ISSN (print): 1698-6180. ISSN (online): 1886-7995
www.ucm.es/info/estratig/journal.htm

Journal of Iberian Geology 34 (2) 2008: 287-298

Journal of Iberian Geology
AN INTERNATIONAL PUBLICATION OF EARTH SCIENCES

Historical trends in Hg, Pb and Zn sedimentation in the central shelf area of Portugal

Tendencias históricas en la sedimentación de Hg, Pb y Zn en el área central de la plataforma continental Portuguesa

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Received: 07/11/06 / Accepted: 26/04/07

Abstract

Temporal records of excess ^{210}Pb, and the determination of major (Al and Ca) and trace elements (Zn, Cr, Ni, Pb, Cu and Hg) in two sediment box-cores, collected in the central area of the Portuguese shelf of North of the Nazaré canyon (offshore from the Lis River), allow evaluation of the deposition of various chemical elements normally associated with anthropogenic activities. In order to compensate for the natural sediment variability, heavy metal contents were normalised to Al. Temporal variations of Hg, Pb and Zn (Al-normalised) show an increasing trend since the beginning of the 1920's, recording the development of industrial activities. Enrichment factors (EF) were calculated to estimate the level of contamination in these sediments. Mercury is the element with the highest average EF values (EF = 3), followed by Pb (EF = 1.5) and Zn (EF = 1.2). The results indicate that since 1991 64% of total Hg, 44% of total Pb and 24% of total Zn are derived from anthropogenic sources. The average anthropogenic fluxes of Hg, Pb and Zn (0.008, 3, 6 μg cm^{-2}yr^{-1}, respectively) for the last 40 years in a ca. 400 km^2 deposition area represent a total accumulation of approximately 30, 12000 and 24400 kg per year of Hg, Pb and Zn, respectively. These results indicate that despite the high-energy conditions and the generally sandy nature of the Portuguese shelf sediments, it is possible to identify significant anthropogenic enrichments in some areas of sediment accumulation. These contaminants are not necessarily related to immediate sources but may instead indicate atmospheric and or marine transport from more distant sources.

Keywords: Portuguese shelf, marine sediments, heavy metals, temporal variations, enrichment factors, anthropogenic fluxes.

Resumen

Los registros temporales del ^{210}Pb en exceso, elementos mayores (Al y Ca), y elementos traza (Zn, Cr, Ni, Pb, Cu y Hg) de 2 box-cores procedentes de la plataforma continental al norte del cañón de Nazaré han permitido caracterizar depósitos de elementos químicos asociados a actividades antropogénicas. Los contenidos de metales pesados han sido normalizados con Al para compensar la variabilidad natural. La variación temporal de Hg, Pb y Zn, normalizados con Al, muestran un incremento desde el inicio de la década de 1920 reflejando el desarrollo de la actividad humana. El nivel de contaminación de los sedimentos ha sido calculado en base a Factores de Enriquecimiento (EF). Los valores medios más altos de FE son de mercurio (EF = 3), seguidos de plomo (EF = 1.5) y zinc (EF = 1.2). Los resultados obtenidos indican que a partir de 1991 el 64% del total de Hg, 44% del total de Pb y 24% del total de Zn son de origen antropogénico. La media para los últimos 40 años de los flujos de Hg, Pb y Zn (0.008, 3, 6 µg cm^{-2} año^{-1}, respectivamente), en un área de deposición de aproximadamente 400 km^2, se traduce en la acumulación de 30, 12000 y 24400 kg por año de Hg, Pb y Zn. Sin embargo, a pesar de las condiciones de alta energía y el carácter arenoso de los sedimentos de la plataforma continental portuguesa, se pueden identificar importantes enriquecimientos antropogénicos en depocentros de sedimentos, no relacionados con fuentes antropogénicas próximas pero que pueden indicar transporte marino y atmosférico de fuentes de contaminación distantes.

Palabras clave: marismas, datación con ^{210}Pb y ^{137}Cs, tasas de sedimentación, metales pesados, impacto antropogénico.

1. Introduction

Metals are released to the marine environment mainly through the weathering of terrestrial rocks and soils. Over the past century, industrial activities are also known to be also a significant source of metals to the coastal environment by atmospheric emissions, runoff and waste effluents (e.g. Alexander *et al.*, 1993; Nolting *et al.*, 1999; Stevenson, 2001). Estuaries and coastal areas of continental shelves act as important sinks for both natural and anthropogenic derived materials, which are mainly incorporated in fine-grained sediments transported in suspension (Windom *et al.*, 1989). Human impacts on these sensitive ecosystems, particularly the negative effects of metals (e.g. Hg, Pb) and persistent organic pollutants on biological resources, can prevent sustainable development and economic growth.

Despite the high-energy conditions and sandy content of the Portuguese shelf (Monteiro *et al.*, 1982; Dias, 1987), certain environmental settings have allowed recent formation of silty-clayey deposits (e.g. Drago *et al.*, 1998; Jouanneau *et al.*, 2002). The history of the accumulation of contaminants as well as a better understanding of the processes and fluxes in the system can be reached by the study of these fine-grained deposits (Finney and Huh, 1989). Metal concentrations in estuarine and marine sediments are commonly used as a tool to monitor time variation of their levels in the environment (e.g. Valette-Silver, 1993), and this is especially justified when sediment resuspension and bioturbation are minimal and diagenetic disturbances are weak.

This paper uses ^{210}Pb combined with geochemical data to reconstruct historical heavy metal input into this sector of the Portuguese shelf. The main goals are to define the level of metal enrichments by the determination of Enrichment Factors (EF) and to estimate the anthropogenic fluxes of Hg, Pb and Zn.

2. Study area

The sector of the Portuguese shelf where the two box-cores were collected is located North of the Nazaré canyon at approximately 120 m depth (Fig. 1, Table 1). The Nazaré canyon cuts across the entire width of the shelf, and therefore intercepts a large portion of the sediment transported laterally, south and southeast along the shelf by waves and wind-driven currents (van Weering *et al.*, 2002).

Both cores were taken in a depocentre located north of the Nazaré canyon, offshore from the Lis River. This fine-grained deposit, first identified by Dias (1987), results from the existence of Cretaceous outcrops, which are responsible for creating a sheltered sea-floor setting at depths of approximately 120 m where fine-grained sediments accumulate, mainly silt with about 10% carbonate. According to Oliveira *et al.* (2002), re-suspension occurs mainly during winter periods due to wave turbulence in areas shallower than 100 m. Winter storm conditions are marked by strong winds blowing from S-SW and are responsible for the development of a downwelling regime over the shelf, which is characterised by persistent pole-

Cruise name	Core number	Field number	Lat. (N)	Long. (W)	Water Depth (m)
PALEO1	3569	PO287-18-1B	39º 51.0’	9º 17.0’	115
	3567	PO287-16-1B	39º 44.0’	9º 16.9’	120

Table 1.– Sediment sampling stations used in this study.

Tabla 1 – Puntos de muestreo utilizados en este estudio.

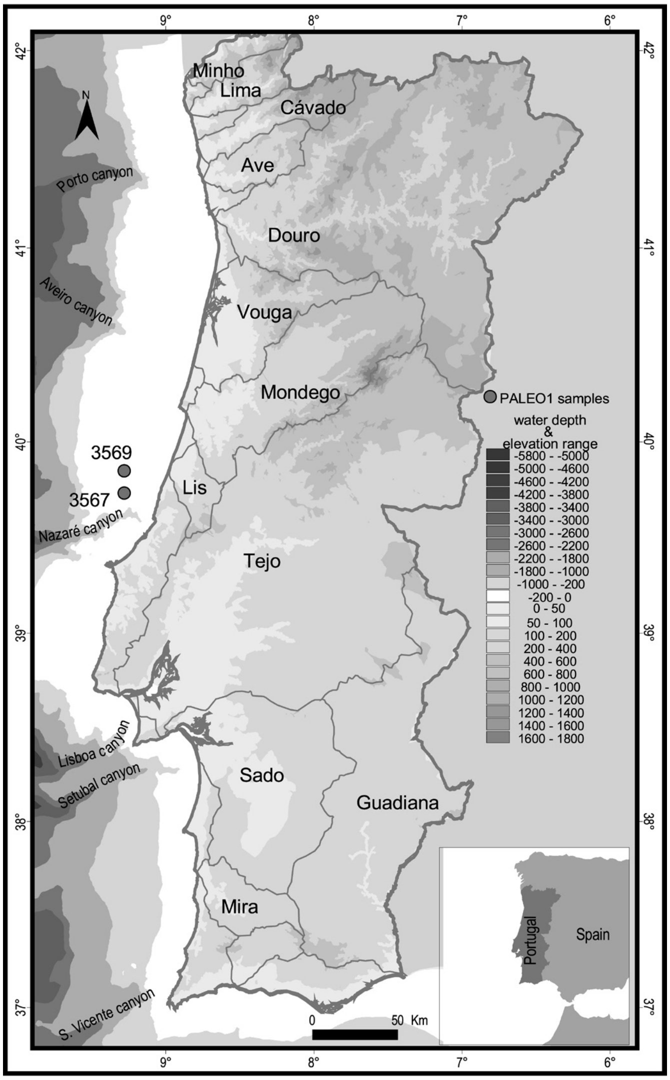

Fig. 1.– Location of the box-cores sampling sites on the shelf area adjacent to the Lis drainage area. Elevation range and tthe boundaries of the main drainage basins are from the "Atlas do Ambiente Digital - Inst. do Ambiente". Bathymetry is a data compilation done at the DGM-INETI.

Fig. 1.– Localización de los box-cores en la plataforma continental adyacente a la cuenca de drenaje del río Lis. Relieve y límites de las cuencas de drenaje procedentes del "Atlas do Ambiente – Instituto do Ambiente". Batimetría recopilada a partir de la base de datos del DGM-INETI.

ward flow at all depths (Ambar and Fiúza, 1994; Vitorino *et al.*, 2002). At depths below 100 m, sediment reworking is less frequent and is mainly induced by strong storms.

The Lis River has a relative low freshwater discharge (0.6 × 10^9 m^3yr^{-1}; Fiúza, 1984), when compared to other important Portuguese rivers, such as Douro (16.8 × 10^9 m^3yr^{-1}; Fiúza, 1984) and Tejo (15.5 × 10^9 m^3yr^{-1}; Fiúza, 1984). The dominant lithologies of the Lis drainage area are carbonate rocks and sandstone. Human activities are essentially rural, but small-scale industries of a wide diversity are dispersed over the drainage area.

3. Materials and Methods

3.1. Sediment samples

Sediment cores were taken with an Oktopus box-corer at two stations in the vicinities of the Lis river mouth at ca. 120 m depth during the PALEO1 cruise (2002) aboard the RV POSEIDON (Fig. 1, Table 1).

Each sediment box-core was described in regard to lithology, colour and structure of sediments (Monteiro *et al.*, 2002). Sub-cores from each box-core were collected using several PVC tubes, which were pressed into the sediment. Each tube was sliced into 1 cm sections and the samples were refrigerated (ca. 4 ºC).

3.2. Sample analyses

Sediments were dated using the ^{210}Pb and ^{226}Ra methods. The uppermost part of each core was more densely sampled for ^{210}Pb analysis (twelve samples analysed from each core). ^{210}Pb measurements were made by means of alpha-spectrometry, following the method described in van Weering *et al.* (1998). ^{226}Ra activity was determined for three distinct levels from each core by using gamma-spectrometry according to the methodology outlined in van den Bergh *et al.* (2003). Sediment accumulation rates were determined using the excess ^{210}Pb values, which is equivalent to the total ^{210}Pb activity minus the supported ^{210}Pb activity that is in equilibrium with sedimentary ^{226}Ra. Supported ^{210}Pb activity can be obtained either from a complete ^{210}Pb profile with depths where a stable background is reached or by measuring the ^{226}Ra activity.

For metal analyses (except Hg), all the samples were totally dissolved by a combination of *Aqua Regia*, hydrofluoric acid (HF) and perchloric acid ($HClO_4$). Determinations were performed using a Perkin-Elmer OPTIMA 4300DV ICP-OES (Inductively Coupled Plasma – Optical Emission Spectrometry) according to an in-house methodology used at the National Oceanography Centre (NOC). Mercury analyses were carried out following the procedure described by Costley *et al.* (2000). Mercury was determined by atomic absorption spectrometry using a silicon UV diode detector Leco AMA-254, after pyrolisys of each sample in a combustion tube at 750 ºC under an oxygen-rich atmosphere and collection on a gold amalgamator.

The accuracy of the analyses for major and heavy metals (except Hg) was checked by analysising 12 replicate samples of the certified reference material MAG-1 (Marine Sediment Reference Material, United States Geological Survey; Table 2). For Hg 8 replicate samples of the certified reference material MESS-2 (Marine Estuarine

Elements	Certified Reference Materials			
	MAG-1 (USGS — USA)		MESS-2 (NRCC — Canada)	
	Certified (mean ± std deviation)	Obtained (mean ± std deviation)	Certified (mean ± std deviation)	Obtained (mean ± std deviation)
Hg (µg g^{-1})	—	—	0.092 ± 0.009	0.096 ± 0.002
Al (%)	8.7 ± 0.2	9.0 ± 0.2	—	—
Ca (%)	1.0 ± 0.1	1.0 ± 0.0	—	—
Cr (µg g^{-1})	97 ± 8	93 ± 4	—	—
Cu (µg g^{-1})	30 ± 3	30 ± 1	—	—
Ni (µg g^{-1})	53 ± 8	53 ± 2	—	—
Pb (µg g^{-1})	24 ± 3	22 ± 2	—	—
Zn (µg g^{-1})	130 ± 6	140 ± 6	—	—

Table 2.– Total Al, Ca (%), Cr, Cu, Hg Ni, Pb and Zn concentrations (µg g^{-1}) determined for this study in certified reference materials (MESS-2 and MAG-1) determined in the present study (for Hg n = 8; and for other studied elements n = 12, where n is the number of replicate samples). The obtained and certified concentrations are presented.

Tabla 2.– Concentración total de Hg, Cr, Cu, Ni, Pb, Zn (µg g^{-1}) y Al y Ca (%) en el material de referencia certificado (MESS-2 y MAG-1). Hg, n=8 para el MESS-2 y n=12 para MAG-1. Se presentan las concentraciones obtenidas y certificadas.

from the National Research Council of Canada; Table 2) were analysed. The results indicate good agreement between certified and analytical values. The recovery (%) of measured elements, based on the mean values calculated for certified reference materials, was practically 100% (Table 2). The analytical precision was assessed by analysis of replicate samples of the certified reference materials and expressed as relative standard deviation (RSD). The precision was less than 5% and 10% ($p < 0.05$) for major elements and heavy metals and less than 4% for Hg ($p < 0.05$).

4. Results and discussion

4.1. Age models

The determination of sediment accumulation rates (g cm^{-2} yr^{-1}) instead of sedimentation rates (cm yr^{-1}) has been used in this study in order to reduce problems related to sediment compactation through time (Robbins, 1978) or core compression during sampling. Sediment accumulation was calculated as cumulative dry mass using the dry bulk density.

The ^{210}Pb profiles indicate sediment accumulation rates of 0.27 g cm^{-2} yr^{-1} and 0.23 g cm^{-2} yr^{-1} for cores 3567 and 3569, respectively (Fig. 2). Both cores are characterised by a reduced surface mixed-layer (SML), involving only the first four centimetres, which can be interpreted as reflecting a low influence of environmental processes (e.g. re-suspension, bioturbation, diagenesis) on sediment accumulation. In core 3567 the existence of two high values associated with bioturbated layers (Fig. 2) can be related to subsurface mixing by burrowing, although this is not documented in this study. Since Al (Fig. 3; reflecting the clay content) does not vary significantly, the similar ^{210}Pb activity at the surface and within this identified layer is best explained by bioturbation (Mil-Homens *et al.*, 2006). Although both ^{210}Pb profiles exhibit a continuous decrease with depth suggesting constant conditions of sedimentation, physical and biological processes can affect the sediment radioisotope profiles.

4.2. Depth variation of metal concentrations

Metal concentrations in the cores 3567 and 3569 are characterised by an absence of any abrupt modifications with depth (Fig. 3). The relatively constant values of Al in sediments younger than 1900 (core 3569) and 1920 (core 3567) suggest the deposition of fine-grained material without significant episodes of higher energy, that would be indicated by the presence of coarser material and lower Al content. Before 1900 Al concentrations gradually increase upward from approximately 6% to 8%, and Ca content decreases concomitantly. The composition in the deepest core samples reflects biogenic sandy sediments and previously different oceanographic conditions (Fig. 3). Cr, Ni, Cu and Zn profiles are mainly marked by similar temporal variation, increasing until 1900-1920 and keeping quite constant towards the modern surface sediments. Pb and Hg show an additional increase about 1950 that cannot be related to natural variations in sediment grain size nor to its composition.

4.3. Metal-metal relationships

Prior to 1910, the Cu-Ni and Cr-Cu relationships (Fig. 5; $Cu = 0.57 * Ni + 0.74$, $r^2=0.74$; $Cr = 0.30 * Cu - 2.90$, $r^2=0.66$) and the Cr, Ni and Cu-Al relationships (Fig. 4)

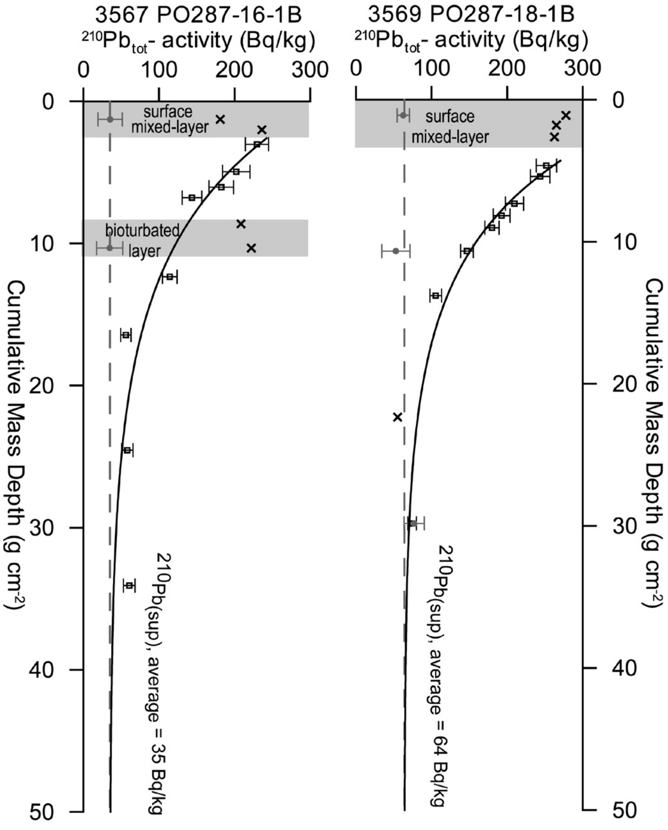

Fig. 2.– Total ^{210}Pb (^{210}Pb$_{tot}$; black square) activities versus depth in *box-cores* 3567 and 3569. Black-cross symbols represent ^{210}Pb values not considered for determination of the accumulation rates. Grey filled circles represent the supported ^{210}Pb activity. Horizontal error bars are 1-σ uncertainties propagated from counting statistics. The vertical dashed lines represent the average ^{226}Ra measurements (supported ^{210}Pb activity).

Fig. 2.– Actividad total de ^{210}Pb (^{210}Pb$_{tot}$; cuadrados negros) *versus* profundidad en los sondeos 3567 y 3569. Las cruces negras representan valores de ^{210}Pb no utilizados para la determinación de tasas de acumulación. Los círculos grises indican la actividad de fondo del ^{210}Pb. Las barras de error horizontal corresponden a 1-σ. Las líneas discontinuas verticales representan los valores medios medidos de ^{226}Ra (actividad de fondo del ^{210}Pb).

and Zn-Al, Pb-Al clearly show the control by grain size (Al is considered as a proxy for the finest grained fraction) of their distribution before the 1910's. After the 1910's, Zn, Pb and Hg show a distinct behaviour compared with that of Cr, Ni and Cu and no relationship between these two groups of samples is evident (Fig. 4). Hg shows the greatest metal enrichment followed by Pb and Zn in modern sediments. This is also shown by the steep gradient in the Hg vs. Pb, Hg, vs. Zn and Pb vs. Zn plots (Fig. 5).

4.4. Temporal variation of metal-Al ratios

In order to minimise the influence of grain-size variability the total metal contents were normalised using Al as a proxy for the fine-grained fraction (Windom *et al.*, 1989).

The normalised profiles of Zn, Pb and Hg show approximately constant values until the 1940s, followed by a significant increase between the 1940s and the 1960s (Fig. 6). After the 1960s the values are approximately constant, showing a slightly increasing trend towards the present (Fig. 6). These variations in normalised metal contents are interpreted not to be due to grain-size variations. The increase of Zn contents in both cores, between the 1880s and 1950s (Fig. 3) is believed to reflect a grain-size dependent change in the detrital supply since the Al-normalised values are approximately constant (Fig. 6). The observation and interpretation are also applicablefor Zn relative to Al plot for Cu values after the 1880s (Fig. 3).

The similar behaviour of Hg, Pb and Zn in the recent sediments (after the 1950s) suggests that similar sources, transport and/or depositional during this time were the dominant influences on metal distributions. Hg, Pb and Zn are interpreted to have an anthropogenic origin considering the absence of natural sources. The Pb anthropogenic enrichments probably represent an increase in supply from leaded gasoline exhausts (Weiss *et al.*, 1999). The major anthropogenic sources of Hg in Portugal are associated with pyrite roast and chloralkali plants located in the Tagus estuary (Figuéres *et al.*, 1985; Canário *et al.*, 2003; Canário *et al.*, 2005) and Aveiro lagoon (Pereira *et al.*, 1998).

4.5. Degree of environmental contamination

Based on the comparison with local pre-industrial background values obtained at the bottom of both box-cores, the degree of environmental contamination was assessed through the definition of the Enrichment Factors (EF). The EFs were calculated based on Al-normalised values to reduce the influence of grain-size and mineralogical variability (Fig. 7).

Conventionally, EF values varying between 0.5 and 1.5 are considered indicative of metal from crustal contributions (Zhang and Liu, 2002). Whereas EF > 1.5 suggests other natural (e.g. biogenic) or anthropogenic contributions in addition to the metals derived from crustal contributions. However, several factors, such as diagenesis, sediment re-working (Christensen and Osuna, 1989), bioturbation, especially in the upper mixed-layers, and dilution by less contaminated sediment, can be responsible for lowering the EF values.

Although there are only slight indications of anthropogenic contamination (shown by relatively low maximum EF values: $EF_{Hg} = 2.9$; $EF_{Pb} = 1.7$; $EF_{Zn} = 1.3$; Fig. 7), at the studied locations of the Lis shelf area, it is still possible to discern human influence in some metal records. In both cores, EFs for Zn (normalised relative to Al) plot

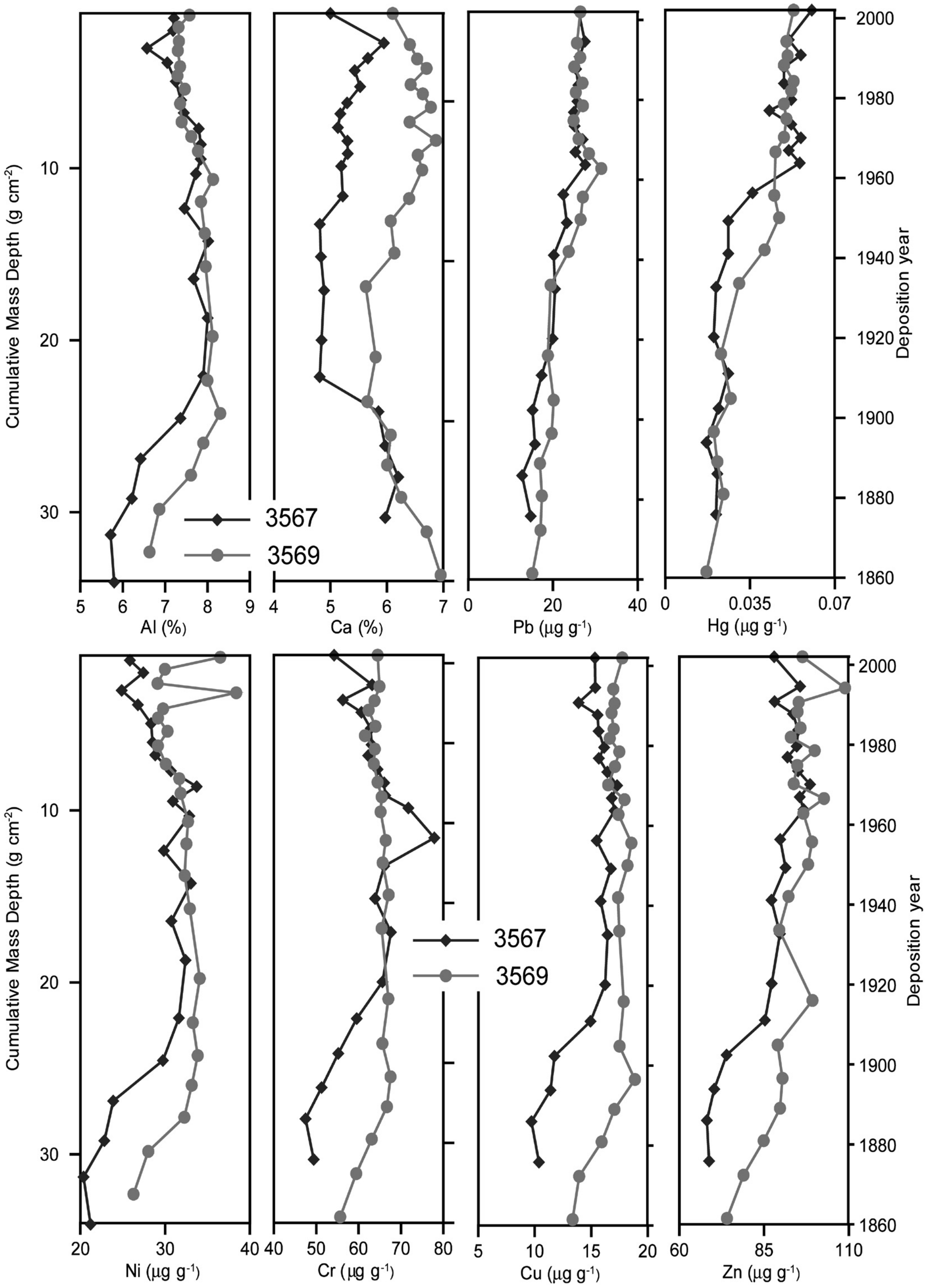

Fig. 3.– Down-core profiles of Al, Ca (%) and Pb, Hg, Ni, Cr, Cu , Zn (µg g^{-1}) in box-cores 3567 (n = 21) and 3569 (n = 22). The geochronology for each core is derived using ^{210}Pb data.

Fig. 3.– Perfil en función de la edad de Al, Ca (%) y Pb, Hg, Ni, Cr, Cu , Zn (µg g^{-1}) en los box-cores 3567 (n = 21) y 3569 (n = 22). La geocronología de cada testigo ha sido derivada a partir de ^{210}Pb.

inside the range of crustal contributions, but the gradual increase in metal enrichment towards the surface is interpreted to reflect a slight anthropogenic influence (Fig. 7). The relatively low Lis River discharge and the absence of natural lithologic metal sources close to this shelf area imply that a diffuse source, perhaps atmospheric deposition and /or marine transport of fine-grained sediments, is most likely. Of the three studied elements, Hg and Pb present the highest EFs, probably reflecting the importance of atmospheric transport as a diffuse source in the

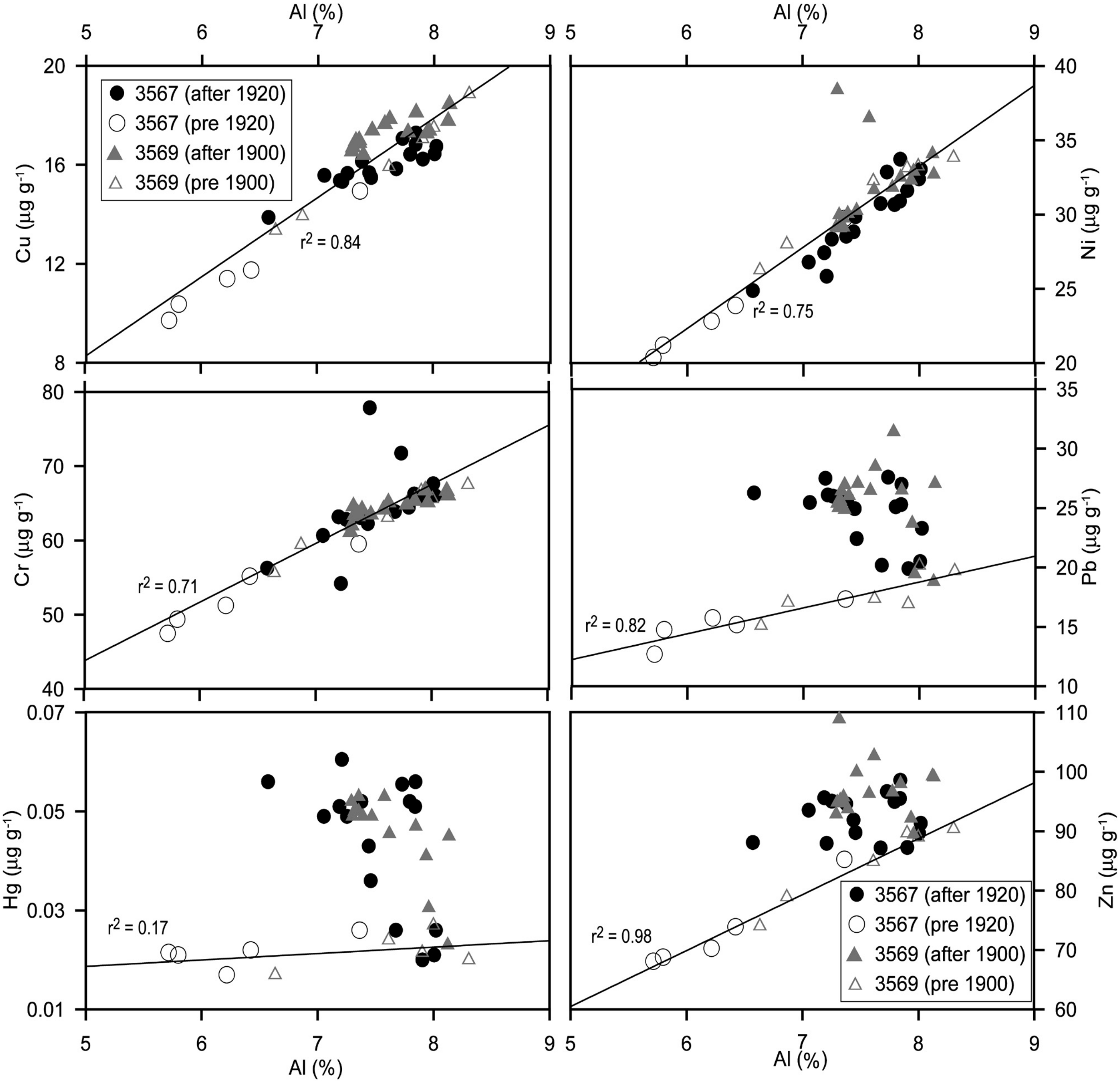

Fig. 4.– Scatterplots showing the relationships between metal contents and Al in down-core samples of the cores 3567 and 3569. Sediment samples from the period after 1900 (core 3569) and 1920 (core 3567) are represented by filled symbols.

Fig. 4.– Gráfico de dispersión con las relaciones entre contenidos de metales y Al en las muestras de los testigos 3567 y 3569. Las muestras pertenecientes al periodo posterior a 1900 (testigo 3569) y 1920 (testigo 3567) aparecen representadas por símbolos rellenos.

Hg and Pb cycles (Nriagu, 1978; Schroeder and Munthe, 1998; Pacyna *et al.*, 2001).

4.6. Anthropogenic fluxes

Previous investigations (e.g. Monna *et al.* (1997); Shotyk *et al.* (1998); Sangster *et al.* (2000); Outridge *et al.* (2002); Miralles *et al.* (2004)) have demonstrated the importance of studying stable Pb isotopes (^{204}Pb, ^{206}Pb, ^{207}Pb and ^{208}Pb) in order to define the origin of Pb. In the absence of stable lead measurements, the proportional estimation of metal associated with anthropogenic activity is based on the determination of the local, pre-industrial background concentrations, which represent the natural metal concentration free of contamination present in these sediment cores. The anthropogenic contribution (in percentage) was obtained by subtracting the background metal concentrations (defined as the average values of the 2 lowermost samples in each core where pre-industrial sedimentation occurred, according to the ^{210}Pb chronology) from the metal contents of the uppermost samples (after 1991) and dividing by the recent contents of these

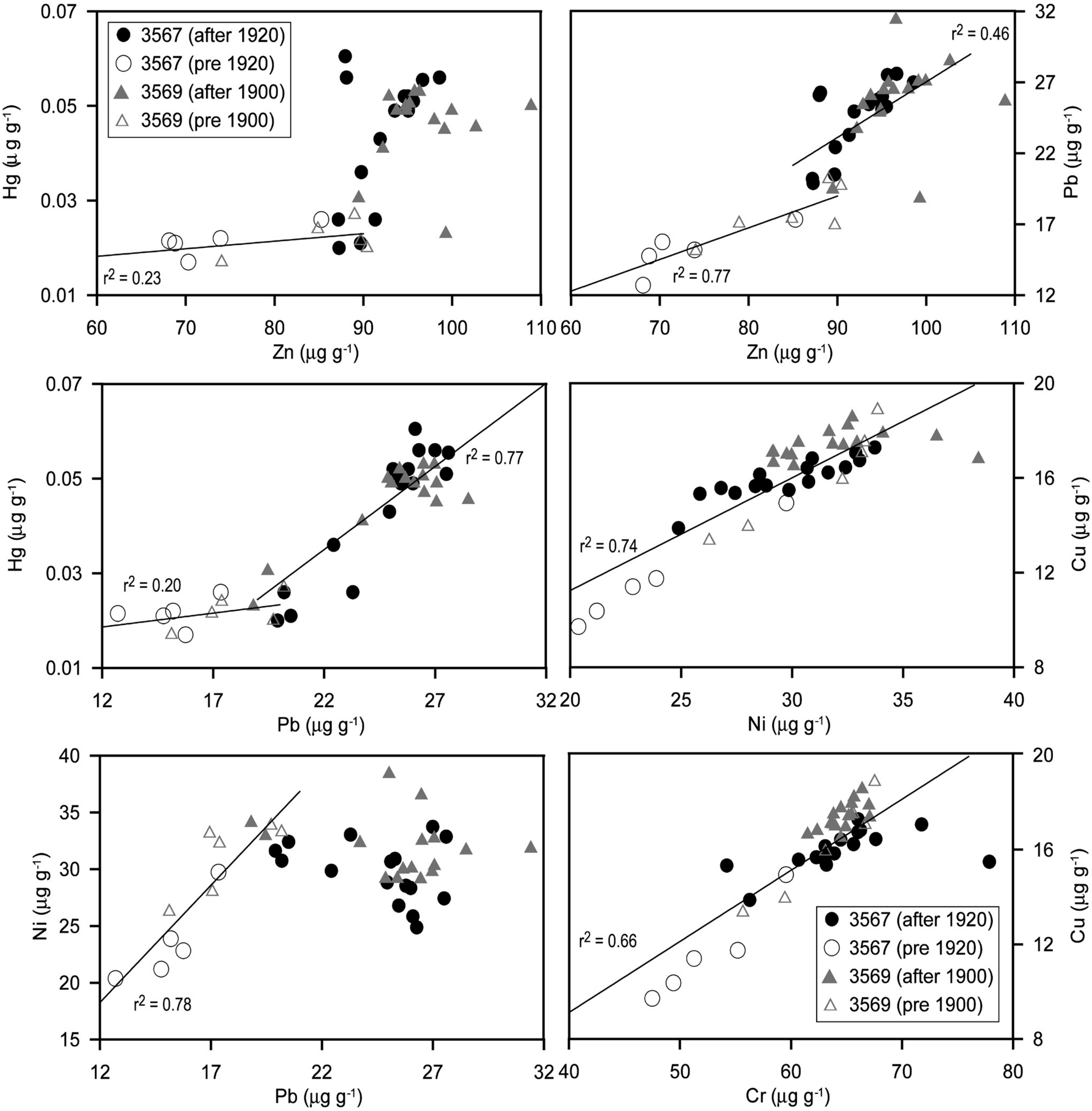

Fig. 5.– Scatterplots showing the relationships between metal contents in down-core samples of the cores 3567 and 3569. Sediment samples from the period after 1900 (core 3569) and 1920 (core 3567) are represented by filled symbols.

Fig. 5.– Gráfico de dispersión con las relaciones entre contenidos de metales en las muestras de los testigos 3567 y 3569. Las muestras pertenecientes al periodo posterior a 1900 (testigo 3569) y 1920 (testigo 3567) aparecen representadas por símbolos rellenos.

upper samples. The average results for both cores indicate that 64% of total Hg, 44% of total Pb and 24% of total Zn in the recent sediments since 1991 were derived from anthropogenic sources. Metal fluxes (Zn, Pb and Hg) were calculated from the ^{210}Pb chronologies and excess metal concentrations according to the equation (Cochran *et al.*, 1998):

$$F_i = \Omega_i \, [Me]^i_{xs}$$

Where, for each depth interval, *i*, F_i is the metal flux (µg cm^{-2} yr^{-1}), Ω_i is the ^{210}Pb-derived accumulation rate (g cm^{-2} yr^{-1}) and $[Me]^i_{xs}$ is the excess metal concentration above background level (µg g^{-1}). The anthropogenic component $[Me]^i_{xs}$ is calculated by subtracting the background fraction from the measured value. The average excess Hg, Pb

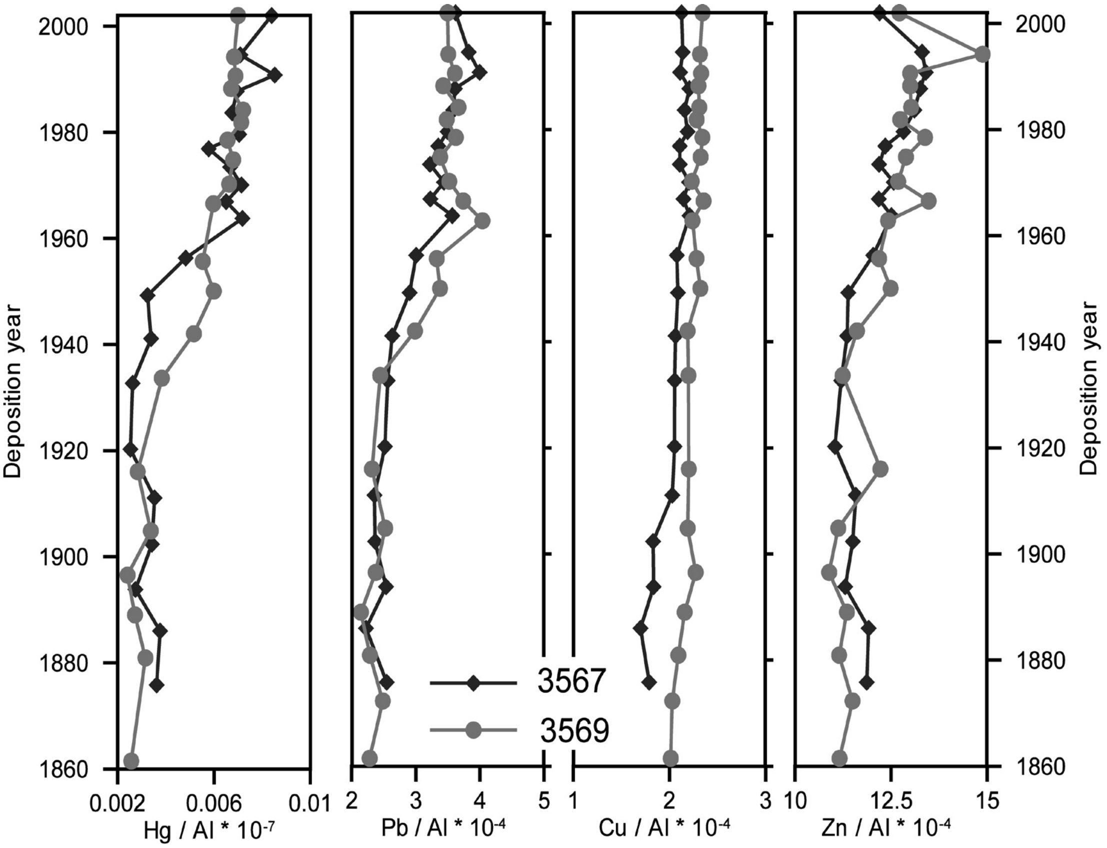

Fig. 6.– The Al-normalised profiles for Hg, Pb, Cu and Zn in box-cores 3567 and 3569. The geochronology for each core is derived using ^{210}Pb data.

Fig. 6.– Perfil en función de la edad de Hg, Pb, Cu y Zn normalizados para el Al en los box-cores 3567 y 3569. La geocronología de cada testigo ha sido derivada a partir de ^{210}Pb.

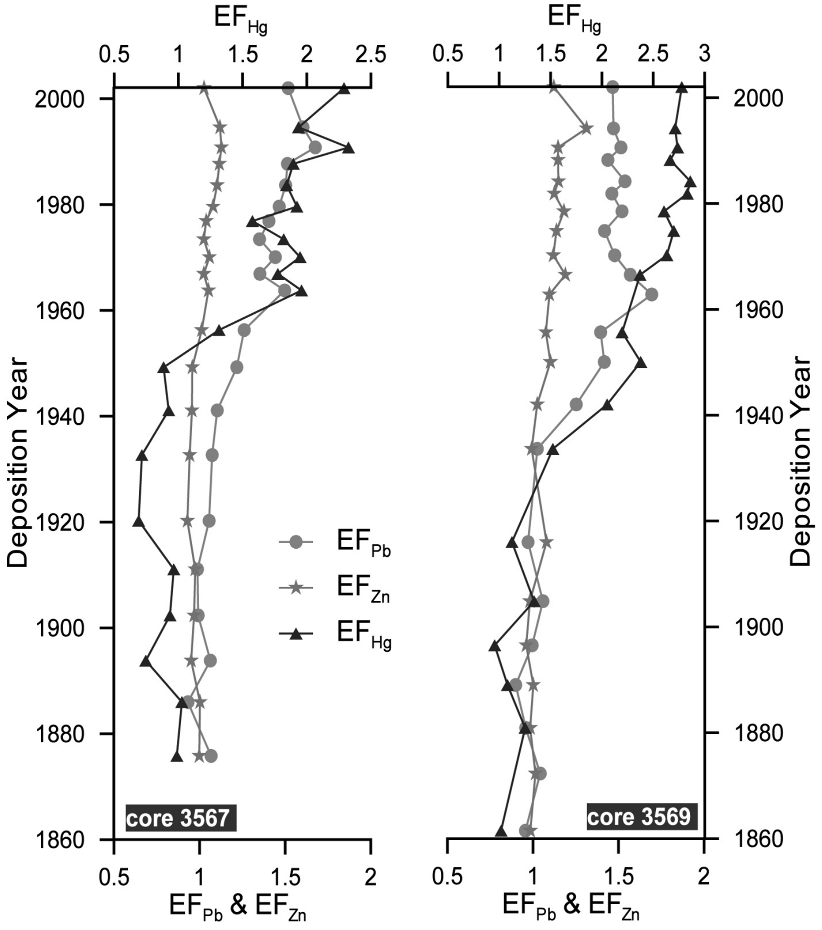

Fig. 7.– Historical trends in normalised enrichment factors for Hg, Pb and Zn in the Lis area. EFs are calculated by dividing the Al-normalised metal contents by the Al-normalised metal background for each core.

Fig. 7.– Tendencias históricas en los factores de enriquecimiento (EF) para Hg, Pb y Zn normalizados para el Al en la zona del río Lis. Los EF han sido calculados dividiendo el contenido de metales normalizados para el Al por el de los valores de fondo para cada metal, en cada testigo.

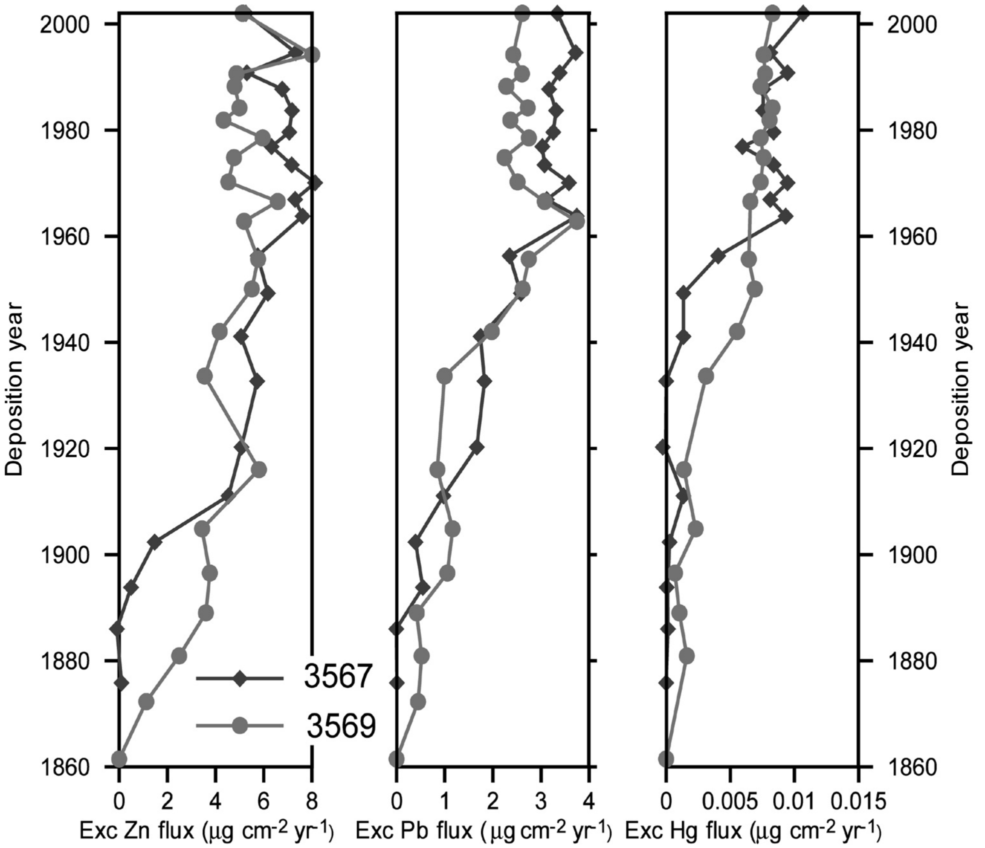

Fig. 8.– Excess metal fluxes for Zn, Pb and Hg in two box-cores from the Lis area: 3567 (dark grey squares) and 3569 (light grey circle).

Fig. 8.– Flujo temporal antropogénico (exc) de Zn, Pb y Hg en los box-cores 3567 (rombos gris oscuro) y 3569 (círculos gris claro) de la zona del Lis.

and Zn fluxes per year for the last 40 years are 0.008 µg cm^{-2}, 3 µg cm^{-2} and 6 µg cm^{-2}, respectively (Fig. 8). Of the three selected elements, Zn shows an earlier increase in anthropogenic fluxes compared with Hg and Pb, probably indicating its prior use by Man (Alderton, 1985). The significant increase in the anthropogenic flux of Hg after the 1940s may reflect the delay of industrial development of Portugal, in comparison to the most of Europe.

Despite the relatively low values for anthropogenic Hg, Pb and Zn fluxes obtained in the Lis area when compared to other contaminated areas (e.g. Long Island Sound (Cochran *et al.*, 1998), San Francisco Bay (Hornberger *et al.*, 1999) and Gota älv estuary (Brack *et al.*, 2001), the approximately 400 km^2 accumulation area of fine-grained sediments based on surface sediments distribution map extracted from Quaresma *et al.* (2005), implies an estimated Hg, Pb and Zn accumulation of 30, 12000 and 24400 kg yr^{-1}, respectively. Considering the interval of time between 1960s and 2000, it is estimated that there was an accumulation of 1.2, 480 and 976 tons of Hg, Pb and Zn, respectively.

5. Conclusions

The distance of large rivers (e.g. Douro and Tejo) from the shelf area under discussion creates conditions for deposition of sediments that are not affected directly by river discharge. Despite the high-energy conditions and the generally sandy character of the Portuguese shelf environment, it is possible to identify slight anthropogenic Hg, Pb and Zn enrichments in local areas of mud accumulation. The identification of metal accumulation is attributed to the use of metals by Man in a much broader area than that of the drainage area of the nearby Lis River.

Due to its higher levels of enrichment, Hg is the element that seems to best reflect anthropogenic activity in these sediments, although it also has had a later use by Man compared to Zn and Pb. The metal enrichments in this shelf area are probably associated with a diffuse and distal source (such as atmospheric and / or marine transport of fine-grained sediments), consistent with the relatively low Lis River discharge and the absence of any other natural lithologic metal sources close to this shelf area.

Acknowledgements

Mário Mil-Homens was supported by a PhD Scholarship awarded by the Portuguese Institute of Geology and Mining (through the INGMAR project financed by the Portuguese Foundation for Science and Technology - FCT), a FCT fellowship (BD/11745/2003) and European Social Fund (ESF) through the 3rd EU Framework Program. The European program SOCFAC funded the analytical work carried out at the National Oceanography Centre, UK. The authors are also grateful to the two anonymous referees for their helpful comments.

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