

Distribution patterns and enrichment of lead, zinc and copper in surface sediments of the central Portuguese shelf and upper slope

Patrones de distribución y enriquecimiento de plomo, zinc y cobre en los sedimentos superficiales de la plataforma y talud superior de la zona central portuguesa

C. C. Jesus^{1*}, H. de Stigter², P. Miranda¹, A. Oliveira³, F. Rocha¹

¹ *GeoBioTec, Department of Geosciences, University of Aveiro, 3810-193 Aveiro, Portugal*
ccesar.jesus@gmail.com; paulo.miranda@ua.pt; tavares.rocha@ua.pt

² *Royal Netherlands Institute for Sea Research (NIOZ), P.O. Box 59, 1790 AB Den Burg, Texel, The Netherlands*
Henko.de.Stigter@nioz.nl

³ *Instituto Hidrográfico, Rua das Trinas, 49, 1249-093 Lisboa, Portugal. anabela.oliveira@hidrografico.pt*

**corresponding author*

Received: 30/04/2013 / Accepted: 01/10/2013

Abstract

Geographic patterns of Cu, Pb and Zn enrichment on the Lisbon-Setúbal-Sines continental shelf and upper slope (central Portuguese margin) were studied in this paper to gain insight into current pathways of trace metal dispersal. Our study is based on the analysis of elemental concentrations and mineralogy of surface sediment samples collected offshore one of the most industrialised areas of Portugal. On the Lisbon-Setúbal-Sines shelf concentrations of Al, Fe, Mg, Ti within the fine-grained sediment fraction appear to a large extent related to the amount of fine-grained fraction in the bulk sediment. The extent of enrichment of trace metals in the studied area follows the sequence: Pb > Zn > Cu. Generally, the enrichment of trace metals tends to decrease in offshore direction suggesting that the excess of trace metals must be derived from land. The areas of the Lisbon-Setúbal-Sines shelf most affected by enrichment of trace metals include the Tagus and Sado mud patches and the inner shelf between Tróia and Sines, including the areas close to the Sado outlet and the area adjacent to the St. André and Melides coastal lagoons, which highlights the nearby estuaries and the lagoons as likely sources for the enrichment. In addition, the more widespread enrichment of Pb in sediments points to contributions from atmospheric inputs. The similarity between the results here presented with later data from other authors allows concluding that our results provide a representative view of trace metal enrichment in surface sediments between 1980 and 2000.

Keywords: Trace Metals, Anthropogenic Contamination, Sediment Distribution Patterns, Continental Shelf, Portugal

Resumen

Los patrones geográficos de enriquecimiento de Cu, Pb y Zn en la plataforma continental y talud superior de el margen central portugués de Lisboa-Setúbal-Sines fueron estudiados en este trabajo Para profundizar en el conocimiento de las vías actuales de dispersión de metales traza. Nuestro estudio se basa en el análisis de las concentraciones elementales y de la mineralogía de muestras de sedimentos superficiales recogidos a lo largo de la zona más industrializada de Portugal. Las concentraciones de Al, Fe, Mg, Ti

[†] *Present affiliation: Nemus, Lda., Campus do LUMIAR, Edificio D, 1649-038 Lisboa, Portugal.*

en la plataforma de Lisboa-Setúbal-Sines dentro de la fracción de sedimento de grano fino aparecen en gran medida relacionadas con la cantidad de fracción fina en el sedimento total. El grado de enriquecimiento de metales traza en el área de estudio sigue la secuencia: $Pb > Zn > Cu$. En general, el enriquecimiento de los metales traza tiende a disminuir en dirección al mar adentro lo que sugiere que el exceso de metales traza se debe derivar de la tierra. Las zonas de la plataforma Lisboa-Setúbal-Sines más afectadas por el enriquecimiento de trazas de metales incluyen los depósitos de lodo de Tajo y de Sado y la plataforma interna entre Tróia y Sines, incluyendo las áreas cercanas a la salida del Sado y de las lagunas costeras de St. André y Melides, que sugiere que estos son las posibles fuentes de enriquecimiento. Además, el enriquecimiento más generalizado de Pb en los sedimentos apunta a las contribuciones de los aportes atmosféricos como fuente principal. La similitud entre los resultados aquí presentados con los datos posteriores de otros autores permite concluir que nuestros resultados proporcionan una visión representativa del enriquecimiento de metales traza en sedimentos superficiales entre 1980 y 2000.

Palabras clave: Metales traza, Contaminación antropogénica, Patrones de distribución de sedimentos, Plataforma continental, Portugal

1. Introduction

The elemental composition of marine sediments is determined primarily by the mixture of particulate components that make up the bulk of the sediment. These components include lithogenic material derived from continental erosion, their composition reflecting the geology of the source area, as well as biogenic material produced in the marine environment (Fütterer, 2006). Trace elements, generally occurring in very low abundance at the Earth's surface, may become enriched in certain marine deposits, due to their high affinity to particulate matter, and under influence of physical sediment sorting and diagenetic alteration. Enhanced concentrations of trace metals in recent surface sediments, especially in the continental shelf environment, often reflect anthropogenic input in addition to input from natural sources. The distinction of contributions from both sources and the study of the anthropogenic fraction of elements may be relevant not only for assessment of anthropogenic impact in marine environment but also to highlight pathways of recent sediment transport (e.g. Jesus et al., 2010). For the latter purpose, particle-reactive chemical species which are adsorbed to the surface of particles are especially good tracers. Since the majority of anthropogenic contaminants are derived from the mainland they may be used to track recent input of terrigenous sediments and to identify the main depocentres of recent sediments. The potential of these tracers increases as the signatures of the potential sources are better known.

The distinction of the natural and anthropogenic fraction through bulk concentrations is complicated by the unequal distribution of trace metals over different grain-size fractions and different components of the mineral and organic matrix (Loring and Rantala, 1992). For this reason, trace metal contents are usually assessed within a defined grain-size fraction, and normalised against a common major element representative for the natural sediment fraction. Such normalisation procedures are

especially important where samples from different sedimentary settings are compared. After normalisation, trace metal contents in contaminated recent sediments can be compared with contents in older, non-contaminated sediments from a similar environmental setting. The observed recent excess in trace metal content can then be directly interpreted as the anthropogenic input.

In this paper we discuss the distribution patterns of major and trace elements in the fine-grained fraction of surface sediments from the central Portuguese shelf and upper slope and assess the geographic patterns of Pb, Zn and Cu enrichment offshore one of the most industrialised areas of Portugal. In addition, we infer about sources of these trace metals in order to gain insight into the pathways of recent trace metal dispersal in the studied shelf area. Our study is based on the analysis of elemental concentrations and mineralogy of surface sediment samples collected from the shelf and upper slope between Cape Raso and Cape Sines (central Portuguese margin). Previous trace metal studies in the same area are scarce and mostly deal with more limited geographic areas, such as the continental shelf adjacent to the Tagus and the Sado rivers (Paiva et al., 1997; Jouanneau et al., 1998) and the Tagus mud patch (Mil-Homens et al., 2009).

2. Regional Setting

We studied a section of the central Portuguese shelf and slope extending between Cape Raso in the north and Cape Sines in the south (Fig. 1). On the landward side, the studied shelf area is bounded by a coast constituted of low mountain ranges ending in cliff coasts, two major estuaries, and coastal arcs with sand beaches, dunes and coastal lagoons. On the seaward side, the shelf ends abruptly in steep and gullied slopes that lead down to deeply incised submarine canyons. In its southern part the shelf passes more gradually into a gentle slope. The shelf, varying in width between 3 and 30 km, is naturally divided in three compartments by protruding capes and

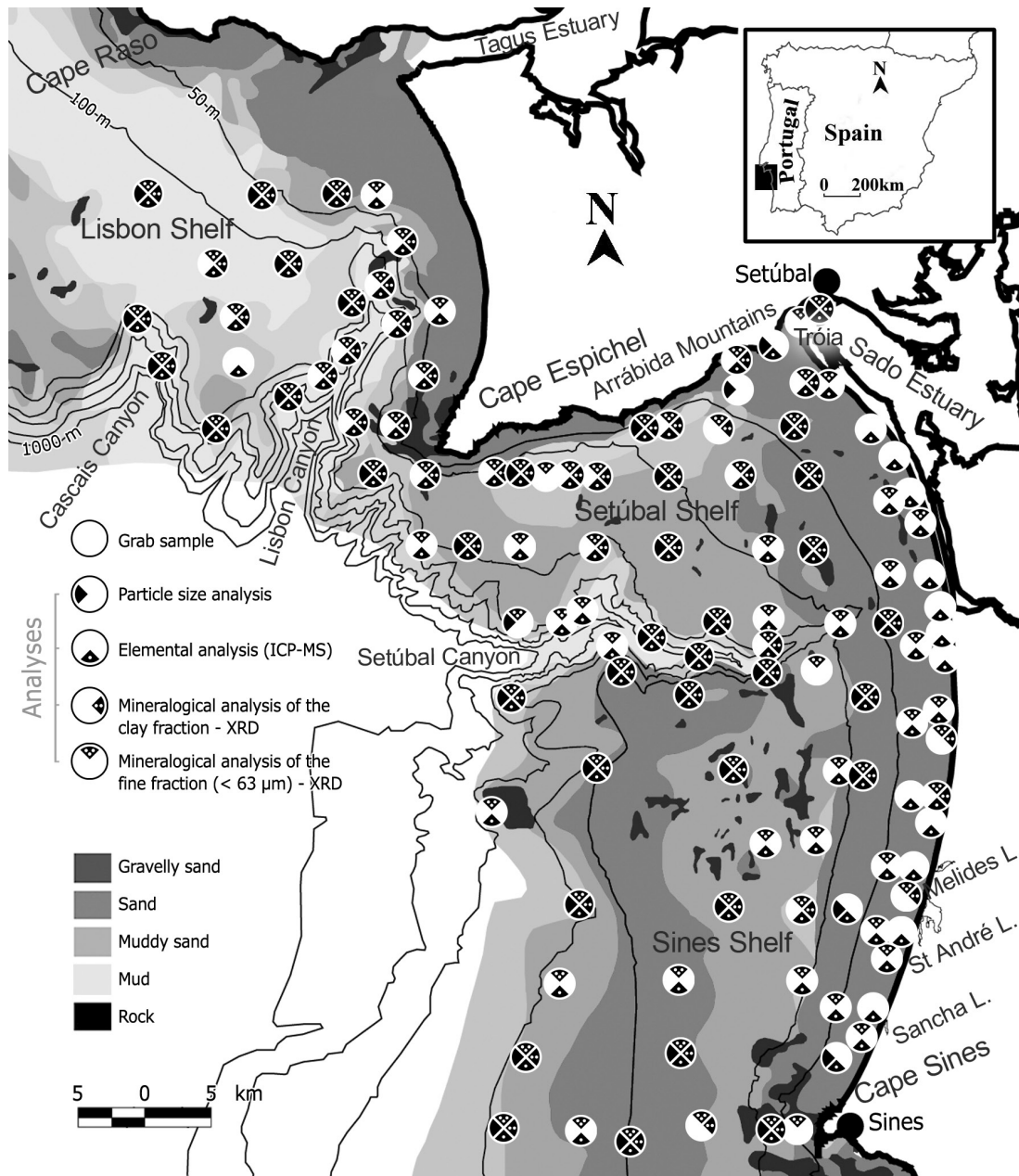


Fig. 1- Surface sediment distribution on the continental shelf between Cape Raso and Cape Sines with location of surface sediment samples analysed in the present study. Different symbols within the circles represent the different analyses performed on the samples.

Fig. 1- Distribución de los sedimentos superficiales de la plataforma continental entre Cabo Raso y Cabo Sines con la ubicación de las muestras de sedimentos analizados en el presente estudio. Los diferentes símbolos dentro de los círculos representan los diferentes análisis realizados sobre las muestras.

deeply incised canyon branches.

The northern compartment, which we refer to as the Lisbon shelf, extends between Cape Raso and Cape Espichel. It is bounded to the north by a stretch of cliffs extending eastwards from Cape Raso to the Tagus River mouth, and to the east by a coastal arc with dunes and low cliffs extending southwards from the Tagus River mouth to Cape Espichel. Parallel to this eastern land boundary, the Lisbon Canyon cuts deeply into the Lisbon shelf, with the canyon head located 13 km off the Tagus River mouth. To the south the Lisbon shelf is delimited by steep

slopes that lead to the Cascais Canyon. The recent sediment cover on the Lisbon shelf is largely determined by sediment discharge from the Tagus (Tejo) River, a major river draining an area of more than 80 000 km² and with a mean annual discharge of 16×10^9 m³ y⁻¹. Sediment discharge onto the shelf has resulted in the formation of a large submarine protofluvial delta in front of the river mouth, which forms part of a large expanse of essentially muddy sediment covering almost the entire Lisbon shelf, and which is known as the Tagus mud patch. The mud patch has an area of about 560 km² and is composed of

sediments with more than 85 % of terrigenous material whereas carbonate contents vary from 5 to 9 % (Alt-Epping et al., 2007 and Jouanneau et al., 1998). Sandy and gravelly deposits occur on the inner shelf, where the energy of littoral currents is sufficiently high to remove the finer-grained sediment fractions.

The central shelf compartment, which we refer to as the Setúbal shelf, extends from Cape Espichel to where the Setúbal Canyon approaches the southern coastline. It is bounded to the north by steep cliffs of the Arrábida Mountains extending westwards from Cape Espichel to the Sado River mouth, and to the east by the long sand spit that closes the Sado Estuary from open sea. To south and west the Setúbal shelf is sharply delimited by steep slopes of, respectively, the upper Setúbal and Lisbon Canyon, which merge at about 2000 m depth. Deposits of the Sado profluvial delta cover only a relatively small area confined to the river outlet, in accordance with the much smaller size of this river compared to the Tagus River. Sandy deposits prevail on the Setúbal shelf, predominantly composed of terrigenous lithoclastic material, mostly quartz, whereas bulk carbonate content is mostly below 30 % (Instituto Hidrográfico, 2005). Muddy sediments are restricted to the northern coast of the bay in front of Sesimbra and to the upper Setúbal Canyon (Moita and Quevauviller, 1986, Monteiro and Moita, 1971).

The southern compartment, which we refer to as the Sines shelf, extends between the Setúbal Canyon and Cape Sines. This shelf area is bounded to the north by the upper Setúbal Canyon, which cuts deeply into the shelf and approaches the coast to only 6 km. To the east the shelf is bounded by the coastal arc that extends from the Sado Estuary southwards to Cape Sines, and is constituted of sand beaches, dunes and low cliffs. To the west, the shelf passes gradually into the gently sloping continental slope. Sandy deposits prevail on the Sines shelf, both on the inner part where finer-grained sediment is removed by littoral wave and current dynamics, and on the outer shelf near the shelfbreak, where they occur as a remnant of an old shoreline dated ~16000 years BP (Dias, 1987). These latter deposits have carbonate contents which can exceed 50 % although contents below 30 % predominate (Instituto Hidrográfico, 2005). Local rock outcrops surrounded by gravelly deposits, although also occurring on the other shelf areas, are most common on the Sines shelf around Cape Sines. Of particular interest with regards to local enrichment of trace metals in near-shore deposits are the Melides, Santo André and Sancha lagoons, located in the coastal arc north of Cape Sines. These lagoons have as common feature a narrow, linear and reflective sand barrier which is attached to the mainland at both ends (Freitas et al., 2002).

Sediments recovered from the edges of the Cascais, Lisbon and Setúbal Canyon canyon invariably consist of fine-grained predominantly terrigenous material, in accordance with observations by Jouanneau et al. (1998) and De Stigter et al. (2011).

3. Materials and Methods

3.1. Field sampling and sample preparation

Hundred and seventeen surface sediment samples from water depths between 1 and 572 m on the continental shelf and upper slope, between Cape Raso and Cape Sines, were collected between 1980 and 1987 during several cruises conducted within the framework of Instituto Hidrográfico internal project SEPLAT (Fig. 1). These samples, representing approximately the first 15 cm of the sediment column, were collected using Shipek, Van Veen and Smith McIntyre grabs. These samples have been kept at Instituto Hidrográfico laboratories in controlled conditions.

Each shelf sample was homogenised and split in two portions for different analyses: 1) mineralogical and grain size analyses and 2) elemental analysis. The first set of samples was treated with hydrogen peroxide (H_2O_2 , 5 %) to remove organic material. H_2O_2 was added stepwise until no more reaction occurred. Subsequently, samples were rinsed several times with distilled water to make sure that all the organic matter was removed. These organic-matter-free samples and the second set of untreated samples were mechanically dispersed by ultrasonication and then wet-sieved through a 63 μm sieve in order to normalise all sediments collected on the continental shelf to the same grain size fraction.

3.2. Grain size analysis

Grain size spectra of the fine-grained fraction of sediment samples from the continental shelf/upper slope were determined with a MALVERN MicroP 2000 laser forward-scattering particle sizer at the Instituto Hidrográfico. The sediment was mechanically dispersed by ultrasonication without use of a chemical dispersant.

3.3. Elemental analysis

Hundred and six shelf sediment samples were analysed through ICP-MS for total concentration of Al, As, Ca, Cr, Cu, Fe, Mg, Mn, Ni, Pb, Th, Ti, U and Zn, at the internationally accredited ACME Analytical Laboratories Ltd – ISO 9002 Accredited Co. According to routine procedure of the laboratory, 0.25 g of sample was heated in HNO_3 -HF-HClO₄ to fuming and then evaporated to dryness. The

residue was dissolved in HCl. The diluted samples were analysed using an ICP-MS. All samples were analysed in a single run to reduce instrumental drift-effects. Several samples were repeated in the beginning and at the end of the run to assess the amount of drift.

Accuracy and precision were assessed through analysis of 8 repeats of reference material DST6. Unidentified repeats (10 % of the total number of samples, according to recommendations of Darnley et al., 1995) and 2 samples of reference material GBW 07309A (China Centre for certified Ref. Mat.) were also included among our samples.

In order to express accuracy, percent recovery calculated from the reference material DST6 was between 90 and 110 % for most elements, except for Zn which seems to have been underestimated (88 %). Percent recovery calculated from the standard reference material GBW 07309A indicated underestimation of Cr (67 %), U (87 %) and Ti (82 %). Precision was assessed through relative standard deviation (RSD) and based on replicate analyses made by the laboratory and 12 replicate samples included in our set of samples. According to Huber (1998) in Ribani et al. (2004) values of RSD < 5 % and < 20 % are acceptable for major and minor elements, respectively. RSD values calculated through the laboratory's replicate analyses were within acceptable limits for all elements except Ti, which had a precision of 9 %. RSD values calculated using the 12 included replicate samples give also percentages within acceptable limits for all elements except again Ti with the same accuracy of 9 %.

3.4. Mineralogical analyses

For the present study a total of 99 surface sediment samples were analysed for bulk mineralogical content and 64 surface sediment samples for clay mineralogical contents, by means of XRD analysis. The majority of analyses were carried out at the Geosciences Department of the University of Aveiro, and a smaller number at the Instituto Hidrográfico in Lisbon. In both laboratories analyses were carried out using a Philips PANalytical diffractometer, with CuK α radiation, following the same analytical procedure. The identification of the main mineral phases in the samples was done by using the database from Brindley and Brown (1980) and MacDiff software's database (Petschick, 2000). An attempt to quantify relative abundance of minerals was also done, on the basis of the percentage approach, which takes the sum of all identified phases in a sample as 100 %. Since this is a relative quantification the term semi-quantification is used in the presented estimates. For semi-quantitative analysis, the peak areas from basal reflections of minerals were estimated using MacDiff software (Petschick, 2000) and afterwards weighted by empirically estimated factors deter-

mined by Huertos and de los Monteros (1974) in Gomes (1988) for the fine-grained fraction and those used by Rocha (1993), Oliveira et al. (2002) and Abrantes (2005) for the clay fraction. The XRD mineralogical analyses were performed on the fine-grained gently homogenised sediment (< 63 μ m) as single runs and on the clay fraction by running three successive XRD scans on the sample: a first scan on the original air dried sample, a second scan after saturating the sample with glycerol, and a third scan after heating the glycerol-saturated sample to 500 °C for 90 minutes.

4. Results

4.1. Grain size of the fine-grained sediment fraction

Relatively higher values of mean grain size of the fine-grained sediment fraction occur in different parts of the study area such as the upper reaches of the Cascais, Lisbon and Setúbal canyons where fine-grained sediments dominate bulk sediments and off the Sado Estuary and in the southernmost part of the study area close to Cape Sines where bulk sediments is dominantly sand. The mean grain size values of the fine-grained sediment fraction seem therefore to have no relationship with water depth or to the type (bulk grain size) of sedimentary deposit (not shown). Modal grain size values of the referred sediment fraction show as well no relationship with water depth or to the type of sedimentary deposit (Fig. 2a). On the other hand, contents of clay-sized particles show a clearer spatial distribution patterns (Fig. 2b). Relatively lower contents of clay-sized particles (17 to 31 %) are found on the Lisbon shelf compared to the other studied shelf areas (Table 1) and also closer to the Cape Sines in the southernmost area (Fig. 2b).

4.2. Fine-grained fraction bulk mineralogy

Seven different minerals / groups of minerals make up the bulk of the fine-grained fraction of surface sediments of the Lisbon-Setúbal-Sines shelf (Table 1). In order of most to least abundant these are: Quartz (Qz), Calcite (Cc), Phyllosilicates (Phy), Plagioclases (Plg), K-Feldspars (K-F), Aragonite (Arg) and Mg-Calcite (Mg-Cc).

Quartz shows the highest contents at shallower water depths at sandy inner shelf deposits, and the lowest contents at fine-grained deposits of the shelfbreak and upper canyons. Concentrations of calcite tend to be higher in sandy deposits however they can also be higher in fine-grained deposits, as it happens in the upper Setúbal Canyon (Fig. 2c). In general, contents of calcite seem more related to the spatial distance from present-day active sediment sources rather than to the dominant grain size

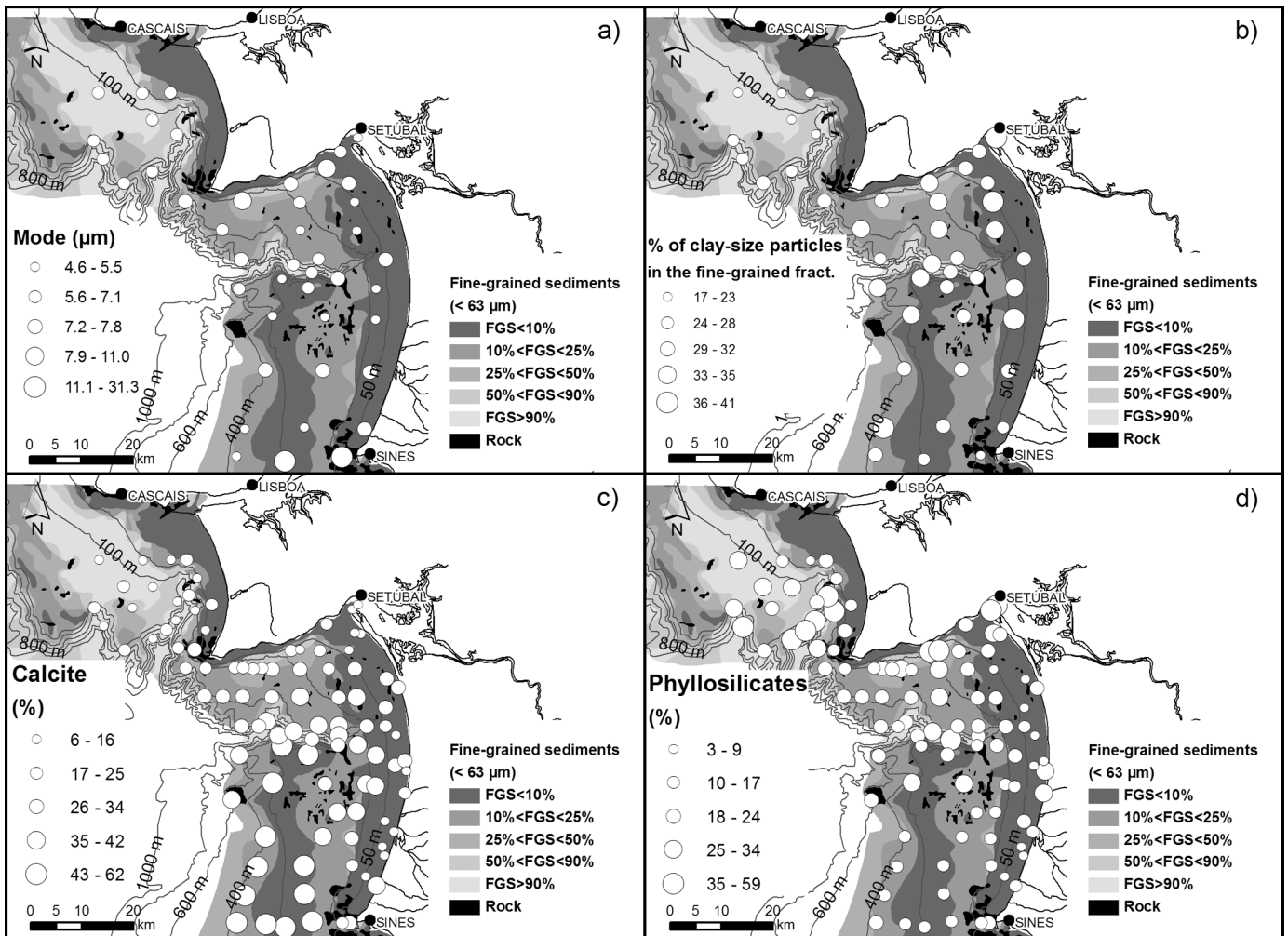


Fig. 2- Grain size mode (a), content of clay-sized particles (b) calcite (c) and phyllosilicates (d) in the fine-grained fraction of surface sediments from the Lisbon-Setúbal-Sines shelf and upper slope.

Fig. 2- Moda (a), contenido de las partículas de tamaño de arcilla (b), calcita (c) y filosilicatos (d) de la fracción de grano fino de los sedimentos superficiales de la plataforma Lisboa-Setúbal-Sines y talud superior adyacente.

of the sedimentary deposit. Contents above 25 % and up to 62 % occur on the Setúbal and Sines shelf, except near the shore, whereas on the Lisbon shelf contents are consistently below 25 % (Fig. 2c). Contents of phyllosilicates seem related to fine-grained sediment deposits. High concentrations (> 25 %) are found in the Tagus mud patch and even higher contents (> 40 %) are found in the Lisbon Canyon (Fig. 2d). On the Setúbal shelf three areas show enrichments in phyllosilicates: sediments in the outlet of the Sado Estuary (59 %), the Sado mud patch and the upper Setúbal Canyon (on both reaching ~40 %). On the Sines shelf, percentages of phyllosilicates tend to be lower than 20 % (Fig. 2d). As for plagioclase, higher values occur in the Tagus and Sado mud patches and also in the inner shelf adjacent to St. André and Melides coastal lagoons (Fig. 3a). Contents seem related to the distance to present-day active sediment sources rather than to the dominant grain size of the sedimentary deposit. The distribution pattern of K-feldspars is similar to that

from plagioclase. Finally, both aragonite and Mg-calcite reach high contents (> 20 %) in inner shelf sandy deposits while they seem absent in most of the other sedimentary deposits.

4.3. Clay-fraction mineralogy

Four different groups of minerals were identified and in most cases their percentages can vary considerably (Table 1): illite (54 – 80 %), kaolinite (18 – 40 %), smectite (1 – 12 %) and chlorite (0 – 3 %).

Contents of illite in the study area show a southward increase and also some enrichment with increasing water depth. Both Tagus and Sado mud patches have contents between 61 and 69 % while values over 72 % occur almost exclusively on the Sines shelf.

The distributions of kaolinite (Fig. 3b) and smectite show opposite trends to that of illite, decreasing in southward direction. For this reason, only the distribution pat-

tern of kaolinite is shown. Generally, the highest concentrations are associated to the outlets of the Tagus and Sado estuaries. The spatial distribution of chlorite shows no clear trend.

4.4. Major and trace elements

Mean concentrations of Al, As, Cu, Fe, Mg, Mn, Pb, Th, Ti, U and Zn are highest on the Lisbon shelf and lowest on the Sines shelf, whereas the reverse pattern is observed for Ca, Cr and Ni (Table 1). Intermediate values are found on the Setúbal shelf. By closer inspection of distribution patterns of these elements in the different shelf areas, four groups of elements with different distribution patterns can be distinguished: 1) Ca, 2) Al, Fe, Mg, Th, Ti, U, 3) As, Cu, Mn, Pb, Zn, 4) Cr, Ni (Figures 4). The groups established according to their distribution

patterns also appear from Spearman correlation analysis, as shown in Fig. 5.

The lowest concentrations of Ca occur on the Tagus and Sado mud patches, yet on the latter contents are slightly higher. Calcium occurs in highest concentrations in the fine-grained fraction of inner shelf sandy deposits. Despite these generally high contents of Ca in the inner shelf, adjacent to the Santo André and Melides lagoons concentrations decrease to values similar to those found in the Tagus and Sado mud patches. The correlation analysis shows, as expected, that Ca correlate with carbonates (Table 2).

Al, Fe, Mg and Ti are closely associated with relatively fine-grained sediments (Fig. 6a and b) rich in quartz and phyllosilicates which prevail on the Tagus and Sado mud patches and along the canyon edges (Fig. 2d). The trace elements Th and U appear in the same association (Fig. 5).

	Lisbon shelf		Setúbal shelf		Sines shelf	
	Mean± Std. Dev. (N)	Min-Max	Mean± Std. Dev. (N)	Min-Max	Mean± Std. Dev. (N)	Min-Max
Clay (%)	24.3±4.7 (10)	17.4 - 31.3	32.5±3.6 (16)	27.0 - 40.7	31.3±3.8 (17)	23.1 - 38.0
Mean grain-size (µm)	6.9±0.4 (10)	6.1 - 7.4	6.4±0.9 (16)	4.9 - 7.7	6.9±1.2 (17)	5.0 - 9.8
Mode grain-size (µm)	6.9±0.4 (10)	6.5 - 7.8	6.9±1.7 (16)	4.6 - 11.0	9.0±7.6 (17)	4.6 - 31.3
Qz (%)	36.6±9.8 (22)	12.2-51.0	30.6±7.4 (38)	16.1-47.0	30.6±8.4 (39)	15.1 - 50.2
Phy (%)	26.8±12.1 (22)	8.7-46.3	22.7±10.2 (38)	5.3-58.6	15.0±6.2 (39)	2.7 - 27.6
Cc (%)	17.1±5.4 (22)	9.3-29.2	26.2±8.7 (38)	6.4-41.4	33.6±13.6 (39)	7.1 - 62.3
Plg (%)	10.2±3.4 (22)	3.2-16.9	7.4±3.3 (38)	1.6-15.1	8.0±5.3 (39)	1.6 - 24.6
FK (%)	6.4±4.4 (22)	1.4-16.4	5.4±2.9 (38)	0-11.5	7.5±5.7 (39)	1.2 - 24.9
Cc-Mg (%)	2.6±8.0 (22)	0-36.2	2.8±5.7 (38)	0-24.4	2.6±6.0 (39)	0 - 26.0
Arag (%)	0.4±1.2 (22)	0-5.0	4.9±6.5 (38)	0-24.2	2.8±2.6 (39)	0 - 12.8
Ill (%)	65.0±2.4 (19)	61.2-70.9	66.5±4.7 (25)	55.3-74.0	70.5±5.7 (20)	54.2-80.4
Kao (%)	31.8±2.4 (19)	26.7-35.5	30.3±4.4 (25)	22.7-39.7	25.5±3.7 (20)	17.7-32.5
Sm (%)	2.3±0.6 (19)	0.9-3.3	2.3±1.0 (25)	0.8-4.8	2.7±2.6 (20)	1.0-11.8
Chl (%)	0.9±0.7 (19)	0-3.2	1.0±0.9 (25)	0-3.2	1.3±0.9 (20)	0-3.4
Al (%)	7.9±1.5 (23)	3.7-9.6	6.2±1.8 (40)	2.2-9.0	5.2±1.5 (43)	2.0 - 7.5
As (µg g ⁻¹)	24±13 (23)	12-60	18±8 (40)	8-42	15±6 (43)	8-41
Ca (%)	5.0±3.5 (23)	2.6-19.5	10.5±4.7 (40)	3.3-22.8	11.0±4.0 (43)	3.2 - 22.4
Cr (µg g ⁻¹)	86±88 (23)	49-400	105±113 (40)	38-559	139±146 (43)	33-651
Cu (µg g ⁻¹)	29±7 (23)	15-45	27±12 (40)	13-74	21±7 (43)	12-52
Fe (%)	3.7±0.6 (23)	2.0-4.8	3.2±0.9 (40)	1.4-5.2	2.7±0.9 (43)	1.1 - 4.8
Mg (%)	1.2±0.1 (23)	1.0-1.6	1.1±0.2 (40)	0.6-1.8	1.0±0.3 (43)	0.4 - 2.0
Mn (µg g ⁻¹)	407±231 (23)	220-1194	413±663 (40)	129-4452	296±165 (43)	118 - 1105
Ni (µg g ⁻¹)	50±58 (23)	24-266	64±65 (40)	20-303	95±103 (43)	12-431
Pb (µg g ⁻¹)	91±54 (23)	40-273	75±54 (40)	19-295	56±47 (43)	21-237
Th (µg g ⁻¹)	21±21 (23)	9-102	14±8 (40)	4-34	10±4 (43)	5-23
Ti (%)	0.4±0.1 (23)	0.2-0.8	0.3±0.1 (40)	0.1-0.6	0.3±0.1 (43)	0.1 - 0.5
U (µg g ⁻¹)	4.4±3.3 (23)	2.1-17.1	3.1±1.3 (40)	1.2-6.4	2.5±0.9 (43)	1.2-4.4
Zn (µg g ⁻¹)	190±66 (23)	93-353	153±69 (40)	57-405	91±20 (43)	36 - 146

Phy – phyllosilicates, Qz – quartz, K-F – K-feldspars, Plg – plagioclase, Cc – calcite, Mg-Cc – Mg-calcite, Arg – aragonite, Kao – Kaolinite, Ill – Illite, Sm – Smectite, Chl – Chlorite

Table 1 - Descriptive statistics of the elemental composition of sediment samples collected in the Lisbon-Setúbal-Sines continental shelf and upper slope
 Tabla 1 – Estadística descriptiva de la composición elemental de las muestras de sedimento recolectadas en la plataforma continental Lisboa-Setúbal-Sines y talud superior adyacente

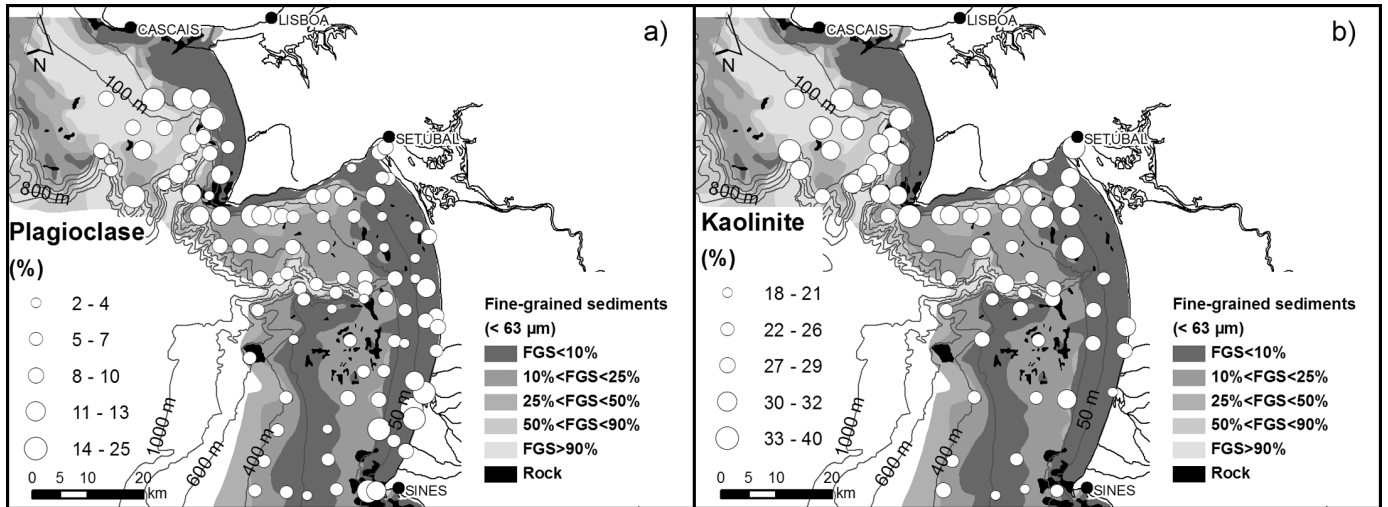


Fig. 3- Content of plagioclase (a) in the fine-grained fraction and content of kaolinite in the clay fraction (b) of surface sediments from the Lisbon-Setúbal-Sines shelf and upper slope.

Fig. 3- Contenido de plagioclasa en la fracción de grano fino (a) y el contenido de caolinita en la fracción de arcilla (b) de los sedimentos superficiales de la plataforma Lisboa-Setúbal-Sines y talud superior adyacente.

Despite the general trend increasing northwards, highest concentrations of As, Cu, Mn, Pb, and Zn are observed on the inner shelf close the mouths of the Tagus and Sado rivers. From this group, Cu and Zn correlate with phyllosilicates in the fine-grained fraction and As, Pb and Zn correlate with kaolinite identified in the clay fraction. The highest Cr and Ni contents are associated with inner shelf sandy deposits of the Setúbal and Sines shelf. The very few samples collected in the inner shelf deposits from the Lisbon shelf do not allow the same conclusion for this area. On Setúbal and Sines inner shelf areas there is a southwards increase of both these elements.

4.6. Enrichment factors for Cu, Pb and Zn

The level of trace metal enrichment in sediments can be assessed through different indices (e.g. Loring and Rantala, 1992). In this study, the enrichment of trace metals in surface sediments was assessed after normalization of trace metal concentrations relative to Fe and using average normalised trace metal concentrations of sediments older than ~150 years from a nearby area (Jesus et al., 2010) as pre-industrial reference. Since Fe had the highest accuracy in the baseline dataset and there were no signs in our data that secondary diagenetic enrichment of trace metals played a significant role, we choose to use Fe for the normalisation of trace metals. Besides, the linear relationships between enrichment factors using Al and Fe as normaliser are close to $Y=X$ and show $R^2 = 0.93$; $R^2 = 0.88$; $R^2 = 0.78$ for Zn, Pb and Cu, respectively.

Enrichment factors (EF) higher than 1.5 are considered to indicate significant enrichment. Considering the elements analysed in both sets and the results obtained by

applying the normalization, we concluded this baseline was mainly suited to analyse the enrichment of Cu, Pb and Zn.

Enrichment factors of Pb and Zn (and Cu to some extent) decrease with increasing water depth (Fig. 7). Lead shows a considerably higher percentage of samples enriched ($EF > 1.5$) compared to Zn and Cu (88 % against 43 % and 30 %, respectively). Most of the samples not enriched in those trace metals occur on the Sines shelf, especially on the outer shelf and upper slope, and in the upper Setúbal Canyon. While sediments enriched in Pb extend over most of the study area, the area with significant enrichment in Zn appears to be more restricted to the Lisbon shelf and a relatively narrow area close to the coast on the Setúbal and Sines shelves. The highest EFs of Pb (7 - 25) occur in the Sado and Tagus pro-delta deposits while the highest EF of Zn (3 - 12) occur in the Sado pro-delta deposit, along the inner shelf between Tróia and Sines and in the Tagus mud patch (Fig. 7 and Table 3). Most of the samples enriched in Cu are from inner shelf sandy deposits and only few from mud patches on the Lisbon and Setúbal shelves. Among various other areas on the inner shelf, high EFs of Cu occur close to the Sado River mouth in the Sado pro-delta deposit.

5. Discussion

5.1. Elemental distribution patterns

On the Lisbon-Setúbal-Sines shelf elemental concentrations of the fine-grained sediment fraction appear to a large extent related to the amount of fine-grained frac-

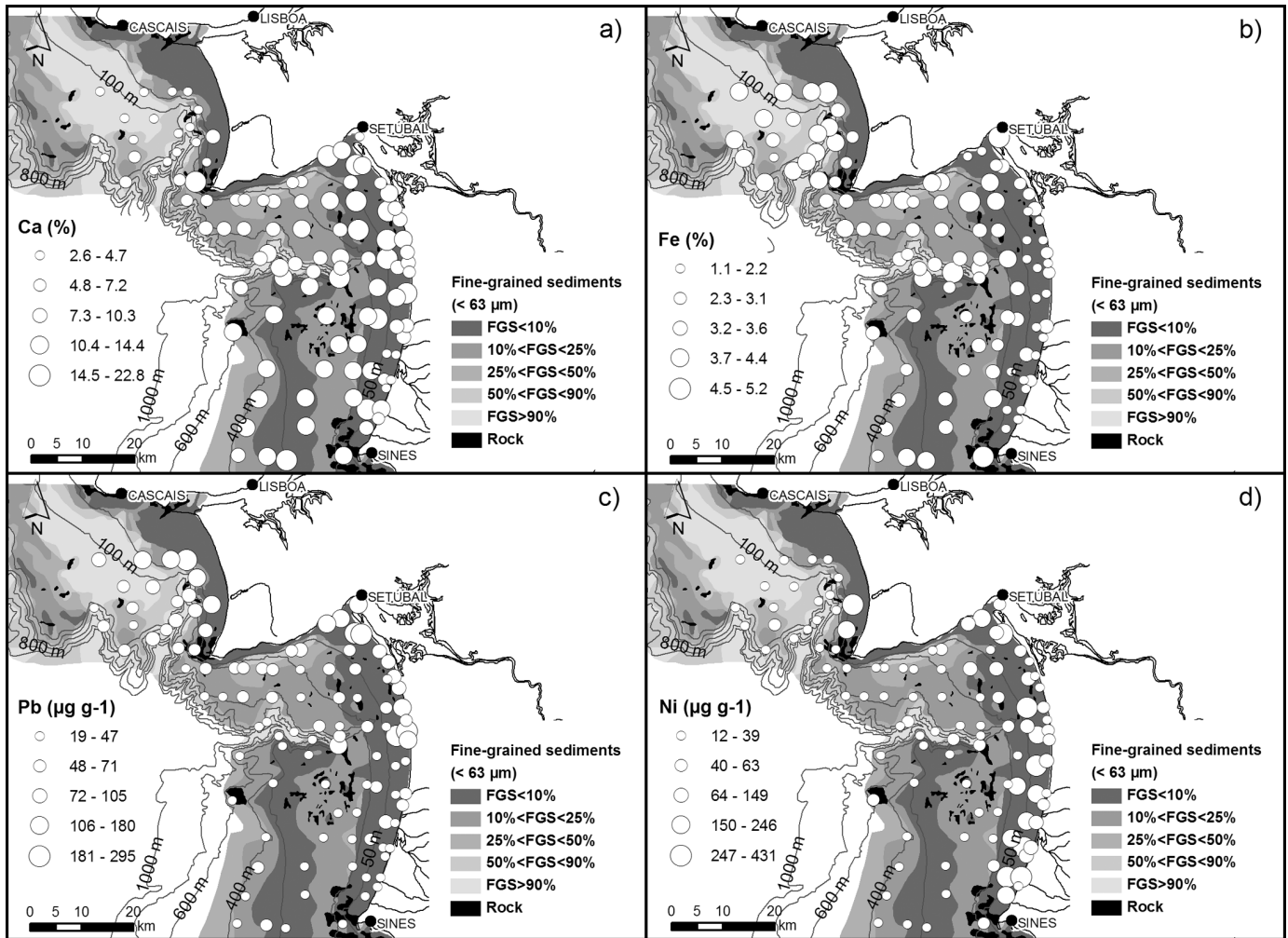


Fig. 4- Content of Ca (a), Fe (b), Pb (c) and Ni (d) in the fine-grained fraction of surface sediments from the Lisbon-Setúbal-Sines shelf and upper slope.

Fig. 4- Contenido de Ca (a), Fe (b), Pb (c) y Ni (d) en la fracción de grano fino de los sedimentos superficiales de la plataforma Lisboa-Setúbal-Sines y el talud superior adyacente.

tion within the bulk sediment. The Lisbon shelf is largely covered by fine-grained deposits derived from the Tagus River, while towards the south, on the Setúbal and Sines shelves, deposits rich in fine-grained material are less widespread (Fig. 1). In accordance, elements typically associated with fine-grained lithogenic sediments (Al, Fe, Mg, Ti) (Fig. 6a, b) show a southward decrease in mean concentrations (Table 1). In the southern area, relatively coarse sediments with high contents of biogenic carbonate are prevalent, which is in turn expressed in the fine-grained fraction by generally high concentrations of Ca.

Although trace metals are in general mostly associated with lithogenic input, the distribution of As, Cu, Mn, Pb and Zn on the Lisbon-Setúbal-Sines shelf show spatial patterns that differ somewhat from the distribution of mineral and elemental proxies of lithogenic input, as well as proxies of biogenic material (calcium and carbonate minerals – calcites and aragonite). The differing patterns of these trace metals indicate that there must be other

trace metal carriers involved and/or that part of the contents of trace metals cannot be explained by the available metal carriers, but may represent anthropogenic enrichment. This is in accordance to findings from other authors that have studied specific areas from this part of the Portuguese continental shelf and slope (e.g. Paiva et al., 1997; Mil-Homens et al., 2009).

The distribution patterns of As, Cu, Mn, Pb and Zn show higher concentrations in sediments close to the outlets of estuaries and coastal lagoons (Fig. 4c illustrates the case of Pb). This is conceivably related to co-precipitation of these trace elements with Mn and Fe (hydr)oxides as observed in several other estuary systems (e.g. Zwolsman and van Eck, 1999 and reference therein). Particularly in the lower Sado Estuary, Cortesão (2002) studied the reactivity of Cd, Co, Cr, Cu and Ni and concluded that co-precipitation with Mn is the main process affecting particulate Co. Furthermore, this author considers that this process may well be critical in the coastal area as well.

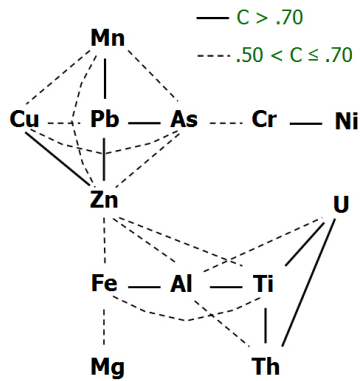


Fig. 5- Schematic diagram showing the positive Spearman correlations (C) between major and trace elements in surface sediments from the Lisbon-Setúbal-Sines shelf and upper open slope. Note: Ca is not represented in the diagram, due to its negative correlation with all other elements except Cr and Ni.

Fig. 5- Diagrama esquemático que muestra las correlaciones (C) de Spearman positivas entre los elementos mayoritarios y traza en sedimentos superficiales de la plataforma de Lisboa-Setúbal-Sines y el talud superior. Nota: Ca no está representado en el diagrama debido a su correlación negativa con todos los demás elementos, excepto Cr y Ni.

Unfortunately, As, Pb and Zn were not considered in the referred study.

As, Cu, Pb, and Zn show as well some relationships with lithogenic material, as represented by significant correlations with Al, Fe, phyllosilicates and kaolinites (Table 2). Kaolinite distribution on the Lisbon and Setúbal shelves appears to reflect river input (Fig. 3b). Since most conceivably the rivers are also the main source of trace metals, it seems logical that trace metals are carried off the estuaries in association with aggregates formed by the more common kaolinites. Coatings of organic matter and Fe and Mn hydroxides precipitated on clay particles may further enhance the adsorptive capacity of these clay

minerals (Jenne, 1976).

Enhanced concentrations of As, Cu, Pb, Zn together with Mn on the inner shelf adjacent to the Melides and St. André lagoons reflect the contribution of trace metals of these lagoons when these are opened to the sea. These coastal lagoons are naturally closed off from the sea by a sand bar, but every spring (and a common practice since the 18th century) both lagoons are artificially opened to promote water exchange with the open sea with the objective of preventing eutrophication (Freitas et al., 1999). When the lagoons are opened to the sea, there is localized erosion and remobilization of superficial sediments and organic matter from the bottom of the lagoon, and export to open sea (Freitas et al., 2000). Several studies (e.g. Cruces et al., 2006) have reported trace metal enrichments from surface sediments in these coastal lagoons. The referred study reported enrichments of Cd, Pb and Zn in the surface sediments of the St. André lagoon. Jesus et al. (2005) found high contents of Mn and various trace metals in beach sediments from the area adjacent to these lagoons, distinctly higher than in other areas of the coastal arc between Tróia and Sines. The high contents of trace metals and Mn in beach and adjacent shelf sediments seem therefore to come from the lagoons. Furthermore, high contents of plagioclase found in the fine-grained fraction of beach and shelf sediments from this area (Fig. 3a), supposedly sourced by the Santo André and Melides lagoons, reinforce this idea of sediment (and trace metals) being nourished by these lagoons into the adjacent shelf and beach. This is a localized increase of plagioclase (Fig. 3a) and according to Jesus (2011) other significant sediment sources (e.g. sea-cliffs) affecting the area do not seem to contribute sediment enriched in these minerals.

	% clay-sized part.	Phy	Qz	K-F	Plg	Cc	Mg-Cc	Arg	Kao	Ill	Sm	Chl
Al	-	0.64	0.29	-	0.44	-0.32	-0.36	-0.74	0.41	-0.31	-	-0.39
As	-	-	-	-	0.38	-0.68	0.23	-	0.52	-0.56	0.37	-
Ca	0.45	-0.45	-0.52	-	-0.69	0.60	0.40	0.72	-0.51	0.43	-	0.35
Cr	-	-	-	-	-	-0.41	0.24	0.30	0.35	-0.38	-	-
Cu	-	0.56	0.27	-	0.47	-0.58	-	-0.40	0.48	-0.47	0.28	-
Fe	-	0.50	-	-	0.27	-0.24	-	-0.43	0.38	-0.29	-	-0.31
Pb	-0.35	0.24	0.26	-	0.30	-0.67	-	-	0.62	-0.74	0.49	-
Mg	-	0.54	-	-	0.28	-0.21	-	-0.32	0.32	-0.29	-	-
Mn	-	0.22	-	-	0.24	-0.45	-	-	0.36	-0.40	0.27	-
Ni	-	-	-	-	-	-0.26	0.36	0.29	-	-	-	-
Th	-0.38	-	0.55	0.21	0.45	-	-0.45	-0.58	0.29	-	-	-
Ti	-0.38	0.32	0.49	-	0.55	-0.38	-0.31	-0.65	0.41	-0.37	-	-0.30
U	-0.33	-	0.46	-	0.40	-	-0.44	-0.56	0.37	-0.31	-	-0.27
Zn	-	0.58	0.25	-	0.38	-0.58	-	-0.33	0.70	-0.71	0.33	-

Phy – phyllosilicates, Qz – quartz, K-F – K-feldspars, Plg – plagioclase, Cc – calcite, Mg-Cc – Mg-calcite, Arg – aragonite, Kao – Kaolinite, Ill – Illite, Sm – Smectite, Chl – Chlorite. Mean and modal grain size show no significant relationship with any element analysed

Table 2 - Spearman correlation matrix: elemental concentrations against bulk and clay mineralogy and contents of clay-sized particles. Only significant correlation coefficients are shown and correlation coefficients higher than |0.50| are highlighted as bold.

Tabla 2 – Matriz de correlación de Spearman: concentraciones elementales contra la mineralogía total y de arcilla y el contenido de partículas del tamaño de las arcillas. Sólo se muestran los coeficientes de correlación significativos. Los coeficientes de correlación superior a |0,50| se destacan en negra

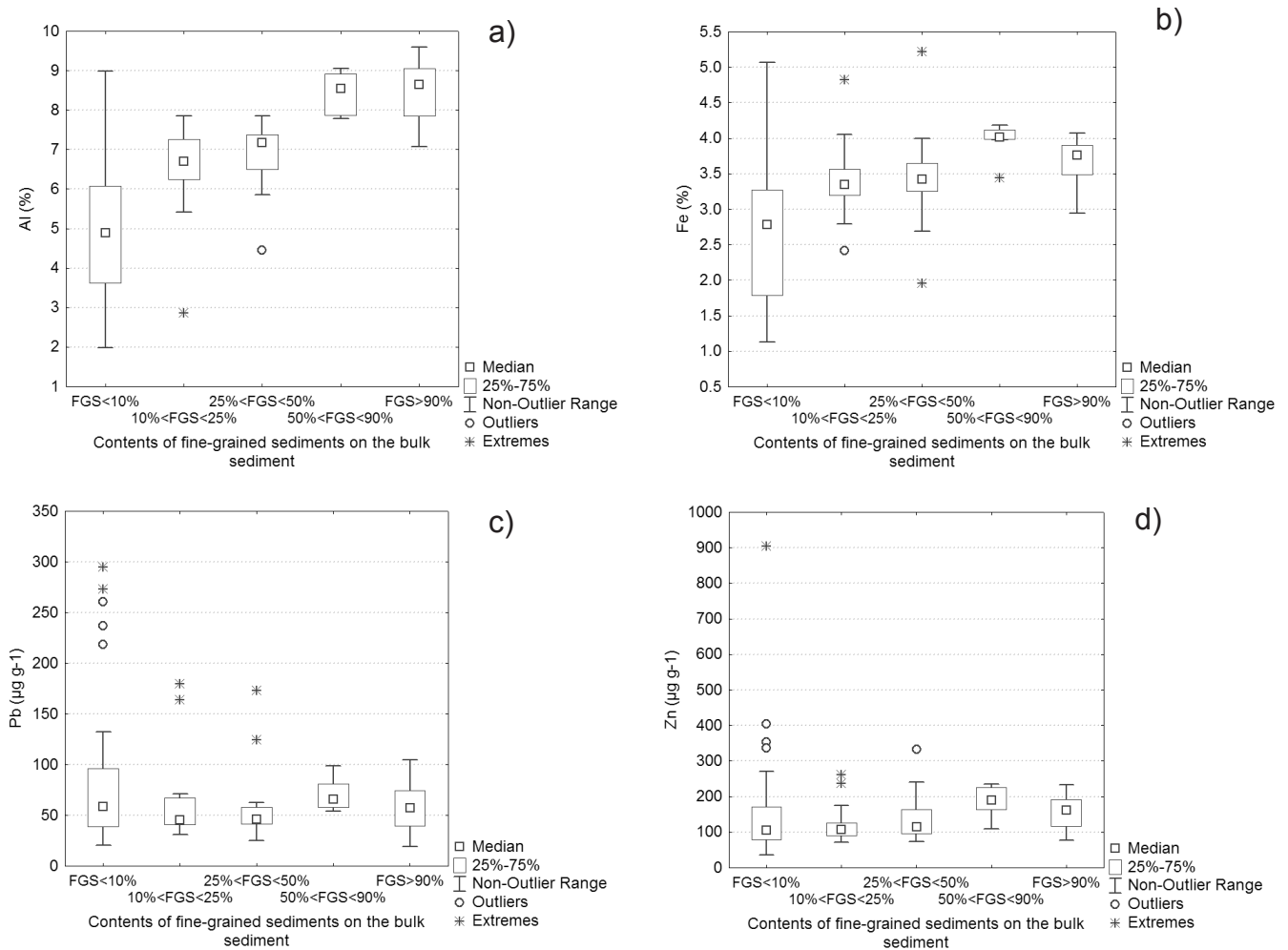


Fig. 6- Contents of fine-grained sediments on the bulk surface sediment against concentrations of Al (a), Fe (b), Pb (c) and Zn (d).

Fig. 6- Contenido de la fracción de grano fino en los sedimentos superficiales contra las concentraciones de Al (a), Fe (b), Pb (c) y Zn (d).

5.2. Enrichment of Cu, Pb and Zn and pathways of trace metal dispersal

The percentage of samples showing significant trace metal enrichment ($EF > 1.5$) per element follows the sequence: Pb (88 %) > Zn (43 %) > Cu (30 %). The areas most affected by enrichment of trace metals include the entire area studied from the Lisbon shelf, the Sado mud patch and the inner shelf between Tróia and Sines. Generally, the enrichment of these three trace metals tends to decrease in offshore direction (Fig. 7 and Table 3), suggesting that the excess of trace metals must be derived from land. This same pattern was found by Richter et al. (2009) and Jesus et al. (2010) for Pb and Zn further offshore in the Lisbon-Setúbal and Cascais submarine canyons and adjacent slope.

Enrichment of Pb and Zn on the Lisbon shelf and the Sado mud patch, and of Cu in the latter area points to the nearby Tagus and Sado estuaries as the likely sources of enrichment. This origin is also highlighted by the significant positive correlations between these trace metals and

kaolinite, whose distribution on the Lisbon and Setúbal shelves appears to reflect river input. Indeed, high trace metal concentrations in water, sediments and biota due to anthropogenic activities have been reported for both estuaries (e.g. Caeiro et al., 2005, Cotté-Krief et al., 2000, França et al., 2005).

On the inner shelf between Tróia and Sines, decreasing levels of enrichment of Cu, Pb and Zn in southward direction, along with the prevailing net longshore drift of sediments towards south (except in the northernmost portion where longshore drift is in the opposite direction) (SNIRLit, 2012 and references therein) suggests once more that the Sado Estuary is the most likely source for these trace metals. In the Sines shelf area, some minor enrichment of trace metals seem to come from the St. André and Melides coastal lagoons, affecting beach and inner shelf sediments in the surrounding area.

Since the enrichment of Pb is found to extend over a much wider area of the shelf and upper open slope than that of other two trace elements, it can be deduced that other sources of pollutant Pb must exist apart from the

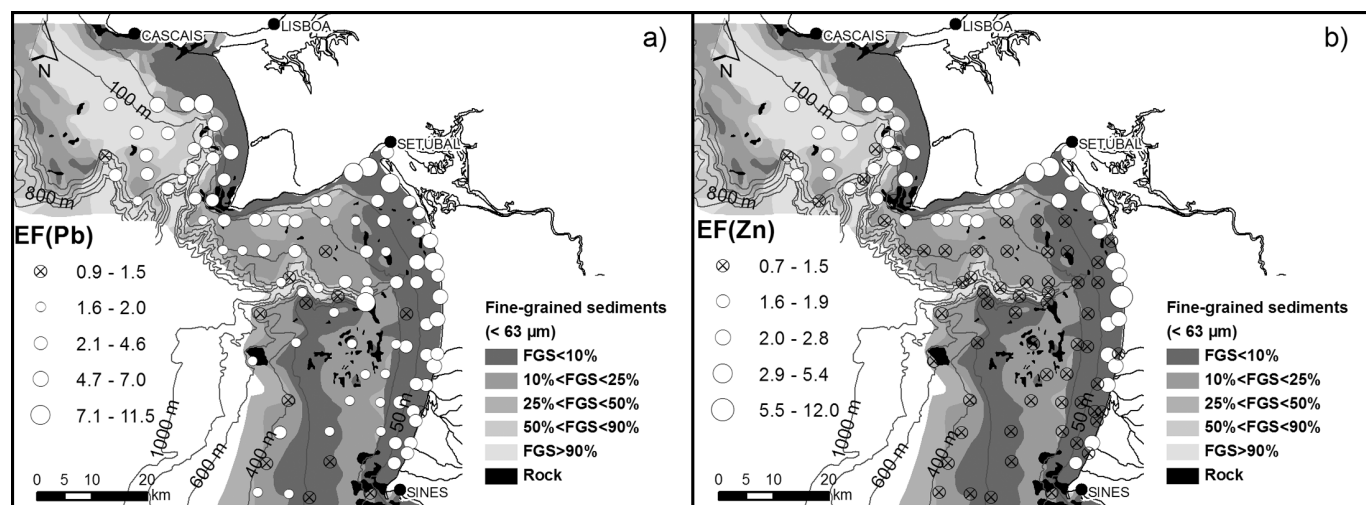


Fig. 7- Enrichment factors of Pb (a) and Zn (b) in the fine-grained fraction of surface sediments from the Lisbon-Setúbal-Sines shelf and upper slope.
Fig. 7- Factores de enriquecimiento de Pb (a) y Zn (b) de la fracción fina de los sedimentos superficiales de la plataforma Lisboa-Setúbal-Sines y el talud superior adyacente.

river discharge. In fact, enrichment factors above 1.5 were also found for most part of the Lisbon-Setúbal and Cascais canyons and adjacent open slope (Jesus et al., 2010). Atmospheric input may well contribute as a source of contamination potentially involving the whole studied shelf area and also the submarine canyons and open slope. Richter et al. (2009) concluded that fly ashes from waste incinerators are the main source for the pollutant lead found in surface sediments (first 0.5 cm) and in settling particulate material from the Lisbon-Setúbal submarine canyon and adjacent slope, based on lead stable isotopes signatures. It is therefore likely that this same source of pollutant lead affects the adjacent shelf area (which is closer to the source). However, between 1980 and 1987, when our samples were collected, leaded gasoline was still in use. This source included atmospheric pathways but also direct inputs into the watercourses and the marine environment via runoff from roads and pavements. Therefore, considering the time of collection of our sediment samples is likely that both leaded gasoline and waste incinerators contributed to Pb enrichment.

5.3. Significance of the presented enrichment factors in terms of time frame

As mentioned above, the sediment samples from the shelf here presented were collected between 1980 and 1987, which implies that they may not represent the present state of contamination of the shelf. Present-day shelf sediments could be expected to be less contaminated with trace metals, after improvement of industrial and domestic effluent treatment and closing of some industrial point sources in both the Tagus and Sado estuaries during the past two decades. During this time leaded gasoline was

also gradually phased out, starting in the early 1990s and completely eliminated in Portugal only in 1999 (Roma-Torres et al., 2007). However, Mil-Homens et al. (2009), in a study of trace metal accumulation in sediments from the Tagus mud patch during the 80 years between 1920 and 2000, concluded that sediments dated between 1980 and 2000 show constant enrichment values of trace metals, presumably due to the homogenizing effect of bioturbation in the surface mixed layer. EFs between 1980 and 2000 obtained by these authors are indeed very similar to those obtained in the present study for the same area (Table 3). Both these sets of results (this study and Mil-Homens et al., 2009) show higher EF (Pb) [and EF(Zn) to some extent] than those calculated from the results of Paiva et al. (1997) for this same area (Table 3). This seems related to the fact these last authors analysed bulk sediment which decreases trace metal concentration through dilution. The enrichment factors found in our grab samples from the Lisbon upper slope (present study) are also comparable to those reported from multicore tops from the same area (Jesus et al., 2010).

The good agreement between this study and the other three independent studies, as shown in Table 3, gives reason for confidence that results presented in this study are a good representation of the enrichment of trace metals in surface sediments over the 20 years between 1980 and 2000, perhaps even further.

6. Conclusions

On the Lisbon-Setúbal-Sines shelf concentrations of major elements Al, Fe, Mg, Ti and trace elements U and Th within the fine-grained sediment fraction appear to a large extent related to the amount of fine-grained frac-

Table 3 - Mean enrichment factors, differentiated per inner-, middle-, and outer shelf and upper slope, for the three studied shelf areas. Mean enrichment factors higher than 1.5 are highlighted in grey. Comparison of enrichment factors obtained for the Tagus mud patch in this study and in Mil-Homens et al. (2009) and Jesus et al. (2010).

Tabla 3 – Factores de enriquecimiento medios para la plataforma interior, media e exterior y en el talud superior para las tres zonas de la plataforma estudiada. La media de factores de enriquecimiento mayor de 1,5 se resaltan en gris. Comparación de factores de enriquecimiento obtenidos para el depósito de lodo del Tajo en este estudio y en Mil-Homens et al. (2009) y Jesus et al. (2010).

		EF (Pb)	EF (Zn)	EF (Cu)
Lisbon Shelf	Inner shelf (n = 4)	5.8	2.3	1.6
	Middle shelf (n = 4)	4.9	2.2	1.5
	Outer shelf (n = 6)	2.8	1.7	1.2
	Upper slope (n = 9)	2.4	1.6	1.2
Setúbal Shelf	Inner shelf (n = 15)	6.6	2.5	2.0
	Middle shelf (n = 7)	2.2	1.4	1.1
	Outer shelf (n = 10)	2.1	1.5	1.2
	Upper slope (n = 9)	1.9	1.1	1.0
Sines Shelf	Inner shelf (n = 17)	5.7	2.6	2.0
	Middle shelf (n = 3)	2.8	0.9	1.4
	Outer shelf (n = 13)	1.6	1.0	1.0
	Upper slope (n = 10)	2.5	1.0	1.0
Tagus mud patch (50-100 m Water Depth - WD)	This study	6.5	3.1	2.0
	Mil-Homens et al. (2009)	~ 5 - 6.5	~ 2.5 - 3.5	~ 2.5 - 3.5
	Paiva et al. (1997)*	4.1	2.6	2.0
Tagus mud patch (>100 m WD)	This study	2.6 - 3.7	1.5 - 2.2	1.1 - 1.5
	Mil-Homens et al. (2009)	~ 4	~ 1.8 - 2.5	~ 2.5
Lisbon upper slope (~300 m WD)	This study	1.9	1.0	0.8
	Jesus et al. (2010)	1.4	1.1	0.7

*EF calculated with the same baseline as in the present study.

tion in the bulk sediment. The above-mentioned elements have highest contents on the Lisbon shelf, which is largely covered by fine-grained lithogenic deposits derived from the Tagus River. On the Setúbal and Sines shelves, deposits rich in fine-grained material are less widespread and coarser carbonate rich sediments prevail. This is in turn expressed by generally high concentrations of Ca.

Distribution of trace metals As, Cu, Mn, Pb and Zn on the other hand show spatial patterns that differ to some extent from the distribution of mineral and elemental proxies of lithogenic and biogenic material. The differing patterns indicate that, most likely, part of trace metal content may represent anthropogenic enrichment.

Higher concentrations of trace metals in sediments close to the inlets of the Tagus and Sado estuaries and the St. André and Melides coastal lagoons indicate these as trace metal sources for the shelf environment.

The extent of enrichment of trace metals in the studied area follows the sequence: Pb > Zn > Cu. Generally, the enrichment of trace metals tends to decrease in offshore direction, as also found in previous studies for the nearby submarine canyons, suggesting that the excess of trace metals must be derived from land. The areas of the Lisbon-Setúbal-Sines shelf most affected by enrichment of trace metals include the entire area studied from the Lisbon shelf (mainly the Tagus mud patch), the Sado mud patch and the inner shelf between Tróia and Sines. Since these mud patches are composed of sediments derived from the Tagus and Sado rivers, enrichment of Pb and Zn on the Lisbon shelf and the Sado mud patch, and of Cu, in the latter area, points to the nearby estuaries as the likely

sources of enrichment. In addition, the more widespread enrichment of Pb in sediments points to contributions from atmospheric inputs. Leaded gasoline and fly ashes from waste incinerators seem to have contributed to Pb enrichment in surface sediment, considering the time of collection of our samples.

The good agreement between the results from the present study and other three independent studies gives reason for confidence that our results provide a representative view of trace metal enrichment in surface sediments between 1980 and 2000, perhaps even further.

Acknowledgements

The Portuguese Science Foundation (FCT) is acknowledged for the Ph.D. grant with reference BD/14125/2003 given to the first author. We thank two anonymous reviewers for constructive comments.

References

- Abrantes, M.I. (2005): *Os sedimentos superficiais da margem continental, sector Espinho – Cabo Mondego: a utilização das fracções finas como traçadores de dinâmica sedimentar actual*. Ph.D. Thesis, University of Aveiro.
- Alt-Epping, U., Mil-Homens, M., Hebbeln, D., Abrantes, F., Schneider, R.R. (2007): Provenance of organic matter and nutrient conditions on a river and upwelling influenced shelf: A case study from the Portuguese Margin. *Marine Geology* 243, 169–179. doi: 10.1016/j.margeo.2007.04.016
- Brindley, G.W., Brown, G. (1980): *Crystal Structures of Clay Minerals and their X-ray Identification*. Mineralogical Society, London.
- Byrd, J.T., Lee, K.W., Lee, D.S., Smith, R.G., Windom, H.L. (1990):

- The behaviour of trace metals in the Geum estuary, Korea. *Estuaries* 13 (1), 8-13. doi: 10.2307/1351426
- Caiiro, S., Costa, M.H., Ramos, T.B., Fernandes F., Silveira, N., Coimbra, A., Medeiros, G., Painho, M. (2005): Assessing heavy metal contamination in Sado Estuary sediment: an index analysis approach. *Ecological Indicators* 5, 151-169. doi: 10.1016/j.ecolind.2005.02.001
- Cearreta, A., Alday, M., Conceição Freitas, M., Andrade, C., Cruces, A. (2002): Modern foraminiferal record of alternating open and restricted environmental conditions in the Santo André lagoon, SW Portugal, in: Orive, E., Elliot, M. and de Jonge V.N. (Eds), *Nutrients and Eutrophication in Estuaries and Coastal Waters*. Kluwer Academic Publishers: 21-27.
- Cortesão, C. (2002): *Distribuição e reactividade do cádmio, cobre, crómio, níquel e cobalto no Estuário do Sado*. Ph.D. Thesis. University of Lisbon .
- Cotté-Krief, M.H., Guieu, C., Thomas, A.J., Martin, J.M. (2000): Sources of Cd, Cu, Ni and Zn in Portuguese coastal waters. *Marine Chemistry* 71, 199-214. doi: 10.1016/S0304-4203(00)00049-9
- Cruces, A., Freitas, M.C., Andrade, C., Munhá, J., Tassinari, C., Vale, C., Jouanneau, J.M. (2006): The importance of geochemistry in multidisciplinary studies of lagoonal environments at different time scales: The case of Santo André lagoon (SW Portugal). *Journal of Coastal Research* SI 39, 1716 – 1722.
- Darnley, A.G., Björklund, A., Bølviken, B., Gustavsson, N., Koval, P.V., Plant, J.A., Steinfelt, A., Tsuchid, M., Xie X. (1995): A global geochemical database for environmental and resource management. Recommendations for international geochemical. Final report of IGCP project 259. UNESCO Publishing.
- De Stigter, H., Jesus, C.C., Boer, W., Richter, T.O., Costa, A., van Weering, T.C.E., (2011): **Recent sediment transport and deposition in the Lisbon-Setúbal and Cascais Canyon, Portuguese margin**. *Deep-Sea Research part1* 58 (23-24), 2321-2344. doi:10.1016/j.dsr2.2011.04.001.
- Dias, J.M.A. (1987): *Dinâmica sedimentar e evolução recente da plataforma continental portuguesa setentrional*. Ph.D. Thesis. University of Lisbon .
- França, S., Vinagre, C., Caçador, I., Cabral, H.N. (2005): Heavy metal concentrations in sediment, benthic invertebrates and fish in three salt march areas subjected to different pollution loads in the Tagus Estuary (Portugal). *Marine Pollution Bulletin* 50, 993-1018. doi:10.1016/j.marpolbul.2005.06.040
- Freitas, M.C., Andrade, C., Cruces, A. (1999): Lagoa de Santo André – Dinâmica do Sistema Lagunar Actual. Comportamento da barra, dinâmica hidrológica e sedimentar da laguna. Evolução holocénica do sistema lagunar. Proceedings of the Eurocoast Seminar. *A Zona Costeira do Alentejo*. Eurocoast – Portugal, 5-11 .
- Freitas, M.C., Andrade, C., Cruces, A. (2000): A importância do conhecimento geológico no ordenamento de ambiente lagunares: exemplos do litoral SW de Portugal. Proceedings of the Eurocoast Seminar. *Perspectivas de gestão integrada de ambientes costeiros*. Eurocoast – Portugal, 127-142 .
- Freitas, M.C., Andrade, C., Cruces, A. (2002): The geological record environmental changes in the southwestern Portuguese coastal lagoons since the Lateglacial. *Quaternary International* 93-94, 161-170.
- Fütterer, D.K. (2006): The solid phase of marine sediments. In *Marine Geochemistry* (eds.) H.D. Schulz and M. Zabel. Springer. 574 p.
- Gomes, C. (1988): *Argilas, o que são e para que servem*. Fundação Calouste Gulbenkian. Lisboa.
- Huber, L. (1998): Validation of analytical methods: review and strategy. *LC-GC Int.* 11, 96-105.
- Huertos, G., de los Monteros, E. (1974): *Les caolinos en España: características, identificación y ensayos cerámicos*. Ed. Soc. Esp. De Cerámica, Madrid.
- Instituto Hidrográfico (2005): Carta dos Sedimentos Superficiais da Plataforma Continental Portuguesa - Folha 5 - Escala 1:150 000.
- Jenne, E. A. (1976): Trace element sorption by sediments and soils - sites and processes, in: *Symposium on Molybdenum*, (Eds.) W. Chapel and K. Petersen. Marcel Dekker, New York: 425-553.
- Jesus, C.C. (2011): *Pathways of recent fine-grained sediment transport on the central Portuguese continental margin*. Ph.D. Thesis, University of Aveiro. p. 278.
- Jesus, C.C., de Stigter, H.C., Richter, T.O., Boer, W., Mil-Homens, M., Oliveira, A., Rocha F. (2010): Trace metal enrichments in Portuguese submarine canyons and open slope: anthropogenic impact and links to sedimentary dynamics. *Marine Geology* 271, 72-83. doi:10.1016/j.margeo.2010.01.011
- Jesus, C.C., Inácio, M., Ferreira da Silva, E., Oliveira, A., Rocha, F. (2005): Enriquecimento de metais em sedimentos de praia (SW Portugal). Proceedings of the X Congresso Brasileiro de Geoquímica dos Países do Mercosul .
- Jouanneau, J.M., Garcia, C., Oliveira, A., Rodrigues, A., Dias, J., Weber, O. (1998): Dispersal and deposition of suspended sediment on the shelf off Tagus and Sado estuaries, SW Portugal. *Progress in Oceanography* 42, 233-257.
- Loring D., Rantala, R. (1992): Manual for the geochemical analyses of marine sediments and suspended particulate matter. *Earth-Science Reviews* 32, 235-283.
- Mil-Homens, M., Branco, V., Vale, C., Boer, W., Alt-Epping, U., Abrantes, F., Vicente, M. (2009): Sedimentary record of anthropogenic metal inputs in the Tagus prodelta (Portugal). *Continental Shelf Research* 29 (2), 381– 392. doi:10.1016/j.csr.2008.10.002
- Moita, I., Quevauviller, P. (1986) : Les différents faciès sédimentaires de la plateforme continentale nord alentejanaise. comparaison avec l'ensemble continental. *Boletim Informação Sociedade Geológica Portugal*. 13, p. 30
- Monteiro, J.H., Moita, I. (1971): Morfologia e sedimentos da plataforma continental e vertente continental superior ao largo da península de Setúbal. *Direcção Geral Minerais e Serviços Geológico*, 301–330 .
- Oliveira, A., Rocha, F., Rodrigues, A., Jouanneau, J., Dias, A., Weber, O., Gomes, C., (2002): Clay minerals from the sedimentary cover from the Northwest Iberian shelf. *Progress in Oceanography* 52, 233-247. doi: 10.1016/S0079-6611(02)00008-3
- Petschick, R. (2000): MacDiff 4.2.2.
- Ribani, M., Bottoli, C., Collins, C., Jardim I. (2004): Validação em métodos cromatográficos e electroforéticos. *Quim. Nova* 27 (5), 771-780.
- Richter, T.O., De Stigter, H.C., Boer, W., Jesus, C.C., Van Weering, T. (2009): **Dispersal of natural and anthropogenic lead through submarine canyons at the Portuguese margin**. *Deep-Sea Research Part I* 56 (2), 267–282.
- Rocha, F. (1993): *Argilas aplicadas a estudos litoestratigráficos e paleoambientais na bacia sedimentar de Aveiro*. Ph.D. Thesis, University of Aveiro .
- Roma-Torres, J., Silva, S., Costa, C., Coelho, P., Henriques, M.A., Teixeira, J.P., Mayan, O. (2007): Lead exposure of children and newborns in Porto, Portugal. *International Journal of Hygiene and Environmental Health* 210, 411–414.
- SNIRLit (2012): <http://geo.snirh.pt/snirlit/site/index.php#> (accessed 05.10.12) .
- Zwolsman, J.J.G., Van Eck, G.T.M. (1999): **Geochemistry of major elements and trace metals in suspended matter of the Scheldt estuary, southwest Netherlands**. *Marine Chemistry* 66, 91-111. doi:10.1016/S0304-4203(99)00026-2.