

Copper in Galician ria sediments: natural levels and harbour contamination

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SUMMARY: Copper distribution, natural background and contamination levels in sediments of the Galician rias were assessed from 389 surface sediment samples and five sediment cores. The natural reference concentration of copper can be estimated using the Cu-Fe relationship obtained from preindustrial sediments of rias: $[\text{Cu (mg kg}^{-1})] / [\text{Fe (g kg}^{-1})] = 0.55$. Severe copper contamination was mainly observed in the harbour, fishing ports and shipyards near shore areas of the Galician coast. Therefore, the rias of Ferrol and Vigo were the most environmentally disturbed, while the northern Galician rias were the least disturbed. The Galician case can be seen as the type of copper contamination due to maritime activities observed in other world harbours.

Keywords: metal, sediment, background concentrations, harbour, ria, NW Iberian Peninsula.

RESUMEN: EL COBRE EN EL SEDIMENTO DE LAS RÍAS GALLEGAS: NIVELES NATURALES Y CONTAMINACIÓN PORTUARIA. — A partir de 389 muestras de sedimento superficial y 5 testigos de sedimento se ha determinado la distribución, concentraciones naturales y niveles de contaminación por cobre en los sedimentos de las rías gallegas. En base a sedimentos preindustriales se ha obtenido una correlación entre hierro y cobre aplicable a las rías: $[\text{Cu (mg kg}^{-1})] / [\text{Fe (g kg}^{-1})] = 0.55$. Al calcular con esta ecuación los factores de enriquecimiento por cobre del sedimento superficial se ha detectado una fuerte contaminación en las zonas portuarias y de astilleros en la costa gallega. Bajo este aspecto son las rías de Ferrol y Vigo las más alteradas mientras que lo contrario ocurre con las rías del norte de Galicia. Este tipo de contaminación por cobre en el noroeste de la península Ibérica se suma a algunos casos derivados del tráfico y construcción de buques observados en otras áreas costeras del planeta.

Keywords: metal, sedimento, concentraciones de fondo, puerto, ría, España.

INTRODUCTION

Copper is a ubiquitous element in the earth's crust, from which it is moved by weathering to coastal sediments. Copper is accumulated in sediments together with its autochthonous sea source due to plankton sedimentation. Although copper is an essential micronutrient for living organisms (Scheinberg 1991), it can become poisonous to marine life when its concentration increases in the surroundings (Long *et al.* 1995). For this reason, copper has been employed as an algicide and molluscicide in water (Schiff *et al.* 2004) and it is a component of antifouling paint for ship bottoms. The typical source of copper in marine environment contamination is industrial discharges and atmospheric deposition. Fungicides, wood preservatives and boat

antifouling paints can also contribute to high levels of copper in the aquatic environment. Most imported and exported goods travel by sea, resulting in a continuous increase in shipyard activities and maritime traffic. Therefore, the copper input in the coastal environment rises every day and the areas around ports decay. Moreover, the ban on using TBT on smaller vessels has resulted in the shift back to the use of copper as the main biocide. Copper present in the water and sediments can be accumulated by benthic animals, causing, for example, reduced respiration rates and impaired growth in mussels, clams and other shellfish (Kennish 1992, Sobral and Widdows 1997).

The influx of copper that leaches from these paints is the main copper load to the Bay of San Diego (Seligman *et al.* 2001, Valkirs *et al.* 2003), and is also the rea-

son for the increase in metal contamination observed in the Pacific harbour sediments (Wolanski 2006). This type of contamination in the sedimentary reservoir has been studied in the main Atlantic harbours of the USA (New York: Feng *et al.* 1998; Baltimore: Mason *et al.* 2004) and France (Fichet *et al.* 1999). Nevertheless, it has been poorly investigated in the Iberian Peninsula and particularly in the Galician rias, where lead and zinc contamination in sediments of the four main harbour areas of Galicia (Ferrol, Coruña, Marín and Vigo) has been observed (Prego *et al.* 2008a).

The biogeochemical cycle of copper in rias was recently surveyed (Prego and Cobelo-García 2003), and the pollution effects were investigated (Fernandez *et al.* 2008, Duran and Beiras 2010). The metal footprint, especially that of copper, in the harbour and shipyard shore-sediments of Vigo Ria was highlighted (Prego *et al.* 2008b). Natural inputs of copper into the Galician rias are usually low (Prego and Cobelo-García 2003). The anthropogenic contributions of dissolved and particulate copper due to sewage from water-treatment plants ($136 \text{ molCu day}^{-1}$) were found to be one order of magnitude higher than the fluvial supply ($15 \text{ molCu day}^{-1}$) in early winter in the Ria of Vigo (Santos-Echeandía, *et al.* 2008). This total flux of copper is similar to the findings of Cobelo-García and Prego (2004) for a small, but industrialized ria in Ferrol where water treatment does not exist. Therefore, copper spillage from diffuse sources must make a significant contribution to the sedimentary zone, which needs to be identified, around shipbuilding and repairing areas, harbours and the maritime traffic routes.

The purpose of this study was to assess the copper concentrations in sediments of the Galician rias and their harbour areas. There were three objectives: (a) to determine the copper distribution in the surface sediments of the Galician rias and their natural backgrounds; (b) to define the copper contamination levels in the harbour and shipyard areas of the rias; and (c) to suggest a simple criterion for identifying copper contamination on the Galician coast.

MATERIALS AND METHODS

Survey area

The Galician rias (Fig. 1) were defined by Evans and Prego (2003) as incised valleys where the estuarine zone can move according to climatic changes. The rias receive the main fluvial flow in the innermost area and, hydrographically, they show a mesotidal and semidiurnal pattern with a ria-ocean water exchange dominated by a positive residual circulation (Prego *et al.* 2001, Varela *et al.* 2005), except the Ferrol and Coruña Rias, in which the outflow is driven by tides (Gómez-Gesteira *et al.* 2002, deCastro *et al.* 2004).

Torre-Enciso (1958) has classified the Galician Rias depending on their geological features into northern, middle and western rias (Fig. 1). The southernmost rias



FIG. 1. – Map of Galicia with the location of harbours and rias under study.

of the Finisterre Cape constitute the western rias, namely, the rias of Vigo, Pontevedra, Arousa and Muros, which are the widest rias of Galicia, with surface areas of 120–230 km² and mouth depths around 50 m. Northern rias are located eastward of Cape Ortegal, while the middle rias are located between the two above-mentioned capes. Watersheds of the rias are composed of granites, schists and gneisses, and fluvial erosion plays the main role in ria sediments compared with lithological and tectonic influences (Torre-Enciso 1958).

Population, harbour activity and industries on the shores of the rias vary depending on each ria. The study of copper in sediments was focussed on the northern, middle and western Galician rias, where the main (La Coruña, Ferrol and Vigo) and secondary harbours of the Galician coast are located (Fig. 1). The maritime traffic in these three aforementioned harbours is 27,000,000 tons per year. In addition, 38% of Spanish shipyards are located in Galicia and receive 40% of the money for the sale of ships. The Ferrol and Vigo Rias have the main shipyards (Prego *et al.* 2008a).

Sampling and analysis

A total of 389 surface sediment samples along the Galician coast were collected in the northern, middle and southern rias and their harbours (Figs 2, 3 and 4, respectively). Sampling zones in the northern rias were: Viveiro (24 samples), O Barqueiro (29), Ortigueira (36) all sampled in July 2008; in the middle rias: Ferrol (33), La Coruña (11) both in September 1998, Laxe (19, in July 2000) and Camariñas (33, in September 2003); and in the southern rias: Corcubión (15, in May 2005), Muros (17), Arousa (66) both in September 1999, Pontevedra (37, in October 1998) and Vigo

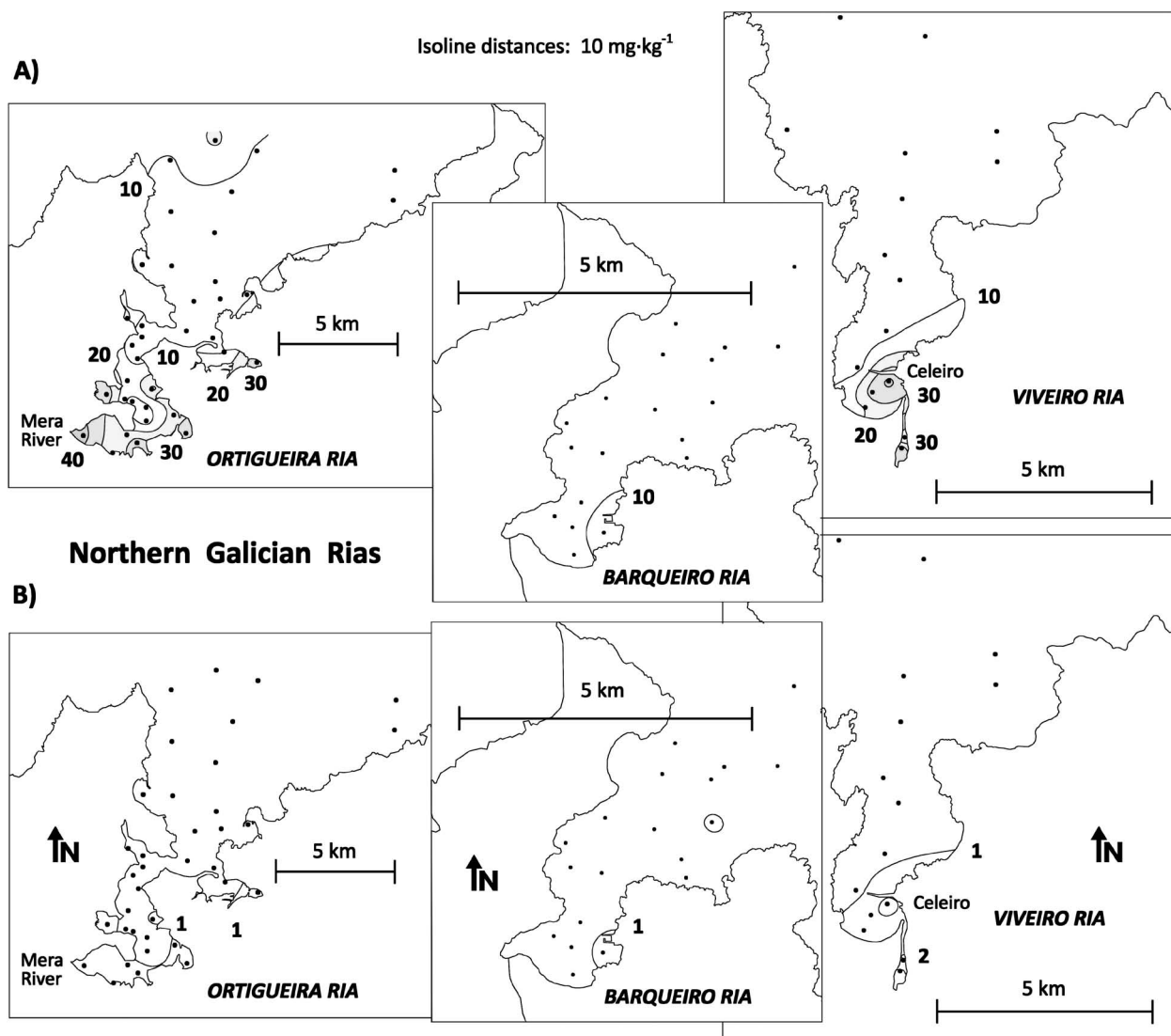


FIG. 2. – Isoline maps showing the fine fraction surface sediments of the northern Galician rias and their harbours: (a) the copper concentrations in mg kg^{-1} , and (b) the copper-iron relationship (NEF). Copper enrichment areas are highlighted with a blank background for negligible-moderate contamination ($\text{NEF} < 3$), light grey for severe contamination ($3 < \text{NEF} < 6$), grey for very severe ($6 < \text{NEF} < 9$) and dark grey for heavy contamination ($9 < \text{NEF}$).

(49, in October 1999). Samples were collected over ten years. The sedimentation rates in the middle-outer ría ranged from 0.5 mm to 3.9 mm per year (Desprat *et al.* 2003, Pena *et al.* 2010), i.e. a period of 3 to 20 years; moreover, the metal contamination pattern should not change in ría surface sediments (Prego *et al.* 2008b).

Sediments were retrieved using two Van Veen grabs (30 L and 3.5 L capacity employed from the R/V and boats respectively) on board R/V *Mytilus* (IIM-CSIC) or its auxiliary boat *Zoea*. In the northern rias and Corcubión Sound samples were collected on board R/V *Lura* (IEO) and small boats in shallow waters. The sediment surface layer (1 cm) was extracted with a polyethylene spatula, stored in 200-mL plastic flasks and placed into refrigerator at 4°C. Later in the laboratory, sediment samples were oven-dried at 50°C and sieved through a 63 μm sieve (Retsch AS-200). Sieved

sediments were stored in plastic tubes until analysis. The plastic laboratory ware that was employed for sampling, storage and sample treatment was previously acid washed and rinsed thoroughly with Milli-Q water.

In order to quantify the background metal concentrations, five cores were retrieved using a Rossfelder P-3 vibrocorer and gravity-corer from R/V *Mytilus*. They were collected in the rias of Ferrol (175 cm length and coordinates: 43°28.11'N 8°14.86'W), Muros (350 cm and 42°45.50'N 8°59.90'W), Arousa (260 cm and 42°33.72'N 8°54.16'W), and Vigo (135 cm and 42°13.37'N 8°49.37'W), and the Corcubión Sound (100 cm and 42°55.06'N 9°10.26'W). The cores were collected in PVC tubes and preserved at 4°C in a refrigerated chamber. The upper layer to a depth of 50 cm was removed in order to work with pre-industrial sediments only. Underneath this depth, cores were

sectioned and slices of 1 cm-thickness were extracted every 10 cm and processed in a similar way to the surface samples.

Around 0.1 g of each sediment sample was digested in Teflon bombs using a microwave oven (Milestone, MLS-1200 Mega), following the EPA guideline for siliceous type matrices (EPA 1996). The copper concentration was analysed by means of electrothermal atomic absorption spectrometry (ETAAS) using a Varian 220 apparatus equipped with the Zeeman background correction. Iron was determined as the normalizing element of the copper concentrations by means of flame atomic absorption spectrometry (FAAS) using a Varian 220-FS apparatus. Samples were handled and analysed in a clean laboratory (ISO 6). The accuracy of the analytical procedures employed for the analysis of both metals in the sediment samples was checked using the PACS-2 (NRC, Canada) certified reference material, and showed good agreement (311 ± 18 mgCu kg⁻¹ and 42.5 ± 2.3 gFe kg⁻¹) with the certified values (310 ± 12 mgCu kg⁻¹ and 40.9 ± 0.6 gFe kg⁻¹).

RESULTS

Concentration and distribution of copper in ria sediments

The distribution of copper in the surface sediment of the eleven studied rias is shown in Figs. 2a, 3a and

4a. The concentration of this metal ranged from 3 to 478 mg kg⁻¹ with the highest levels in the Vigo Ria and the lowest in the northern rias together with the small rias of Camariñas and Laxe, with values up to 100 mg kg⁻¹. In general, the copper values showed a decreasing trend from the contamination source towards the ocean. In the middle-outer ria areas the copper concentrations were usually lower than 30 mg kg⁻¹. However, there was a local maximum in the harbour and/or shipyard areas, e.g. in the Bay of Bouzas and Teis of the Vigo Ria, in the Marin zone of Pontevedra Ria, in the harbour zone of Coruña Ria, and Ferrol-Caranza zones as well as in the shipyard areas in the southern-middle littoral of the Ferrol Ria. Furthermore, the copper concentration was also high in sediments of the fishing ports of Celeiro, Muxía, Camariñas, Laxe and Corme, the area for repairing small fishing boats at the head of Laxe Ria, and the Cee port next to the metallic carbide factory (55 mg kg⁻¹; a figure of copper concentrations in the Sound of Corcubión was not included because its sampling was only a straight section). However, high values of copper were detected in surface sediments that are not directly related to harbour activities, e.g. those located at the semi-enclosed inlets of 'Grove' and Rianxo in the Arousa Ria, the Punta Corbeira shipyard area and intertidal zone around Noia town, the innermost zone of Ferrol Ria where there is an iron and steel recovery industry, and the mouth of Mera River in the Ortigueira Ria.

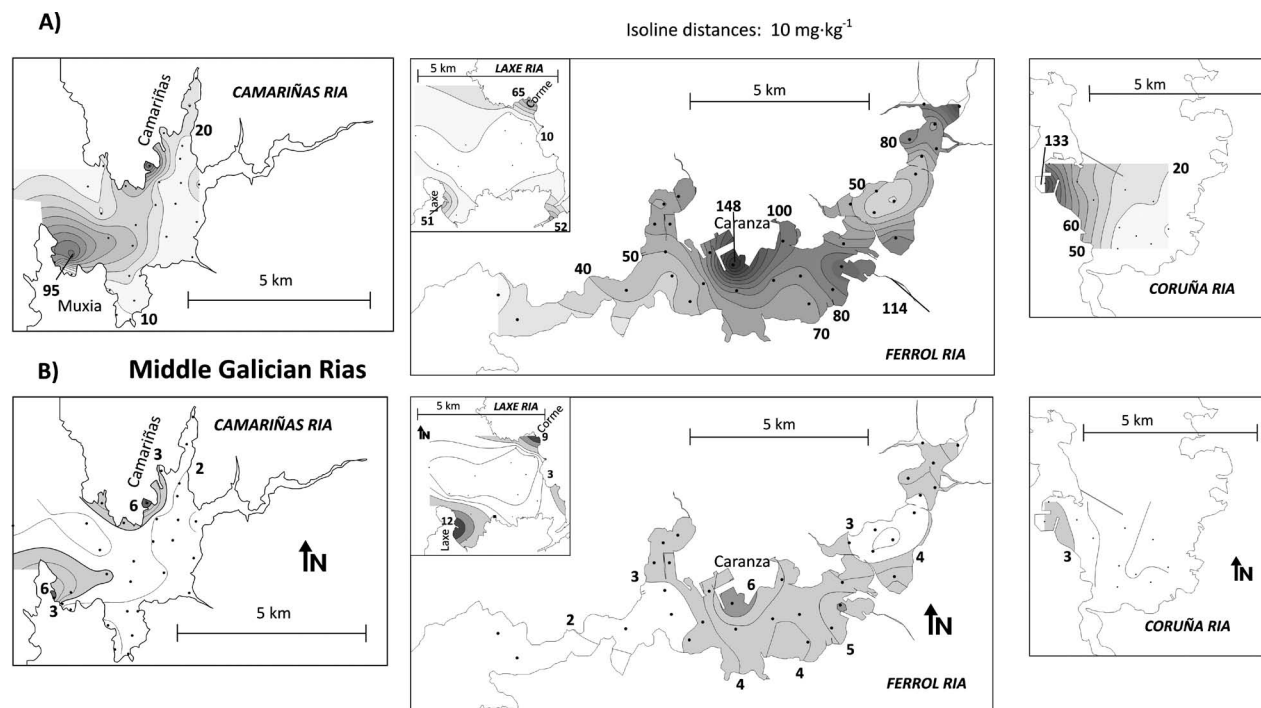


FIG. 3. – Isoline maps showing the fine fraction surface sediments of the middle Galician rias and their harbours: (a) the copper concentrations in mg kg⁻¹, and (b) the copper-iron relationship (NEF). Copper enrichment areas are highlighted with a blank background for negligible-moderate contamination ($NEF < 3$), light grey for severe contamination ($3 < NEF < 6$), grey for very severe ($6 < NEF < 9$) and dark grey for heavy contamination ($9 < NEF$).

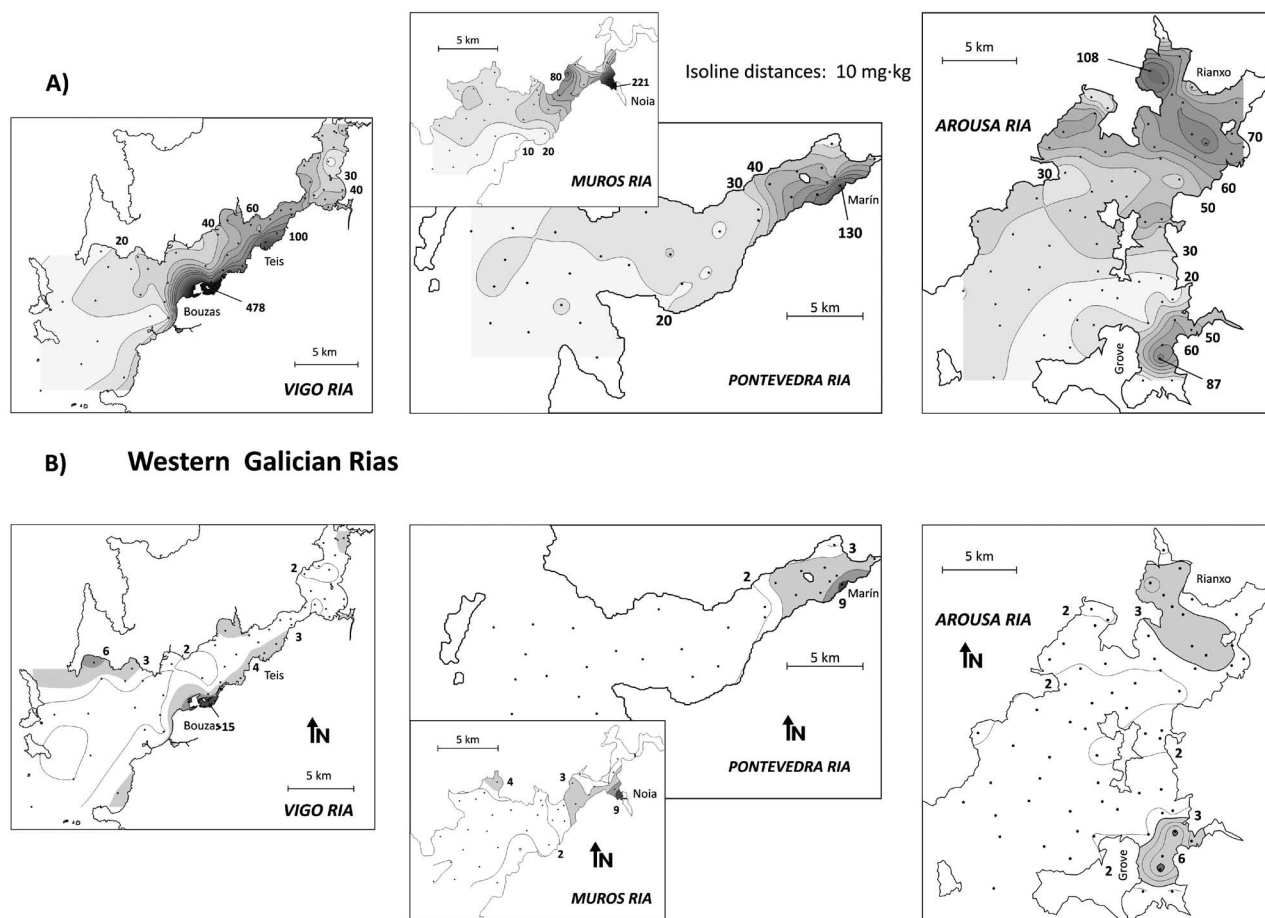


FIG. 4. – Isoline maps showing the fine fraction surface sediments of the western Galician rias and their harbours: (a) the copper concentrations in mg kg^{-1} , and (b) the copper-iron relationship (NEF). Copper enrichment areas are highlighted with a blank background for negligible-moderate contamination ($\text{NEF} < 3$), light grey for severe contamination ($3 < \text{NEF} < 6$), grey for very severe ($6 < \text{NEF} < 9$) and dark grey for heavy contamination ($9 < \text{NEF}$).

Background copper ranges in ria sediments

In order to distinguish the natural copper concentrations from anthropogenic additions in the sediments and to diagnose the contamination level, it is essential to establish a reference background concentration (BC), which is assumed to correspond to the pre-civilization metal concentrations (Prego and Cobelo-García 2003). Therefore, some conditions were followed to obtain a precise quantification of the BC for the sediments of the Galician rias:

(a) The natural presence of copper in the ria could be defined from its average level in the continental crust (Wedepohl 1991) or from its level in pristine sediments (Bryan and Langston 1992). This is not the most suitable approach because it does not take into account that the background concentration of copper in sediments varies according to the local geochemical composition. Therefore, the background concentration of copper in rias must be calculated from local data.

(b) Using a single copper concentration as the natural reference level for sediment normalization in rias is not appropriate. This was done in the rias (vg. Carbal-

leira *et al.* 2000); however, copper richness depends on the geochemical sources and a metal-copper normalization equation based on local samples is desirable.

(c) The normalization equation needs to be established with respect to a conservative element of natural origin unaffected by anthropogenic contributions. The selection of the normalizer element cannot be solved by guesswork, but rather on the basis of geochemical characteristics of the river basins flowing to the rias. In this way, Fe can be used as a normalizer metal of Cu because it is an abundant element in the Galician granitic soils (Guitián 1992), its natural concentration in sediments is high (Prego and Cobelo-García 2003), it does not vary due to anthropogenic contributions and it is easy and fast to analyse by Flame AAS. Therefore, iron has already been used as a normalizing element in coastal systems and rias (Macías-Zamora *et al.* 1999, Cobelo-García and Prego 2003a, Chon Lin *et al.* 1998).

(d) Sediment from rias shows a wide range of grain size distributions in the extensive geographical area considered. The grain size distribution varies from siliciclastic sands associated with the river mouths, to siliciclastic mud with high organic matter content

located under the mussel rafts and biogenic sands with gravel and low organic matter at the ria mouths (Vilas *et al.* 2005). Since particles smaller than 63 µm have a very strong adsorptive potential for trace metals, contaminants are predominantly distributed and pre-concentrated in this fraction (Hanson *et al.* 1993). For these reasons, it is best to carry out a second type of normalization with respect to sediment texture, and the fine fraction (<63 µm) was selected to compare ria sediments in relation to adsorption and transport capacities related to metallic traces (Förstner 1987).

(e) The metal concentrations in surface sediments of the Galician rias were considered by means of regression techniques to determine the background concentrations (Carballeira *et al.* 2000). However, the BC determined from sediment cores is a more appropriate tool than selecting potential clean-contaminated sites in the rias. This has already been applied in the Ferrol Ria (Cobelo-García and Prego 2003a), where the sediment cores were accurately dated and iron was the element chosen for normalization as the pre-industrial deep sediment reference. Similarly, it could be applied to other rias, and the upper layer (~50 cm) of cores will not be considered in the equation of copper normalization with iron.

Taking into account the above conditions, a linear relationship between copper and iron (Fig. 5) was obtained in sediment samples of five cores sampled along the Galician coast in the rias of Ferrol, Muros, Arousa and Vigo and Corcubión Sound. Consequently, the copper concentration (mg kg^{-1}) in the sediment can be defined as a function of its iron content (g kg^{-1}) expressed by the following equation:

$$[\text{Cu}]_{\text{BC}} = 0.52 [\text{Fe}] + 1.0 \quad (r=0.91; n=73) \quad (1)$$

Copper enrichment and contamination of ria sediment

The evaluation of the copper contamination levels in the rias and their harbour areas is based in the normalized enrichment factor (NEF), which was defined as the number of times that the reference concentration of natural conditions is exceeded (Tanner *et al.* 2000). Therefore, the NEF of copper is calculated by the following mathematical expression:

$$\text{NEF}_{\text{Cu}} = [\text{Cu}] / [\text{Cu}]_{\text{BC}} \quad (2)$$

where $[\text{Cu}]_{\text{BC}}$ is the value of the background concentration of copper, provided by the copper-iron normalization equation (1).

Thus, the copper contamination state of the sediment can be defined in basis of NEF value (Prego *et al.* 2008b adapted from Hakanson 1980) as follows:

negligible <1 ≤ possible <2 ≤ moderate <3 ≤
severe <6 ≤ very severe <9 ≤ heavy

Applying the above-mentioned criterion, the sediment of the rias can be considered as not or moderately

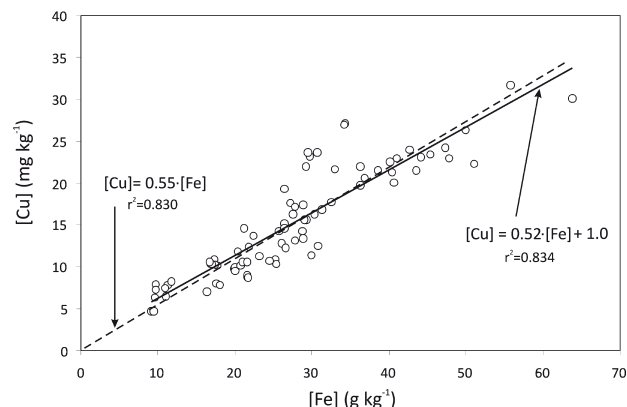


FIG. 5. – Regression line of copper versus iron concentrations in sediments from cores retrieved in the rias ($n=73$). Dashed line depicts the regression line forced to go through the coordinates' origin.

contaminated in relation to copper (Figs 2b, 3b and 4b). Nevertheless, Ferrol Ria was an exception as the NEF ranges indicated severe contamination throughout the ria, except in the areas located at its mouth. On the contrary, the northern rias are almost pristine. In the remaining Galician rias there were isolated areas where the contamination state was detected. These areas corresponded to the harbour and shipyard shores, which have severe-heavy copper contamination in sediments, and were the following:

- Vigo Ria: all its southern middle part, i.e. the harbour zone, which had severe contamination, and particularly the shipyard area of Bouzas, which had heavy contamination;
- Pontevedra Ria: the shipyard and harbour of Marín, which had very severe contamination;
- Corcubión Sound: its inner part close to the Metallic Carbides Factory, which had severe contamination;
- Camariñas Ria: the zones close to the fishing ports of Muxia and Camariñas, which had severe contamination;
- Laxe Ria: the zones close to the fishing ports of Corme and Laxe, which had very severe contamination
- Coruña Ria: its harbour, which had severe contamination.

Occasionally, several areas in the rias showed a rise in the copper levels, i.e., those located near towns with small harbours in semi-enclosed bays such as Rianxo and Grove (severely contaminated) in Arousa Ria, and the Noia Town coast (severely contaminated) in Muros Ria.

DISCUSSION

The granitic nature of the Galician soils determines the lithological characteristics of the sediment components carried out to the rias (Vilas *et al.* 2005). The copper concentration in the land soils near the shoreline and fluvial basins running into the rias is usually low, in general it does not exceed 25 mg kg^{-1} (Guitián 1992). The results obtained in ria sediments are in good

TABLE 1. – Copper concentration ranges in fine surface sediment of the main Galician Ria harbours compared to some world harbours.

Harbour (country or ria)	[Cu] (mg kg ⁻¹)	Goods traffic (10 ⁶ t yr ⁻¹)	Reference
Bouzas-Teis (Ria of Vigo)	100-478	5.1	This study
Coruña (Ria of La Coruña)	50-133	12.8	This study
Ferrol (Ria of Ferrol)	100-148	12.9	This study
Marin (Ria of Pontevedra)	40-130	1.7	This study
Vilagarcía (Ria of Arousa)	50-80	1.1	This study
Barcelona (Spain)	70-530	51	Guevara-Riba <i>et al.</i> 2004
Bergen (Norway)	25-1090	38	Paetzel <i>et al.</i> 2003
Ceuta (Spain)	5-865	1.4	Guerra-García and García-Gómez 2005
Cork (Ireland)	8-54	4.0	Kilemade <i>et al.</i> 2004
Elizabeth (South Africa)	9-82	31	Fatoki and Mathabatha 2001
Hamilton (Canada)	8-135	12.0	Poulton <i>et al.</i> 1996
Kaohsiung (Taiwan)	5-946	9.5	Chen <i>et al.</i> 2007
Kembla (Australia)	150-485	27	He and Morrison 2001
Keratsin (Greece)	195-518	–	Galanopoulou <i>et al.</i> 2009
Montevideo (Uruguay)	58-135	8.7	Muñiz <i>et al.</i> 2004
Port Reitz (Kenya)	50-229	–	Muhoi <i>et al.</i> 2003
Singapore (Singapore)	138-248	483	Orlic and Tang 1999
Sydney (Australia)	20-701	28	McCready <i>et al.</i> 2006
Tolo (Hong Kong)	6-231	295	Owen and Shandu 2000
Ventspils (Latvia)	3-29	28	Müller-Karulis <i>et al.</i> 2003

agreement with this pristine limitation due to the allochthonous continental source of copper. This source is quasi-homogeneous along the entire Galician coastal zone and fluvial basins; for this reason a significant Fe-Cu correlation was obtained using preindustrial sediments from different rias as a whole (Fig. 5). Therefore, equation (1) can be applied to all the ria sediments in order to define their contamination level. As a reference, a simple criterion is proposed according to the following relationship (concentration of copper and iron in mg kg⁻¹ and g kg⁻¹ respectively):

$$[\text{Cu}] / [\text{Fe}] = 0.55 \quad (r = 0.91; n = 73) \quad (3)$$

Now, the simple equation (3) can be used to define the copper contamination state in the Galician rias by analysing only the copper and iron concentrations in a sediment sample. Moreover, because the average copper concentrations in world soils commonly range from 20 to 30 mg kg⁻¹ (Scheinberg 1991) the advanced ratio value could be applied in other coastal systems.

The anthropogenic influence is shown in the contaminated areas highlighted by the enrichment factor (Fig. 2b, 3b and 4b). According to the NEF distribution maps the non-natural source of sedimentary copper in the rias may be associated with harbours and shipyard littorals. This metal trend distribution was observed in previous studies in the Ferrol (Cobelo-García and Prego 2003a) and Pontevedra Rias (Cobelo-García and Prego 2003b). Although there are other possible sources of copper, such as the sewage and fluvial load (Cobelo-García and Prego 2003; Santos-Echeandía *et al.* 2008), these are not as important as the diffuse sources from shipping activities: antifouling release (Valkirs *et al.* 2003; Schiff *et al.* 2004) and shipyard loading (Turner 2010).

The focus of this copper contamination is mainly localized in the industrial bays of the rias. In these zones,

the copper concentration reaches the sediment limits of marine quality (Klapow and Lewis 1979). The limit values are 34 mg kg⁻¹, considered as the ERL (effects range-low; Byrkit 1975), and 270 mg kg⁻¹ as the ERM (effects range-median), at which adverse biological effects usually occur (Long *et al.* 1995). The ria ecotoxicological status defined using the sea-urchin embryo test with sediment elutriates (Duran and Beiras 2010) has identified the Vigo and Marin harbours as polluted areas. In Galicia, copper contamination of sediments ranges from the coastal industrial areas and ports of Ferrol and Vigo, the most environmentally changed rias, to the pristine northern Galician rias, which are the most commercially isolated. Therefore, the Galician case exemplifies the type of copper contamination that is also observed in the world's harbours (Table 1), and which is especially significant in the Bergen (Paetzel *et al.* 2003), Sydney (McCready *et al.* 2006) and Kaohsiung (Chen *et al.* 2007) harbours.

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