary of the River Guadalquivir, and in littoral sediments under the influence of the Odiel system (Alastuey *et al.*, 1999; Usero *et al.*, 2005; Sáinz and Ruiz, 2006).

^{210}Pb and ^{137}Cs profiles and sediment accumulation rate

The magnitude of calculated sedimentation rate and sediment accumulation rate (SAR) in the outer Bay of Cádiz broadly reflects values that have also been found in shelves of the mid-Atlantic, the western Mediterranean, and the North Iberian Margin (Sánchez-Cabeza

et al., 1999; Masqué *et al.*, 2003; Sommerfield, 2006; Jouanneau *et al.*, 2008). Bioturbation rates closely resemble mixing in deep-sea sediments rather than the much more rapid mixing seen in shallow-water environments (Schmidt *et al.*, 2002; Masqué *et al.*, 2003; Schmidt *et al.*, 2007). The effects of mixing are therefore reasonably low for the Cádiz shelf environment, but should be considered for high resolution or precise geochronological studies.

^{137}Cs activities detected were well below 10 Bq kg^{-1} (Fig. 5), in agreement with the findings of Ligeró *et al.* (2002; 2005), but the ^{137}Cs inventory (26 mBq cm^{-2}) was lower than the average inventory found in the inner Bay of Cádiz (Ligeró *et al.*, 2005). A strong positive correlation between ^{137}Cs and organic carbon was found ($r^2 = 0.84$, $p = 0.0002$), suggesting that the capacity of retention of ^{137}Cs in the sediment is linked to the organic matter (Rubio *et al.*, 2003). However, mobility of ^{137}Cs in the sediment column through processes of molecular diffusion and biological activity cannot be excluded in this area, considering that BC sites showed slightly higher faunal density and biomass than GL sites, as well as greater species richness according to the findings of Ferrón *et al.* (2009).

The core (BC4) does not show maximum values that can be directly associated with the historical fallout of ^{137}Cs , in agreement with other studies carried out in Spanish coastal and marine ecosystems (Gascó *et al.*, 1999; Rubio *et al.*, 2003; Ligeró *et al.*, 2005). The impact of the Chernobyl disaster has not been great in Spain, as can be inferred from the data reported by UNSCEAR (1988) and De Cort *et al.* (1998). Average deposition densities for ^{137}Cs after the Chernobyl disaster were about 0.02 kBq m^{-2} in the western Spanish regions, and about 0.07 kBq m^{-2} in the eastern regions. Finally, despite the close proximity, the Gulf of Cádiz was probably not contaminated by fallout from the accident in Algeciras in 1998; this conclusion agrees with plume trajectory simulations carried out by Vogt *et al.* (1998) and Quelo *et al.* (2007).

CONCLUSIONS

Sediment cores from the outer Bay of Cádiz display a similar composition, reflecting a relatively coarse grained texture, whereas sediments in the Guadalquivir prodelta area are dominated by finer grain sizes, as suggested from bulk geochemical analyses. Levels of trace metals (V, Ni, Cu, Zn, Pb and Hg) are higher in the Guadalquivir prodelta area than in the Bay of Cádiz area and are influenced by the contribution of the heavily contaminated sediments from the River Guadalquivir. In this area, trace metals do not vary with depth, whereas a shift in concentration is observed in the Bay of Cádiz cores. Future studies are needed to extend the application of the ^{210}Pb mixing model for estimating bioturbation and sediment accumulation rates to other locations in the Bay of Cádiz and to the Guadalquivir area, where no previous data are available.

ACKNOWLEDGEMENTS

This research was supported by the Spanish Inter-Ministerial Science and Technology Commission by means of the “EMIGAS” project (CTM2005-01364/MAR).

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Received November 1, 2008. Accepted July 30, 2010.
Published online November 13, 2010.