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Lead and Zinc contamination of surface sediments in the main harbours of the Galician Rias

Contaminación del sedimento superficial por plomo y cinc en los principales puertos de las rías gallegas

R. Prego*, P. Ferro, C. Trujillo

Instituto de Investigaciones Marinas (CSIC), 36208 Vigo (Spain).
**corresponding author: prego@iim.csic.es*

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Abstract

The concentration ranges and degree of contamination of lead and zinc in the four principal harbour areas of the northwest Iberian Peninsula have been defined from 130 surface sediment samples (<63 µm fraction) using the pre-industrial background equations obtained from metal analysis of four sediment cores. The increase of metals may be associated with the ria-harbour areas: (a) for lead to values of 140 mg·kg^{-1} in Pontevedra, 160 mg·kg^{-1} in Ferrol and Coruña and 320 mg·kg^{-1} in Vigo; (b) for zinc to values of 150 mg·kg^{-1} in Pontevedra, 380 mg·kg^{-1} in Coruña, 600 mg·kg^{-1} in Ferrol and 1960 mg·kg^{-1} in Vigo. The areal distribution patterns of lead and zinc in sediments, with higher concentrations at locations close to the metal sources, reflect firstly the influence of harbour activities and secondly the shipyard works in the rias. The degree of lead and zinc contamination in these harbour sediments, based on the calculation of normalized factors of sediment enrichment, can be defined as moderate to considerable in the harbours of La Coruña and Pontevedra and severe in Ferrol and Vigo. In other parts of the rias the contamination usually decreases, as is generally observed for other world estuaries or coastal zones where there are harbours.

Keywords: Pb, Zn, contamination, sediment, harbour, ria, Spain

Resumen

A partir de la fracción fina en 130 muestras de sedimento superficial se han cuantificado los niveles de concentración para plomo y cinc en las rías donde se encuentran los principales puertos de la costa gallega. Los patrones de distribución de Pb y Zn en el sedimento muestran altos contenidos en el litoral próximo a las áreas de actividad portuaria y astilleros: las concentraciones llegan hasta 140, 160, 160 y 320 mg·kg^{-1} para Pb y hasta 150, 380, 600 y 1960 mg·kg^{-1} para Zn en Pontevedra, Coruña, Ferrol y Vigo, respectivamente. En base a sus niveles naturales, establecidos mediante cuatro testigos de sedimento, se han definido sus grados de contaminación mediante factores de enriquecimiento. Consecuentemente, se puede definir entre moderada y considerable la contaminación de Pb y Zn en los puertos de La Coruña y Pontevedra, así como severa en Ferrol y Vigo. En otras zonas de las rías la contaminación normalmente decrece, como suele ocurrir en estuarios y costas de nuestro planeta donde existen puertos o astilleros.

Palabras clave: Pb, Zn, contamination, sediment, harbour, ria, España.

1. Introduction

Metals are natural constituents of the sediments in coastal zones and they may be oligoelements, such as zinc for example, which is a natural element essential for living organisms when present in small amounts, or do not have any known biological role, as is the case for lead. However, both can become toxic for living organisms at high concentrations (Ewers and Schlipkoter, 1991; Ohnesorge and Wilhein, 1991). Metals enter the environment by means of natural processes or are derived from human activities. For some metals, natural and anthropogenic inputs may be of the same order (Zn), whereas for others (Pb) inputs due to human activities dwarf natural inputs (Clark, 2001). Much of those human activities are located in the fluvial watersheds and in the margins of estuaries (Salomons and Förstner, 1984), being important areas for the concentration of contaminants, due to coastal industrial activity and human settlement. There, trade is growing rapidly and much of it depends on shipping, most of import and export travel by sea, and the marine harbour environment is degraded. The increase of metal concentrations in the sediment is a symptom of this process as has been observed in the Pacific harbours (Wolanski, 2006). In the Atlantic and Mediterranean harbours these changes in the sediment reservoir have been occasionally studied. Generally, the presence of contamination by metals have been considered only in important harbours such as New York (Feng *et al.*, 1998), Boston (Manheim *et al.*, 1998), the Atlantic French harbours (Fichet *et al.*, 1999) and, more recently, in Baltimore (Mason *et al.*, 2004), Montevideo (Muniz *et al.*, 2004) and Naples (Adamo *et al.*, 2005). In all of these Pb and Zn were taken in account and its contamination noticed. The objective of this study is to define the ranges and state of contamination of these two metals of the four principal harbour areas inside the Galician Rias of the northwest of Iberian Peninsula, i.e. Ferrol, La Coruña, Marín and Vigo (Fig. 1).

2. Material and Methods

2.1. Survey area

Rias were classified by Torres-Enciso (1958) in basis of their geological features into Northern, Central and Western Rias and he considered that fluvial erosion played the main role in ria sediments in comparison with lithological and tectonic influences. Rias were defined by Evans and Prego (2003) as incised valleys where the estuarine zone moves according to climatic changes and their hydrography is characterized by mesotidal and semidiurnal pattern with a ria-ocean water exchange being dominated by a positive residual circulation in the case of large Western Rias of Pontevedra and Vigo (Prego and Fraga, 1992; Prego *et al.*, 2001) and driven by tides in the case of the small Central Ferrol and Coruña Rias (deCastro *et al.*, 2004; Gómez-Gesteira *et al.*, 2002). The littoral of these four selected rias is heavily populated, with populations ranging from 200,000 to 450,000 inhabitants. Their residual waters flow into the Ferrol Ria without pre-treatment, in the Vigo and Pontevedra Rias after sewage plants processing whilst in La Coruña none flows into the ria. Moreover, there is intense harbour activity, with between 2,000,000 and 14,000,000 tonnes of goods each year passing through these harbours and the shipyard works are important, particularly in the Ferrol and Vigo areas.

Fig. 1.- Map of the Galicia with their rias and the main harbours.
Fig. 1.- Mapa de Galicia con sus rías y principales puertos.

2.2. Sampling

The surface sediment collected in the four rias are shown in figure 1. A total of 33 samples in Ferrol (September 11, 1998), 11 in La Coruña (September 1998), 37 in Pontevedra (October 1998) and 49 in Vigo (October 1999). These were taken using a Van Veen grab (30 and 3.5 L of capacity) from R/V *Mytilus* and its auxiliary boat *Zoea*. Samples of the top surface centimetre were collected with a polyethylene spatula of 200 mL and stored in plastic flasks, which were stored in refrigerator at 4ºC. Later, in the Institute laboratories, sediment samples were oven-dried at 50ºC and sieved through a nylon mesh to obtain the fraction less than 63 µm; this fraction was then stored in plastic tubes until analysis.

In order to quantify the background metal concentrations, two cores of 150 and 175 cm length were sampled in the middle Ferrol Ria using a Rossfelder P-3 vibrocorer and another two cores of 270 and 134 cm length were taken in the middle of Vigo Ria using a gravity-corer. The four cores collected in PVC tubes were preserved at 4ºC in a refrigerated chamber until they were sectioned and slices of 1 cm of thickness every 10 cm were extracted from each core to depth of 50 cm to reach beneath the level of the anthropogenic influence. They were processed in a similar way to the surface samples. Handling and analysis of samples were carried out in a clean laboratory (ISO 6); plastic laboratory ware employed for sampling, storage and sample treatment were all previously acid-washed (HNO_3 10%) for 48 h and rinsed throughout with Milli-Q water (Millipore).

2.3. Analysis

The sub-samples of the fine fraction (<63 µm) were digested, following the EPA guideline for siliceous sediments (EPA, 1996), in Teflon bombs using a microwave oven (Milestone, MLS-1200 Mega). Pb was analysed by means of electrothermal atomic absorption spectrometry (ETAAS) using Varian 220 apparatus equipped with the Zeeman background correction. Fe and Zn were determinated by means of flame atomic absorption spectrometry (FAAS) using a Varian 220-FS apparatus. The accuracy of the analytical procedures employed for the analysis of metals in sediment samples was checked using the PACS-2 (NRC, Canada) certified reference material, and showed good agreement with the certified values (table 1).

Metal	measured	certified
Fe ($g \cdot kg^{-1}$)	42.0 ± 0.5	40.9 ± 0.6
Pb ($mg \cdot kg^{-1}$)	176 ± 16	183 ± 8
Zn ($mg \cdot kg^{-1}$)	356 ± 6	364 ± 23

Table 1.- Metal analysis of CRM PACS-2.
Tabla 1.- Análisis de metales de CRM PACS-2

3. Results and Discussion

3.1. Surface sediment concentration and distributions

In general, the areal distribution of metals in the Galician Rias reflects the inputs from anthropogenic origins, with higher concentrations at locations close to the metal sources (Prego and Cobelo-García, 2003). So, lead levels in the main ria harbours were in the range of 10 to 1100 $mg \cdot kg^{-1}$. The highest lead values occur in the San Simón Inlet due to the porcelain factory wastes outflow at the head of the Vigo Ria (Prego and Cobelo-García, 2002). When this local area is not considered, the increase of lead concentrations in the surface sediments of the four rias are associated with the harbour areas (Fig. 2a): up to 140 $mg \cdot kg^{-1}$ in Pontevedra Ria, to 160 $mg \cdot kg^{-1}$ in Ferrol and Coruña Rias and to 320 $mg \cdot kg^{-1}$ in Vigo Ria. Thus, the pattern of distribution of this metal shows the affect of the firstly harbour activities and secondly the shipyard such as is observed in the middle of the southern margin of Ferrol Ria and the Vigo littoral (Fig. 2a). These results validate the industrial effects already pointed out by Besada *et al.*, (1997) and Rubio *et al.*, (2000) for lead.

The strong gradient in the harbour lead pattern observed around the Galician harbours is different in the Pontevedra Ria because in this area the lead concentration increases slowly from the outer parts towards the inner parts of the ria, although maximum values (Fig. 2a) are found just beyond the river mouth, in the Marin harbour zone. The anthropogenic origin is clear in the sedimentary register (Rubio et. al., 1995), however the lead is dispersed throughout the ria and is not concentrated in the harbour area.

Zinc has a similar trend to lead with local differences (Fig. 2b): the highest concentrations in the fine sediment occur in the shipyard zone of the Ferrol Ria (600 $mg \cdot kg^{-1}$) and the shipyard-harbour area of the Vigo Ria (1960 $mg \cdot kg^{-1}$). The influence of the harbours is low, however it is obvious (Fig. 2b), in the La Coruña (380 $mg \cdot kg^{-1}$) and, to a lesser way, in Pontevedra Ria (150 $mg \cdot kg^{-1}$). Another difference is that the zinc levels in the San Simón Inlet show small signs of anthropogenic enrichment, as stated by Evans *et al.*, (2003) and Howarth *et al.*, (2005). The zinc contamination in the area of Samil noticed by Carballeira *et al.*, (2000) was not found because the intertidal sediments of river Lagares outflow were not sampled. Similarly, in the innermost part of the Coruña Ria (O Burgo zone) the high concentrations measured by Barreiro *et al.*, (1988), attaining 640 $mg \cdot kg^{-1}$, was not verified.

Once the lead and zinc levels in the surficial sediments are established, the contamination state could be ascertained by comparison with typical concentrations of these two metals in the unpolluted sediments and/or their natural presence in the lithosphere. The measured values in the four ria-harbour areas are higher than average concentration in the earth's crust (16-32 $mg \cdot kg^{-1}$ of Pb and 50-65 $mg \cdot kg^{-1}$ of Zn; Wedepohl, 1991) and also exceed the range for unpolluted sediments (5-25 $mg \cdot kg^{-1}$ of Pb

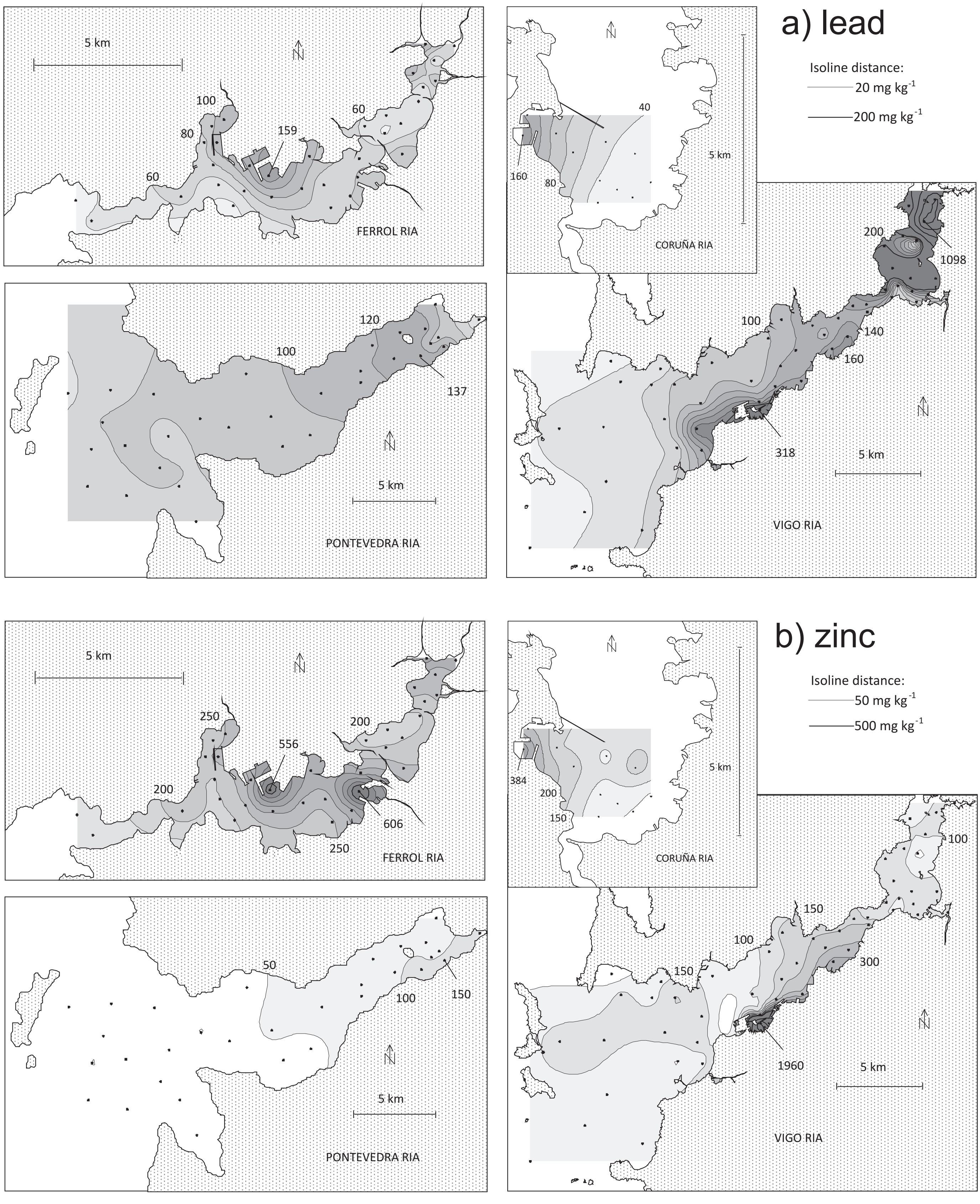
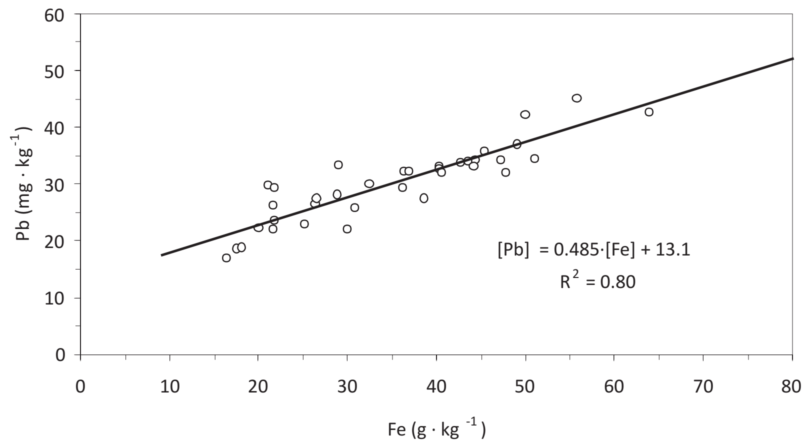


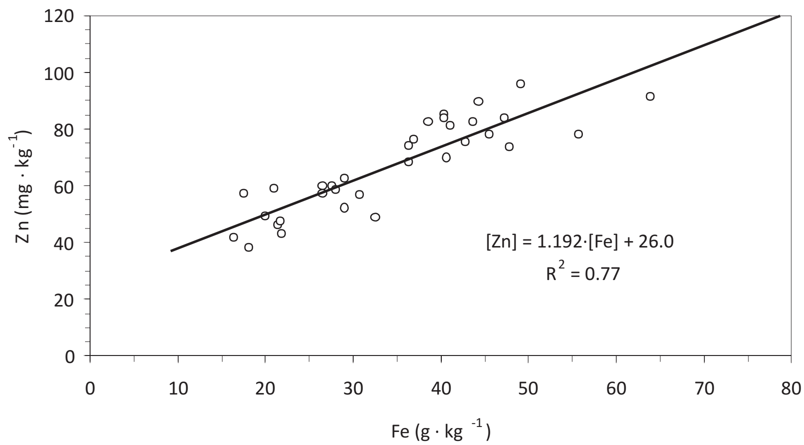
Fig. 2.- Contour plots of (a) lead and (b) zinc concentrations (mg·kg^{-1}) in fine fraction surface sediment of the ria-harbours.

Fig. 2.- Isolíneas de las concentraciones de (a) plomo y (b) cinc en la fracción fina del sedimento superficial en las rías con los principales puertos gallegos.

Fig. 3.- Regression lines of the lead and zinc concentrations vs. Fe in the sediments in the cores.

Fig. 3.- Rectas de ajuste para las concentraciones de plomo y cinc respecto a las de hierro en el sedimento de los testigos.





and 20-100 mg·kg^{-1} of Zn; Bryan and Langston, 1992; Hornberger, *et al.*, 1999; Doherty *et al.*, 2000). However, it is more appropriate to use local background equations (Prego and Cobelo-García, 2003) to define the degree of contamination.

3.2. Background ranges of lead and zinc

In order to distinguish the natural metal concentrations from that of anthropogenic additions in the sediments of the rias where the main harbours and shipyards zones are located, and to make a diagnosis of the degree of contamination, there is a need to establish a reference, i.e., *a background value*. The quantification of the natural background range of Pb and Zn in the four rias is the first necessary step in an attempt to determine the levels of metal enrichment in the sediments. They should not be referenced to those of the crust (Wedephol, 1991) nor to pristine coastal zones, because the local geochemical composition determines the reference concentrations. Lithogenic elements such as aluminium (Hanson *et al.*, 1993), iron (Chon Lin el al., 1998) or scandium (Luoma *et al.*, 1990) were used as normalizing elements; of these three possibilities iron was choose because it was already used successfully in the study of the rias (Cobelo-García and Prego, 2003; Marmolejo *et al.*, in press). Iron concentration in surface sediment ranged 24-41, 16-48, 17-30 and 11-59 g·kg^{-1} to Ferrol, Coruña, Pontevedra and Vigo Rias, respectively.

Since particles smaller than 63 μm present a very strong adsorptive potential for trace metals (Salomons and Förstner, 1984), contaminants are predominantly distributed and concentrated in this fraction. For these reasons, Pb and Zn will be considered only this grain-size fraction. The surface sediment is affected by the anthropogenic activities, but it is assumed that the metal concentrations in sediment from the deeper part of the core represent preindustrial conditions (Cobelo-García and Prego, 2003).

Previously, a constant background concentration was assumed for the ria sediment (Carballeira *et al.*, 2000) but the metal content changes according to the granulometric and geochemical compositions of the sediment, so metal versus reference element equations were employed to avoid this problem (Cobelo-García and Prego, 2003). However, the equation was obtained for each ria. In this study, only one equation was used for the rias of Ferrol, La Coruña, Pontevedra and Vigo based in four cores sampled in the northeast and the southeast ria.

Pb-Fe and Zn-Fe representations are shown in figure 3 to the four cores together. The equations obtained from sediments below 50 cm, to avoid anthropogenic enrichment, are:

$$[Pb]_{cal} = 0.485\ [Fe] + 13.1 \qquad r = 0.90 \qquad (1)$$

$$[Zn]_{cal} = 1.192\ [Fe] + 26.0 \qquad r = 0.88 \qquad (2)$$

where $[Me]_{cal}$ is the Pb or Zn concentration (in $mg \cdot kg^{-1}$) calculated from the iron content (in $mg \cdot g^{-1}$) of the sediment. Then, equations (1) and (2) are applied to the surface sediment of the four rias and so the background or pre-industrial value can be established.

3.3. Metal enrichment and contamination

The metal contamination of the surface sediment in the rias is based on the calculation of normalized factors of sediment enrichment (NFSE) from the measured concentrations and the theoretical background levels calculated from the equations (1) and (2):

$$Pb_{NFSE} = [Pb]_{measured} / [Pb]_{calculated} \qquad (3)$$

$$Zn_{NFSE} = [Zn]_{measured} / [Zn]_{calculated} \qquad (4)$$

The NFSE isopleths maps for lead and zinc in the four rias considered are shown in figure 4. According to the criteria of Hakanson (1980), the degree of contamination in the ria sediments can be defined by the NFSE relationship as:

null < 1 < moderate < 3 < considerable/severe < 6 < very severe

Consequently, the NESF isolines of figure 4 define particular ria areas with a clear anthropogenic influence generated by local contamination. Between these areas are the Galician harbours (Fig. 4) where metals tend to be accumulated in their sediments as observed in other world harbours (see table 2). The degree of contamination of ria-harbours may be defined as:

- Coruña harbour: Moderate-considerable (NESF: 2-4) to Pb and Zn,
- Pontevedra harbour: Moderate (Zn: 2-3) and considerable (Pb: 4-5),
- Ferrol harbour: Considerable (Pb: 4-5) and severe (Zn: 4-6),
- Vigo harbour: Considerable-very severe to Pb (4-7) and Zn (3-10).

When all the rias are considered, the pattern of contamination is similar to other world estuaries or coastal zones where harbours are situated (Bolton *et al.*, 2003; Guerra-

Harbour	Pb	Zn	Reference
Barcelona (Spain)	85 - 590	180 - 1130	Guevara-Riba *et al.*, 2004
Bergen (Norway)	24 - 1920	45 - 2900	Paetzel *et al.*, 2003
Ceuta (Spain)	10 - 520	295 - 695	Guerra-García and García-Gómez, 2005
Cork (Ireland)	15 - 50	100 - 215	Kilemade *et al.*, 2004
East London (South Africa)	5 - 85	25 - 330	Fatoki and Mathabatha, 2001
Hamilton (Canada)	20 - 1250	340 - 5930	Poulton *et al.*, 1996
Kembla (Australia)	150 - 485	1210 - 2220	He and Morrison, 2001
Makupa (Kenya)	55 - 165	276 - 3193	Muhoi *et al.*, 2003
Montevideo (Uruguay)	85 ± 31	312 ± 102	Muñiz *et al.*, 2004
Singapore (Singapore)	88 ± 34	451 ± 195	Orlic and Tang, 1999
Sydney (Australia)	78 - 1050	75 - 8820	McCready *et al.*, 2006
Ventspils (Latvia)	3 - 44	17 - 254	Müller-Karulis *et al.*, 2003
Coruña (Spain)	85 - 160	155 - 385	This study
Ferrol (Spain)	70 - 160	240 - 560	This study
Marin (Pontevedra, Spain)	95 - 135	90 - 150	This study
Vigo (Spain)	160 - 320	265 - 1960	This study

Table 2.- Lead and zinc concentration ranges ($mg \cdot kg^{-1}$) in the surface sediment (<63 µm fraction) of some world ports and the main Galician rias harbours.

Tabla 2.- Rangos de concentración de plomo y cinc ($mg \cdot kg^{-1}$) en el sedimento superficial (<63 µm fraction) de diferentes puertos del mundo y de los principales puertos de las rías gallegas.

Fig. 4-. Contour plots of normalised factors of sediment enrichment (NFSE) of (a) lead and (b) zinc in fine fraction of the surface sediment fine fraction of the ria-harbours.

Fig. 4.- Isolíneas de los factores de enriquecimiento normalizados en el sedimento (NFSE) para (a) plomo y (b) cinc en la fracción fina del sedimento superficial en las rías con los principales puertos gallegos.

García and García-Gómez, 2005; Tam, 2006). Harbour areas are usually the main source of contamination as result of the commercial transporting activities and occasionally shipyard works and industrial and urban effluents spill (Cobelo-García *et al.*, 2004). In these cases, Pb and Zn are always present. Moreover, there is another area, beyond the harbour influence, where the degree of contamination decreases, eg lead in Ferrol Ria (Fig. 4a), it is low (Zn in Vigo; Fig. 4b), or quasi-pristine even (Zn in Pontevedra, Fig. 4b).

In conclusion, although lead and zinc have been shown to be strong contaminants at several locations in some rias (Prego and Cobelo-García, 2003) there is clear evidence of considerable localized anthropogenic enrichments of these two metals in the harbour and shipyard zones of the four main industrial and commercial maritime Galician Rias. The environmental state of these requires monitoring of the contaminated sediment areas and the ria harbours in general with systematic and periodic analysis in order to decide if regeneration actions will be needed in the future.

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