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Factors Controlling the Incorporation of Trace Metals to Coastal Marine Sediments: Cases of Study in the Galician Rías Baixas (NW Spain)

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1. Introduction

Transitional coastal environments such as the Galician Rías in the Atlantic coast of NW Spain are densely populated areas. Their environmental problems are highlighted by the conflicting interests of different economic sectors: extensive mariculture activities are located in its waters and intertidal zone; shipbuilding, carbuilding, canning and other industries compete with tourism on their shores; and dairy farming is the main agricultural activity in its surrounding hills and hinterland (Vilas et al., 2008). As a result, the management of the coastal zone is highly complex and it is difficult to balance quality of coastal waters with economic activities. For instance, in the Ría de Vigo, the southernmost of the Rías Baixas, wastewater treatment plants were not installed until the 1990s, and in spite of regional environmental legislation (Lei 8/2001), their capacity was still insufficient in 2005 when the European Court of Justice found Spain guilty of failure to fulfill its obligations under the Article 5 of the Council Directive 79/923/EEC on the quality required for shellfish waters (Case C-26/04 ECJ). This case was closed following Spain's submission of a pollution-reducing programme specifically pertinent to shellfish waters; success of this plan will depend critically on the behaviour of the sediments on the ría bottom.

Galician Rías experience seasonal upwelling, which increases marine productivity. This promotes the deposition of high organic matter contents in the bottom sediments and contributes to the observed intense sedimentation rates of 1-6 mm yr⁻¹ (Álvarez-Iglesias et al., 2007; Rubio et al., 2001). Current levels of trace metals (Prego & Cobelo, 2003) in sediments of these Rías have caused a significant concern by local and European authorities in the last ten years, especially in relation to the application of the Water Framework Directive (WFD), aimed to ensure that all waters reach "good status" by 2015. Some of these studies (Álvarez-Iglesias et al., 2003; Belzunce-Segarra et al., 2008; Rubio et al., 2000a) showed that the highest concentration of trace metals occurs in the muddiest surficial

sediments of the rías, and that their fate and bioavailability depends on the intensity and speed of bacterial-mediated redoxomorphic post-sedimentary processes (Álvarez-Iglesias & Rubio, 2008, 2009; Rubio et al., 2010). This chapter will review the main factors that control the incorporation of metals to the sediments in these environments, with a focus on the forcing factors and their temporal evolution in the recent sedimentary record.

This study will also show the critical importance of distinguishing and quantifying the various metal forms by using sequential extractions and by the determination of magnetic properties in order to reach a full understanding of the potential and present environmental impacts of contaminated sediments. Special emphasis will be put in the role of mussel rafts on the diagenetic immobilization of heavy metals. Finally, the solubility of these metals by aerobic oxidation will be analyzed in some laboratory experiments in order to improve coastal risks prevention and management.

2. Sediments as trace metal sinks and sources

Water analyses proposed in the WFD (Directive 2000/60/CE) are the most obvious way to quantify the degree of metal contamination in an area. However, these analyses are not easy because concentrations of metals in solution are very low, contamination can occur during collection and analysis, and sampling needs to be repeated in specific time intervals (weeks, months, and seasons). Moreover, most metals transported in aquatic ecosystems quickly set on the solid material, due to their low solubility (Forstner & Wittman, 1981). Binding of metals in suspension will eventually lead to their incorporation into the sediment (Fig. 1).

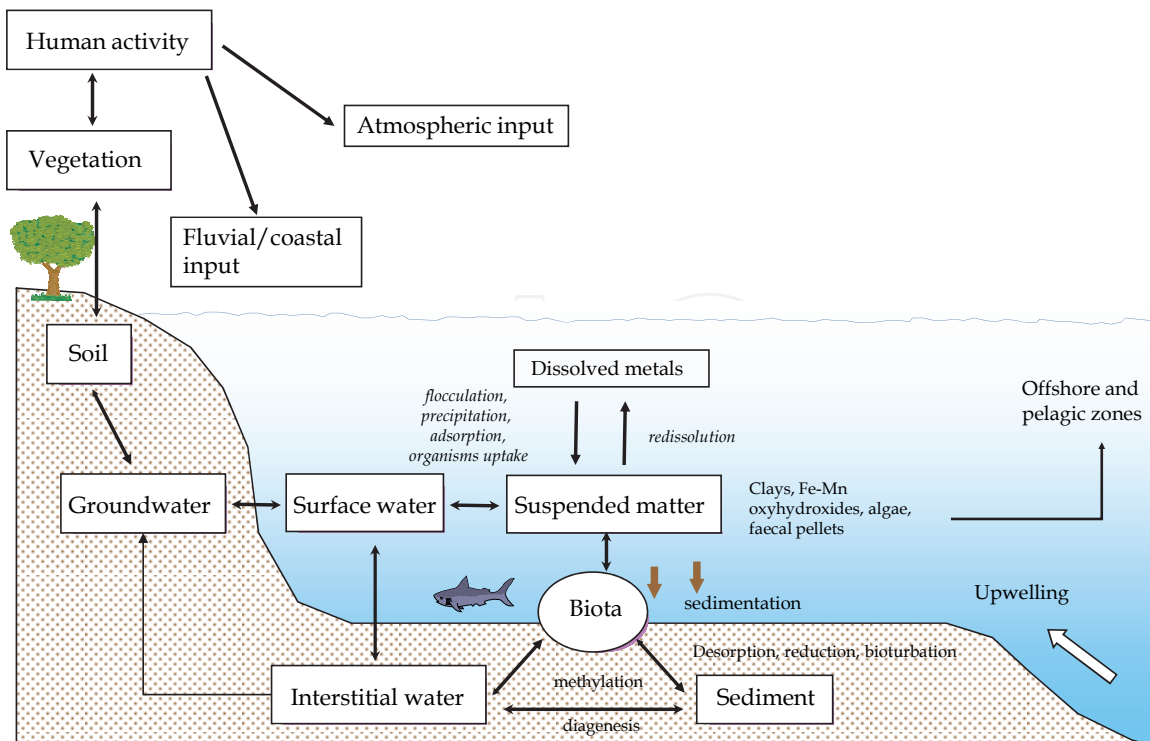


Fig. 1. Schematic representation of metals reservoirs and their interactions in coastal systems.

Therefore, sediments are a sink of metals with concentrations several orders of magnitude higher than those in the adjacent waters, both interstitial and overlying (Tessier & Campbell, 1988). Nevertheless, sediments are dynamic reservoirs subject to rapidly changing conditions. When the environmental variables change, remobilization of metals can occur. Although there are different mechanisms of metal binding to sediments, adsorbed metals appear to be more readily available, and therefore can be recycled. In these cases, the sediment acts as a source of metals to other biotic and abiotic compartments (Fig. 1).

In addition, sediments can be considered as archives of environmental information due to their "memory capacity", so that the sedimentary record allows us to reconstruct the recent historical record of coastal pollution (Álvarez-Iglesias et al., 2007; Rubio et al., 2001, 2010; Valette-Silver, 1993; among others).

3. Incorporation of metals to the sediment

Human activities have drastically altered the biogeochemical cycles and equilibria of some trace metals. These metals cannot be degraded or destroyed and become stable and persistent contaminants that tend to accumulate in sediments. Metals can be transferred from sediments to benthic organisms and then become a potential risk to human consumers by incorporation through the food web (Soto-Jiménez et al., 2011).

The main anthropogenic metals sources are industrial point sources, including present and former mining activities, foundries and smelters, shipbuilding, chemical industries, metallic industries, and diffuse sources such as combustion by-products. Dispersion of metals in the particulate phase is usually small, but relatively volatile metals and those that become attached to air-borne particles can be widely dispersed over very large scales. Trace metals carried in dissolved or particulate forms (e.g., river run-off) enter the normal coastal biogeochemical cycle and are largely retained within near-shore and shelf regions (Fig. 1).

3.1 Processes affecting the cycles of metals in coastal zones

Trace elements may suffer varying degrees of internal recycling before they are buried in the sediment and/or carried into the ocean (Fig.1). Such recycling may involve processes such as flocculation, precipitation, release from living or dead particulate phases, and subsequent regeneration when these particles undergo redissolution. Recycling of metals in suspended solids takes place by coprecipitation, adsorption, desorption and flocculation (Fig. 1). The suspended matter and deposited sediments are linked through processes of sedimentation and erosion. Diagenetic processes release high concentrations of trace metals to interstitial waters, which can influence metal concentrations in the overlying waters through diffusion, consolidation and bioturbation. This element recycling can occur within the water column or within the sediment. If the metal residence time is short an element can be recycled several times.

In addition to physical processes, recycling in the sediment can also be biologically mediated (i.e. methylation) (Fig. 1). The concentration of suspended matter may also influence these processes, especially in estuaries and rías, where suspended matter concentration is much larger than in other systems of the hydrologic cycle, such as most lakes and oceans.

3.2 The interaction between trace metals and aquaculture

In the last decades, marine aquaculture has experienced an important development around the world. Galicia is the second largest producer of mussels in the world after China. They are cultivated in wood frames called mussel rafts. Most of these are concentrated in the Rías Baixas, with more than 3,000 rafts located in Arousa, Pontevedra and Vigo rías.

An important environmental impact of these activities is the high amount of particulate matter discharged by mussels from faeces. Although the concentration of heavy metals in these particles is relatively low, the amount of solids is so high that the total accumulation of metals in the sediments may become an important problem. This fact has been mentioned in previous works (Otero et al., 2005; Prego et al., 2006), but it has not been studied in depth. Table 1 compares the accumulation of some trace metals (especially Pb, Ni, and V) in sediments collected below mussel rafts and in adjacent areas in the Ría de Pontevedra. Despite intensive marine aquaculture these results indicate that the differences are not very high, and they seem to be more related to textural differences than to aquaculture activities. However, there are very significant differences in the elements and ratios of the organic matter characterization (table 1). Sediments collected below mussel rafts areas showed higher contents of total organic carbon (TOC), total N (TN) and total S (TS) than those collected in adjacent areas (table 1). Significant differences were also observed in the mean values for the ratios C/N and S/C, showing that the increase in TOC in mussel rafts areas influences the redoxomorphic organic matter degradation. C/N ratios are, on average, higher than those reported for biodeposits by other authors (<10; Calvo de Anta, 1999; Otero et al., 2006). S/C ratios are below the global average in normal marine sediments (Raiswell & Berner, 1986), indicating a moderate stage of diagenetic evolution.

Trace elements ($\mu\text{g g}^{-1}$)	Mussel rafts areas	Adjacent areas
Sr	865 \pm 504	1888 \pm 438
Rb	210 \pm 31	169 \pm 41
Ba	403 \pm 73	341 \pm 58
Co	13 \pm 2	14 \pm 1
Cu	20 \pm 7	29 \pm 20
Zn	77 \pm 20	89 \pm 32
Ni	34 \pm 12	24 \pm 4
Pb	18 \pm 15	3 \pm 8
Cr	65 \pm 12	66 \pm 11
V	89 \pm 29	65 \pm 17
Other parameters (%)		
TOC	3.69 \pm 1.76	2.42 \pm 0.68
TN	0.24 \pm 0.13	0.13 \pm 0.77
TS	0.95 \pm 0.62	0.37 \pm 0.16
C/N	19.83 \pm 10.18	25.19 \pm 13.33
S/C	0.25 \pm 0.13	0.16 \pm 0.09

Table 1. Comparison of trace elements concentration obtained by X-ray Fluorescence (XRF) and other sediment parameters (TOC, TN, TS, C/N and S/C) for a group of sediment cores (101 samples) collected below mussel rafts and in adjacent areas (35 samples) in the Ría de Pontevedra.

4. The ría environment - Factors controlling trace metal contents in ría sediments

The Rías Baixas are a characteristic geomorphological coastal feature of the Northwest Iberian Margin consisting of four deep and narrow V-shaped Tertiary river valleys that have been flooded during the last sea-level transgression.

Most regional studies in rías have shown that although the hydrodynamic processes are similar to those identified in estuaries, the rías are clearly dominated by the waves while the estuarine circulation is restricted to the innermost areas (Piedracoba et al., 2005; Ruiz-Villarreal et al., 2002; Souto et al., 2003; Vilas et al., 2005). These environments are also characterized by a lesser continental freshwater input, and a higher primary productivity due to seasonal upwelling (Fraga, 1981) in comparison to estuarine environments.

In addition, the sediment characteristics and distribution of the Galician Rías Baixas (Vilas et al., 2005) also show significant differences from the facies models of wave- or tide-dominated estuaries (Vilas et al., 2010) as we will discuss in the following sections.

4.1 Factors and forcings controlling grain-size distributions

Wave conditions exert an important control on sediment distribution (Rey et al., 2005; Vilas et al., 2005, 2010). Organic-rich fine-grained sediments accumulate in low-energy areas along the deep central axis, and in protected areas of the inner ría sector with maximum mud percentages near 100% (Fig. 2).

Mud accumulation is also promoted by the agglutinating effect of organic matter. As a result, organic matter content is higher in muds, and increases towards the inner ría to values in excess of 10% (Vilas et al., 2005).

Sediment composition inside the rías is predominantly siliciclastic, as a result of the granitic and metamorphic rocks of their catchment areas. As an example, figure 2 shows the similarities between quartz distribution and mud contents. On the contrary, biogenic carbonates are predominant in the sand and gravel fractions. Production of these coarse calcareous bioclastic sediments is favoured by upwelling fertilization of the rías. CaCO_3 abundance is greatest at the margins of the ría and towards the outer areas (Fig. 2), where wave energy is stronger. In these areas CaCO_3 contents can reach values higher than 90%.

Many authors have recognized the sediment grain size as a factor directly related to the ability for retaining trace elements (Horowitz & Elrick, 1987). This relationship is clearly observed in the sediments of the rías by the surficial distribution of Pb (Fig. 2) and other trace elements. This is also shown by the strong positive correlations between mud percentage and trace elements concentrations (Fig. 3). This correlation is explained by a combination of physico-chemical factors, since materials with a higher capacity to retain contaminants have smaller particle sizes and therefore also have higher specific surfaces and cation exchange capacities.

In addition, the effect of grain size is enhanced by organic matter, which is a complexing agent for some pollutant metals and is concentrated in fine-grained particles (Wangersky, 1986). Note in figure 3 the typical association of Pb and Cu with organic matter and the strong relationship of Co with finer fractions. The diluent effect, expressed as a negative correlation, caused by coarser fractions and/or carbonates, is exemplified by the concentration of Zn vs the percentage of CaCO_3 or the concentration of Cu vs the percentage of sand.

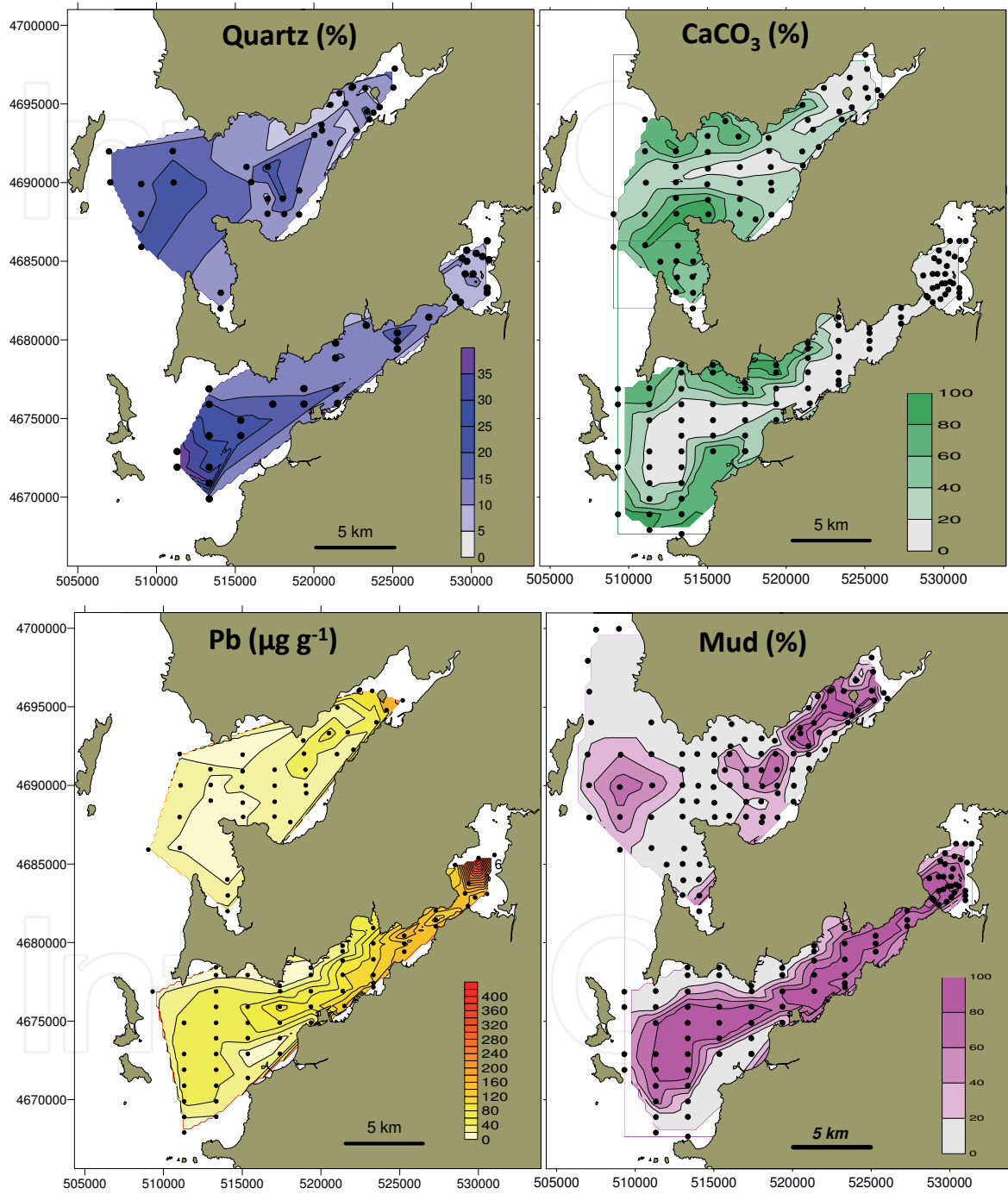


Fig. 2. Distribution maps of quartz, calcium carbonate, lead and mud concentrations in surface sediments of the Rías de Vigo and Pontevedra (NW Spain) measured on more than 100 samples (black dots).

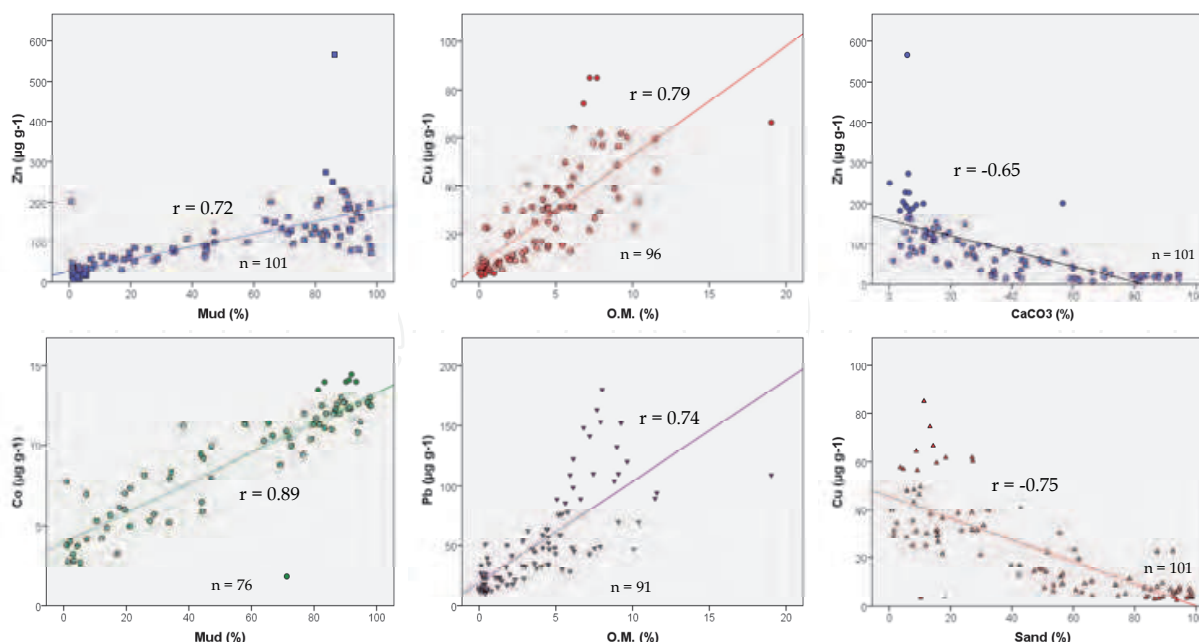


Fig. 3. Relationships between some trace elements and some properties of about one hundred of surficial sediment samples located in the Rías de Vigo and Pontevedra (data from Ría de Vigo from Rubio et al., 2000a). Sample location in figure 2 (black dots).

4.2 Grain-size effect: Proxies and normalization procedures

A very simple method used to detect whether a sediment is contaminated is to map the surface concentration of the target element and try to detect geochemical anomalies (Chester & Voutsinou, 1981) that highlight areas or regions with anomalous contents. For instance, too high values of Pb were detected in the inner part of the Ría de Vigo (San Simón Bay) (Fig. 2). In addition, the distribution patterns of conservative elements indicative of grain size should be compared to the distribution of trace metals in order to detect whether or not these metals are supplied by anthropogenic activities.

However, a first approach to determine the presence of contamination is to analyze the relationships between a normalizer element or grain-size proxy (Al, Ti, Rb, among others) and the potential contaminant element. If there is no linear relationship between them, this is usually due to contamination. For example for the relationship between Zn and mud (Fig. 3), those data points that are far from the correlation line are indicative of contamination.

5. Anthropogenic evidences on metal concentration in ría sediments

Several indexes (contamination factor, enrichment factor, geoaccumulation index, among others) have been developed to assess the degree of metal contamination in a given area. These indexes compare the metal content of the samples with natural values for each metal. The determination of these so-called background levels is a key factor in assessing the degree of contamination or the anthropogenic effect in a given area. Rubio et al. (2000a) showed how the choice of these values determines the geochemical interpretation of a given area, hence the importance of establishing background values adequately.

Also the comparison with Sediment Quality Guidelines (SQGs) that allows calculating the effects range low (ERL), effects range medium (ERM) and probable effect levels according to

Long et al. (1995) has been used by several authors (Mucha et al., 2003; Pekey et al., 2004). In the following sections we will review some examples for the sediments of the Rías Baixas.

5.1 Background levels

The background value or "background" of a given trace metal in sediments is the natural content of the metal without human intervention. This value will depend on the geochemistry of the source area sediment. Several possibilities have been set up to establish background values for trace metals (Forstner & Wittmann, 1981):

1. Mean values of metals in the crust (Taylor, 1964) or average shale values (Turekian & Wedepohl, 1961; Wedepohl, 1971, 1991).
2. Values determined by various methods, in the same study area, including:
 - a. Selection of presumably clean stations (Barreiro et al., 1988; Subramanian & Mohanachandran, 1990).
 - b. Statistical methods, among others, include: multiple regression techniques (Summers et al., 1996a), principal component analysis (Rubio et al., 2000), selection of the first percentile of the cumulative distributions of the concentration of metals (Barreiro et al., 1988), and determination of homogeneous populations based on the analysis of frequency distribution curves (Carral et al., 1995).
3. Analysis of sediment cores deep enough to contain the preindustrial record in the sediment (Angelidis & Aloupi, 1995), which is the best recommended technique for establishing background values for a particular area. For example, Rubio et al. (2000b) proposed background values for the Ría de Vigo from a core about 3 m long, with an approximate age of over 1000 years BP enough to reach preindustrial levels (Table 2).

Table 2 gives some examples of background concentrations obtained for several authors for typical trace metals found in the rías compared with global background values. In many cases background values at the global level can be inadequate for a particular area and it is necessary to obtain background values at local or regional level.

Metal	B (1)	C (2)	R(3)	R (4)	A (5)	T (6)
Al	--	--	6.48	6.48	9.82	8.0
Fe	2.69	2.95	3.51	3.51	3.53	4.72
Ti	--	--	0.34	0.34	0.36	0.46
Mn	225	273	244	244	216	850
Zn	100	133	105	105	110	95
Cu	25	22	29	20	21	45
Pb	25	73	51	25	51	20
Cr	43	34	34	55	65	90
Ni	30	32	30	30	33	68
Co	16	12	12	12		19

(1) Barreiro 1991. (2) Carral et al., 1995. (3) Rubio et al., (2000a). (4) Rubio et al. (2000b). (5) Álvarez-Iglesias et al., 2006. (6) Average shale values from Turekian & Wedepohl (1961).

Table 2. Regional background values obtained by different authors for ría sediments, and its comparison to average shale values from Turekian & Wedepohl (1961). Shaded values are similar between the different authors.

5.2 Studies on sediment cores in the rías: The need of dating with ^{137}Cs and ^{210}Pb

During the last decade, radionuclide dating of sediment cores has been used to establish sources and input rates of pollutants such as trace metals (Lee & Cundy, 2001; Ligeró et al., 2002). However they have been very rarely used in sediments for the Galician Rías (Álvarez-Iglesias et al., 2007; Rubio et al., 2001). Among the latest methods to determine these rates the depth distribution of ^{210}Pb and ^{137}Cs specific activities have proven to be valid. ^{137}Cs is a good tracer for erosion and sedimentation because there are no natural sources of this radioisotope that is produced during nuclear fission. Its presence in the environment, therefore, is due to nuclear testing or release from nuclear reactors. The distribution of this radioisotope in a sediment core would reflect variations in their inputs to the environment. Average sedimentation rates are obtained by identifying their maximum inputs in the activity profiles if mixing or radionuclide diffusion has not occurred. ^{210}Pb can be used for dating sediments because it is a natural daughter radionuclide in the decay series of ^{238}U . The decay of ^{226}Ra (half-life 1600 years) in soils and sediments produces the rare gas ^{222}Rn (half-life of 3.8 days) which partially diffuses into the atmosphere or into the water column where it decays to ^{210}Pb (half-life of approximately 22 years). ^{210}Pb becomes absorbed onto particles and finally deposits in the bottom sediments (Allen et al., 1993). The ^{210}Pb method is very useful for dating events that have occurred over the last 100-150 years. It has been successfully applied in the sediments of the Ría de Vigo by Álvarez-Iglesias et al. (2007) to obtain sedimentation rates of about 5 mm yr^{-1} in intertidal sediments, whereas Rubio et al. (2001) determined values between 1 and 3 mm yr^{-1} for sediments in inner areas of the Ría de Pontevedra. The analysis of dated sediment cores is tremendously useful because it provides a historical record of natural background levels while it also records the anthropogenic accumulation of metals over the last century.

5.3 The assessment of metal pollution

In order to assess metal pollution in sediment cores it is essential to account for grain-size effects first. The two basic procedures for this purpose are to make analytical determinations on a separate grain-size fraction (Ackerman et al., 1983), or use a normalizing factor to correct the results so that regardless of the sediment size distribution, the analytical results can be compared.

Some authors disagree with the grain-size separation because they think that some metals are associated with the coarser fractions, either as aggregates or pellets composed of fine-grained particles and organic matter, or as grain coatings, that may contain high concentrations of metals. For instance, Rubio et al. (1999) have confirmed the occurrence of pellets and coatings enriched in metals in the sediments of the Rías Baixas. On the contrary, other authors (Araujo et al., 1988; Salomons & Forstner 1984) recommend the use of the fraction smaller than $63 \mu\text{m}$ in order to minimize grain-size biases on the results of heavy metal content. However, Rubio et al. (1996) concluded that the analysis of this fraction could not compensate for the grain size effect in sediments of the Ría de Pontevedra. For this reason it is always recommended to normalize the metal content to a conservative element such as Al or Rb. In the case of the Galician Rías, the best results for sediments have been obtained with aluminium (Nombela et al. 1994; Marcet Miramontes et al., 1997, Rubio et al., 2000a, 2001). An example for a sediment core from San Simón Bay (inner Ría de Vigo) is shown in figure 4. The similarity of the profiles of the absolute metal concentrations and the Al-normalized results confirm that the increase of Cu, Pb and Zn concentration towards the

top of the core is not due to textural effects but anthropogenic inputs. Therefore, the effectiveness of standardization is itself a way to detect metal contamination.

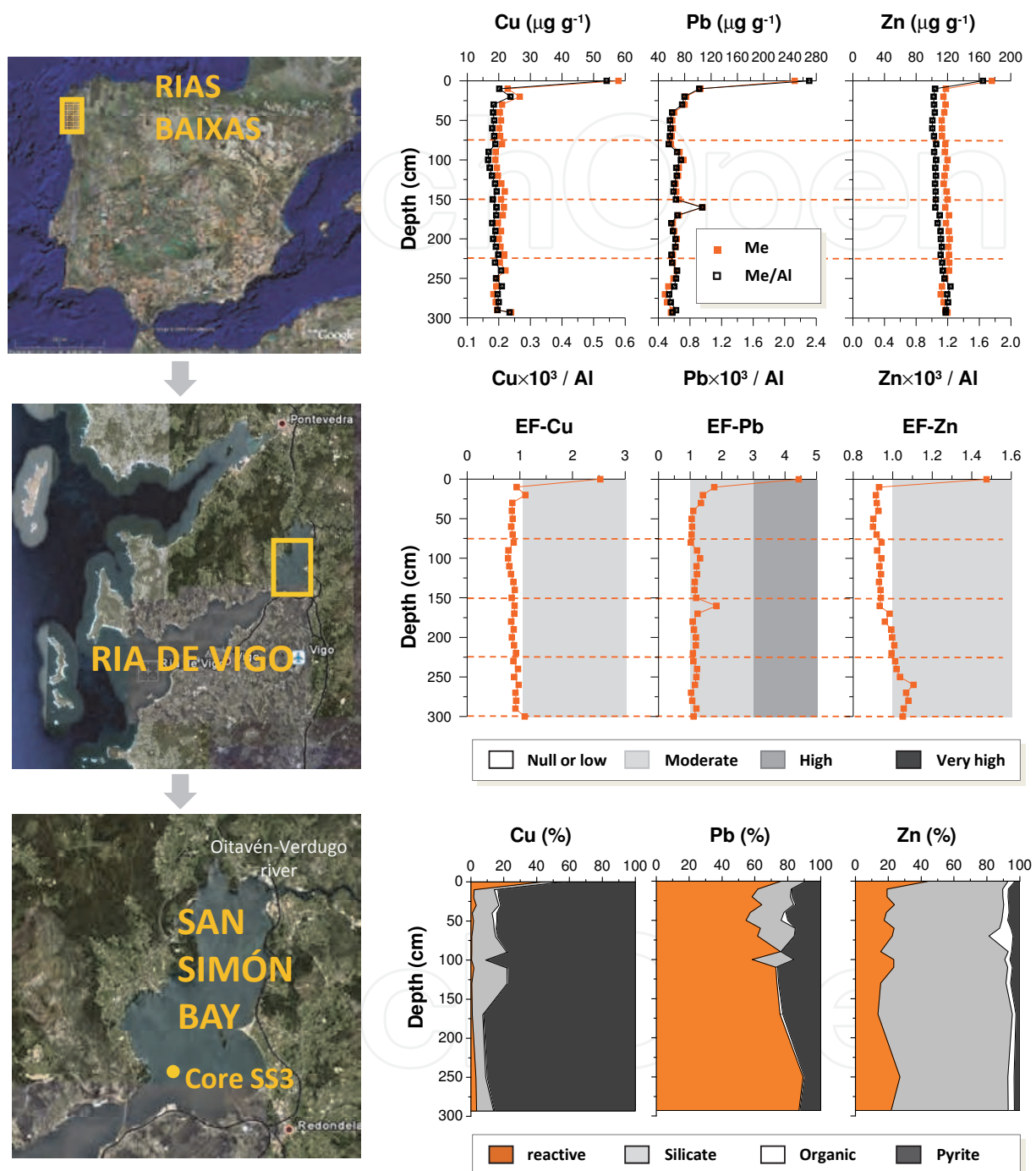


Fig. 4. Left: Location of the core SS3 in the inner area of Ría de Vigo (San Simón Bay). Right: Top, concentrations of Cu, Pb and Zn (orange; data from Álvarez-Iglesias et al., 2006) in a core from San Simón Bay and corresponding metal/Al ratios (black). Middle, enrichment factors (EF) for the same elements and classification of the level of contamination. Bottom, depth distribution of reactive, organic, silicate and pyrite fractions of Cu, Pb and Zn obtained from sequential extractions according to the procedure of Huerta-Díaz & Morse (1990).

Normalized enrichment factors (EF) (Zoller et al., 1974) are also a useful tool where $EF = (M/Al)_{\text{sample}} / (M/Al)_{\text{background}}$. EFs for Zn, Pb and Cu in core SS3 are shown in figure 4. These results show high contamination for Pb, and moderate for Cu and Zn in the upper part of the core, whereas for the core bottom contamination is moderate for Pb and absent, for Cu and Zn.

5.4 The need to carry out sequential extractions

The total amount of metals in the sediment is unrepresentative of the potential toxicity of the metal. To assess the toxicity appropriately it is essential to know the chemical forms in which a metal is presented, i.e. speciation. The chemical form (as dissolved, adsorbed, bound or precipitated) of an element will not only regulate its degree of toxicity but also its availability.

Total concentrations are still used very frequently in studies of contamination due to its easy measurement and reproducibility, in spite of the fact that the type of contaminant and the form in which it appears (soluble, exchangeable, bound, adsorbed, occluded, etc.) will decisively influence the pollution effect. For this reason, sequential extractions are usually performed and several operationally defined fractions obtained, which depend on the ability of the chemical extractant to remove certain components. These extractions allow us to determine the chemical forms in which each element is found in the sediment. However, very few studies on trace metals in the Galician Rías have considered the forms adopted by different metals. One example of a sequential extraction following the method of Huerta-Díaz & Morse (1990) is shown in figure 4 for inner Ría de Vigo sediments (core SS3). Here we distinguish operationally defined reactive, organic, pyrite and silicate-bound fractions for several trace elements. Pb appeared mostly in the reactive fraction (average, 68.5%), Cu in the pyrite fraction (81.0% on average) and Zn in the silicate-bound fraction (68.7% on average), being the organic fraction very low in all cases (usually lower than 4%). In terms of toxicity these results show that the most problematic trace elements are Pb, because it is found in more bioavailable forms, and Cu, because it is found in oxidizable forms. Zn toxicity will mostly come from its reactive fraction. These detailed interpretations confirm the interest of the determination of chemical forms when contamination is suspected in a target area.

5.5 The magnetic properties as a proxy for trace metals in sediments

The measurement of trace elements in sediments is very laborious and expensive and, therefore, the use of fast and economic alternative techniques is desirable. Environmental magnetism –the use of magnetic properties for environmental applications– can be used to estimate contamination levels and assess possible patterns of dispersion of contaminants. Some authors have shown that certain magnetic properties such as magnetic susceptibility (χ) or the isothermal remanent magnetization (IRM) show significant positive correlations with the concentrations of trace metals in the fine-grained fraction of sediments (Chan et al., 1998, 2001; Scoullou & Oldfield, 1984; Spassov et al., 2004), whereas other researchers (Petrovsky et al., 1998) have reported the contrary. In some studies both behaviours are observed depending on the element considered (Berry & Plater 1998; Georgeaud et al., 1997). A positive association is explained by these authors in terms of the preferential absorption of the metals by the clay fraction and Fe oxides, whereas a negative correlation is sometimes explained in terms of diversity of sources of contamination or due to diagenetical processes.

Some studies in the Rías Baixas pointed out that the distribution of magnetic susceptibility in surficial sediments could be explained mostly by the textural and hydrodynamic interplay (Rey et al., 2000, 2005; Mohamed et al., 2011). The increase in diamagnetic carbonate content toward the ría margins, where coarse-grained material accumulates, results in generally low susceptibility values. The highest susceptibilities lie along the central axis, where the clay content is high and carbonate bioclasts are scarce; and also toward the outer sector of the ría, where oxygenation is more intense and formation of authigenic Fe oxides and oxyhydroxides is favoured. The analysis of the susceptibility of the mud fraction (χ_{mud}) that was correlated with trace metals and other properties of the sediments (Fig. 5) revealed a strong negative correlation of susceptibility with Pb. The organic matter content is also correlated with the distribution of elements like Pb, as it is shown in figure 3. Magnetic susceptibility gradually decreases toward the inner part of the central axis because the organic matter decomposition causes reducing conditions and the establishment of an anoxic/sulphidic environment where the magnetic oxides and oxyhydroxides that carry out the susceptibility signal in the outer part of the ría are dissolved. Therefore, low magnetic susceptibility values in sediments of the rías can be a good indicator of reducing conditions, related to organic-rich fine-grained sediments in low-energy environments where trace metals tend to accumulate.

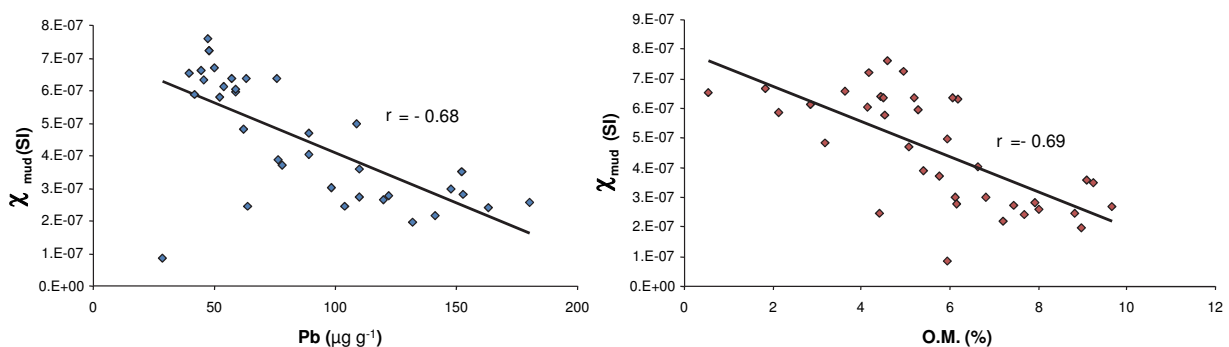


Fig. 5. Relationships between magnetic susceptibility of the mud fraction (χ_{mud}) vs Pb concentration and vs organic matter (O.M.) in surficial sediments from the Rías de Pontevedra and Vigo (modified from López-Rodríguez et al., 1999).

6. Early diagenesis of metals in ría sediments

The early diagenetic reactions that control the formation of authigenic minerals are driven by the oxidation of organic matter, initially by aerobic respiration and subsequently by a series of reactions controlled by anaerobic bacteria, such as reduction of Fe and Mn oxides, reduction of nitrates and sulfates and methanogenesis (Canfield et al., 1993). These reactions release products (e.g., HCO_3^- , HS^- , Fe^{+2} , Mn^{+2}) to the sediment pore waters, which will precipitate forming new minerals when the saturation is reached (Gaillard et al., 1989). These processes occur ideally sequentially starting with oxic, suboxic, sulfidic and finally methanogenic reactions (Berner, 1981). This diagenetic sequence of events can be evaluated from the analysis of pore-waters and the mineral concentration of typical diagenetic mineral phases in sediment cores, or by using sequential extractions in the sediments.

6.1 Diagenetic zonation in ría environments: The hydrodynamic role

Previous studies in the Rías Baixas allowed the definition of a diagenetic zonation model in these environments by using a combination of geochemical sequential extractions and magnetic properties (Mohamed et al., 2011; Rey et al., 2005; Rubio et al., 2001, 2010). In particular, speciation data of redox sensitive elements such as Fe and Mn are indicative of the different reducing conditions in sediments. Magnetic properties are useful to identify the magnetic minerals and their concentration, which can be used as proxies for the different diagenetic environments. Figure 6 shows the deepening of the redox boundaries from inner to outer ría. The oxic zone expands as it gets deeper toward the outer ría, in a similar way as the suboxic, anoxic and methanogenic zones. The observed redoxcline deepening can also be related to the different depths at which shallow gas fields have been described in the Ría de Vigo sediments (García-Gil et al., 2002; Kitidis et al., 2006; Iglesias and García-Gil, 2007).

This spatial trend can be explained by several factors: 1) A progressive change in the hydrodynamic conditions along the ría, 2) The different origin (marine or terrestrial) of the organic matter and their aging in the water column.

Regarding hydrodynamics the outermost ría areas are affected by severe storms in winter that remobilize and oxygenate the top sediments due to wave action. This process buffers sulphate reduction and contributes to the formation of authigenic iron oxides by precipitation of dissolved iron diffusing from underlying anoxic layers (Rubio et al., 2001). This process also seems to contribute to the gradual depletion of organic matter in fine-grained sediments observed toward the outer areas of the ría mouth.

As for the organic matter characteristics, the decrease in terrestrial sedimentary organic matter toward the outer-ría (Álvarez-Iglesias 2006; Andrade et al. 2011), in addition to the longer aging of organic matter in deeper waters of the outer-ría areas compared to the inner-ría, could contribute to explain the mentioned diagenetic zonation.

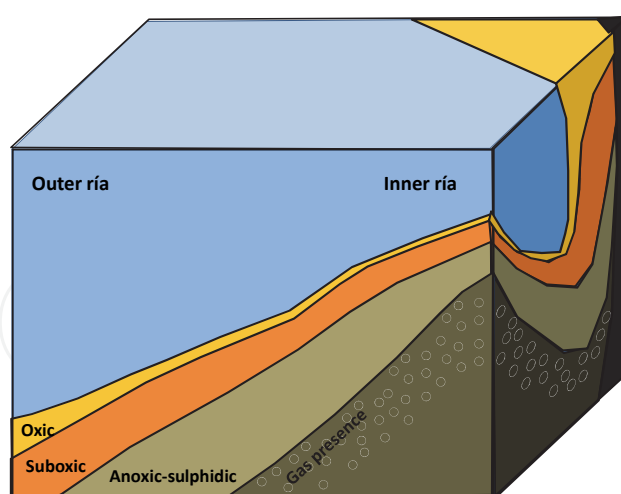


Fig. 6. Block diagram illustrating the variation in depth of the diagenetic zones in the different sectors of the ría.

6.2 Diagenetic mobilization of trace metals: Influence of mussel rafts

In the last fifty years mussel culture in the Rías Baixas has caused significant changes in the sediment due to the large amounts of detritus originated by these filter feeders, which are deposited mostly as pellets enriched in organic matter on the ría bottoms. Each mussel raft

produces approximately 190 kg day⁻¹ of dry biodeposit that contains between 31 and 32 kg day⁻¹ of organic matter (Cabanas et al., 1979). In addition, sedimentation rate is increased significantly in areas below mussel rafts, with values that range between 5 and 15 mm yr⁻¹ (Tenore & González, 1975; Cabanas et al., 1979). This elevated sediment accumulation together with its high concentration of organic matter has led to a change in the physico-chemical properties of sediments towards more anoxic environments (Cabanas et al., 1982; León et al., 2004).

In these sediments, anoxic degradation of organic matter is responsible for the early diagenesis of sedimentary Fe sulfides that eventually are transformed into pyrite (FeS₂), which is thermodynamically the more stable compound (Luther, 1991; Morse & Luther, 1999).

The study of diagenesis and organic matter degradation can provide very important information about retention and/or mobility of contaminants such as trace metals. Some authors considered that formation of insoluble sulfides under reducing conditions would immobilize and trap trace metals such as Cu, Zn and Pb. On the contrary, other studies (Álvarez-Iglesias & Rubio, 2008, 2009; Rae & Allen, 1993; Rubio et al., 2010; Varekamp, 1991) indicated that these elements can be mobilized or relocated during the degradation of organic matter. It is also important to distinguish between the fraction of the elements incorporated in detrital phases and the fraction which may be available in response to changes in redox conditions, such as variations in the chemical conditions of the bottom water or interstitial water. The two main approaches to make this separation are: 1) The use of statistical techniques of separation of these phases (Calvert, 1976; Dymond, 1981). 2) The application of chemical treatments to remove certain phases or fractions of elements (Huerta-Díaz & Morse, 1990; Tessier et al., 1979; Ure et al., 1993, among others). As we have seen in section 5.4 the latter approach, sequential extractions, are a key tool to assessing the bioavailability of a particular metal.

The availability of trace metals in the sediment depends on the fractions to which they are associated to (carbonates, organic matter, sulfides, silicates, oxyhydroxides of Fe and Mn). When conditions are favorable for the formation of pyrite, metals can co-precipitate with it, and pyrite becomes an important metal sink. If environmental conditions change (i.e. oxidation of sediments) metals can be released and pyrite becomes a source.

6.3 Degree of pyritization (DOP) and degree of trace metal pyritization (DTMP) as proxies for predicting mobilization of metals

Two parameters (DOP and DTMP) can be used as proxies for predicting mobilization of metals. The DOP has been used to classify sedimentary marine environments because it is a useful paleoenvironmental geochemical index that has been correlated and corroborated with paleoecological data (Raiswell et al., 1988). The DOP is calculated from the reactive fractions (extracted with HCl) and pyrite (Berner, 1970) as $DOP = [Fe_{pyr} / (Fe_{react} + Fe_{pyr})] * 100$. Similarly we can determine DTMP according to Huerta-Díaz & Morse (1990) as $DTMP = [M_{pyr} / (M_{react} + M_{pyr})] * 100$, where M is the metal of interest.

In order to homogenize the differences in nomenclatures, León et al. (2004) proposed a new classification that combines the Berner's (1981) pioneering geochemical classification of sedimentary environments and the above mentioned work of Raiswell et al. (1988) based on the DOP. This new classification establishes that the sedimentary environments are oxic when DOP is <42%, dioxic or suboxic (42% - 55%), anoxic (55% - 75%), and euxinic (DOP >75%).

Based on this classification we compared the DOP for sediment cores in inner and middle sectors of the Ría de Pontevedra (Fig. 7). The cores of the middle sector, on average, have lower DOP values and fall into the oxic category, whilst the redox status of the cores of the inner sector, vary from suboxic to anoxic. The presence of anoxic areas in the rías is an unusual situation in an ecosystem where the dissolved oxygen in the water column is not completely exhausted, in spite of the high biological productivity in these areas resulting from the upwelling process (Figueiras et al., 1986). However, due to the high sedimentation rate of organic-rich material, especially under mussel rafts, anoxic environments can be developed at the sediment-water interface. Regarding the DTMP (Fig. 7), and its differences between mussel rafts areas and adjacent sediments the highest values correspond to Hg in both cases. The sources of Hg in the Ría de Pontevedra are paper pulp and electrochemical companies (ELNOSA-ENCE complex), in operation since the 1950's. This is a typical example of point-source contamination, where total Hg concentrations in sediments above $2 \mu\text{g g}^{-1}$ (Fig. 8) are detected close to the discharge area of this industrial complex. However, Hg was mainly associated with pyrite phases (Hg_{pyr}), while reactive Hg (Hg_{react}) is only detected in the upper 25 cm of the core and in much lower concentrations than Hg_{pyr} .

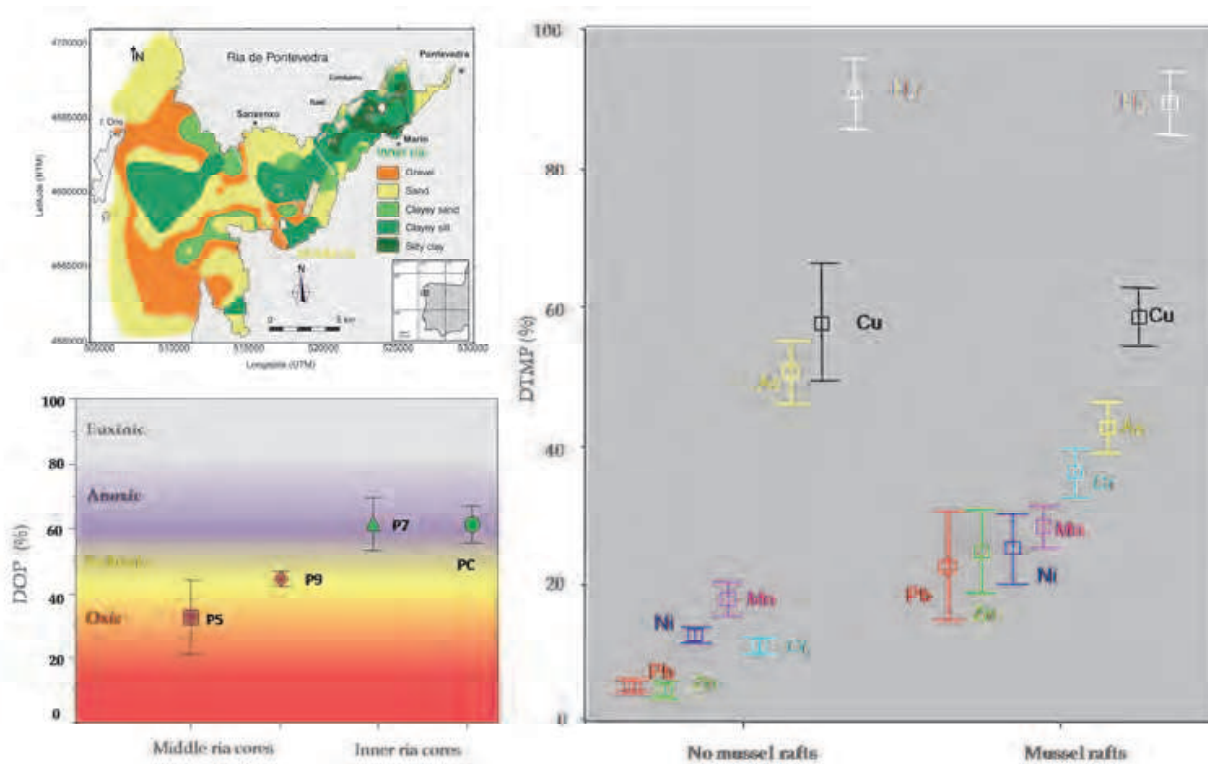


Fig. 7. a) Sediment distribution map of the Ría de Pontevedra (modified from Vilas et al., 1995) and core location. b) Sedimentary environments of the Ría de Pontevedra based on the degree of pyritization (DOP, % mean values) for these cores. The limits for oxic, suboxic, anoxic and euxinic are from León et al. (2004). c) Mean DTMP (%) values for cores both influenced by mussel rafts and from adjacent areas with no mussel rafts.

The Hg_{react} is weakly adsorbed to the components of the sediment matrix and can be released, relatively easily, into the water column due to changes in environmental conditions such as sediment resuspension. In addition, pyrite can be oxidized and release the Hg bound to its structure, constituting a serious threat to aquatic fauna, especially fish

and filter feeders. In general terms, the action of water currents, bioturbation, or human activities can provoke remobilization of trace metals associated with organic matter or reduced forms (Otero et al., 2000, 2005; Rubio et al., 2008) that may eventually contaminate the interstitial and suprajacent waters. For a more precise assessment of the water pollution risks that such events can produce, aerobic oxidation experiments such as the one shown in the next section are needed.

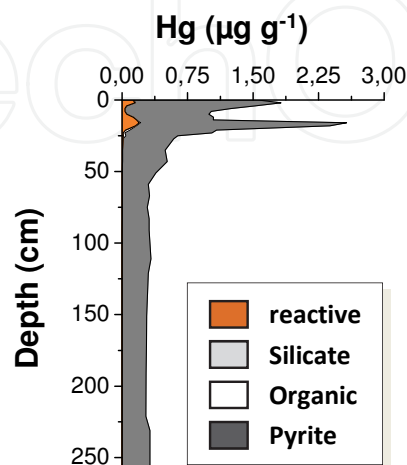


Fig. 8. Depth-distribution of Hg concentrations in reactive, silicate, organic and pyrite fractions according to Huerta-Díaz & Morse (1990) in a core from the Ría de Pontevedra (core PC). Core location in figure 7.

6.4 Solubility of heavy metals during controlled aerobic oxidation of anoxic sediments: Some laboratory experiments

As we have seen in previous sections the concentration levels of certain metal and metalloids in the sediments of the Galician Rías Baixas have shown an increasing trend in the last decades. It is likely that a transfer of these elements to the water column may occur during remobilization of sediments caused by natural events or anthropogenic activities. The inner areas of the rías are exposed to activities that remobilize the sediment such as intense maritime traffic or dredging and cleaning operations. Selected samples of surficial sediments from inner and middle ría sediments of Ría de Pontevedra were subjected to an aerobic oxidation procedure to determine the concentration of some elements (Fe, Mn, Cu, Cr, Pb and Hg) released from the sediment to the aqueous phase. The experiment was done over five days and measurements of pH and total metal concentrations were made both in water and in sediment samples. Metal concentrations were lower in the sediments during aerobic oxidation due to their release to the aqueous phase.

The net release of metals was higher in sediments from the inner sector than those from the middle sector of the Ría de Pontevedra (Fig. 9), with the exception of Cu. The high standard deviation of Fe and Mn in the inner sector samples is mainly due to the high redox sensitivity of these two metals and their high abundance as sulphides, as we have mentioned concerning the DOP values, which are rapidly oxidized causing the release of these metals to the aqueous phase. The concentrations of these metals together with those of Cu, Cr and Zn increased significantly in the aqueous phase after the experiment. This demonstrates that remobilization of marine sediments tends to increase the mobility and availability of those trace metals.

Metal concentrations in the aqueous phase varied between elements (Fig. 9). Hg and Pb concentrations were below the detection limits in all cases. Cr and Zn concentrations were in general quite low and remained almost constant over time. In contrast, Fe and Mn were released very rapidly although their concentrations decreased sharply to reach undetectable limits, because they precipitated as oxides and oxyhydroxides. Finally, the release of Cu increased with time for most of the samples, with a maximum concentration of total dissolved Cu of 8.9 mg L⁻¹. This concentration is higher than the toxicity threshold for organisms of the Galician Rías reported by other authors (Beiras & Albentosa, 2004).

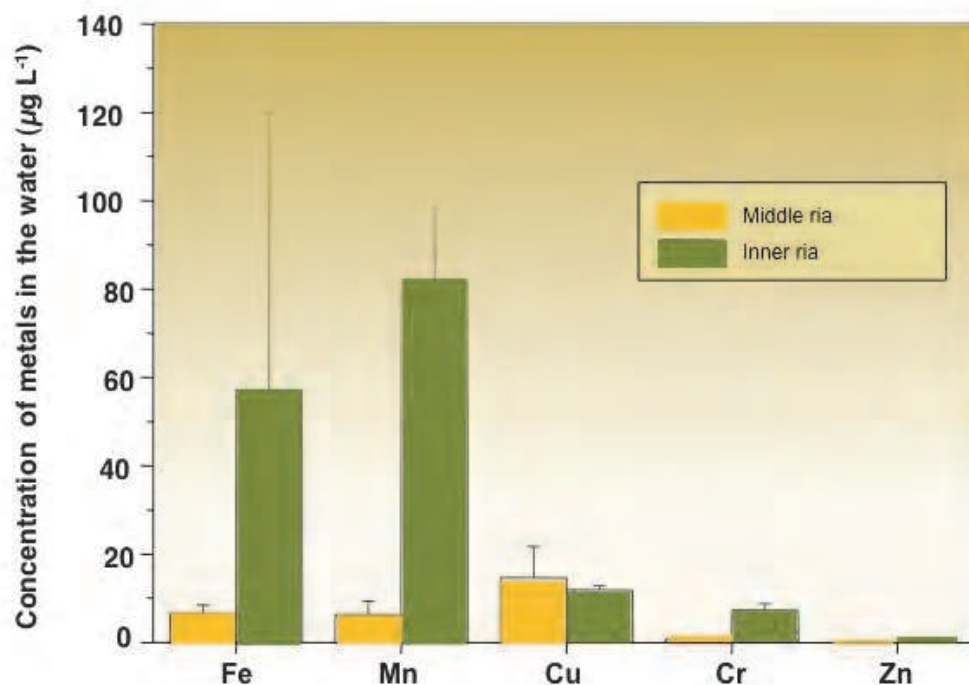


Fig. 9. Mean concentrations of trace metals in water after oxidation of sediments from inner and middle areas of Ría de Pontevedra. Sampling location in figure 7.

7. Conclusion

The main factors controlling the incorporation of metals to the sediments in transitional coastal environments like the Galician Rías Baixas in the NW Spain have been revised in this chapter. It is essential to understand the behaviour of trace metals in the sediments from the ría bottoms in order to improve coastal risks prevention and management, as well as to reach a good status in water quality as one of the great challenges for the European Union in the new millennium.

In the rías, wave conditions exert an important control on sediment distribution and in the subsequent diagenetic evolution of the sediments, and thus on trace metal accumulation and immobilization. A strong positive correlation is found between fine-grained sediments and trace metals. Organic matter enhances the grain-size effect on metal concentration, especially in areas influenced by mussel culture. The procedures for normalizing and minimizing grain-size effects have also been revised in order to distinguish natural from anthropogenic metal signals in the sediments.

Inner ría sediments are highly contaminated by Pb, and moderately by Cu and Zn, especially in the most recent sedimentary record. Some examples of point-source Hg contamination have also been shown for the Ría de Pontevedra. The importance of distinguishing and quantifying the various metal forms by using sequential extractions have also been demonstrated with several examples for sediment cores, highlighting the role of the diagenetic processes in the immobilization and/or relocation of trace metals. A characteristic diagenetic zonation in ría environments is attributed to the local water depth, the distribution of wave energy and the subsequent sediment grain-size distribution. The diagenetic processes have also been emphasized by the results of the magnetic properties, showing that low magnetic susceptibility values in sediments of the rías can be a good indicator of reducing conditions. In such conditions, trace metals are mostly concentrated in sulfide fractions. The degrees of pyritization of iron and trace elements can be valid indicators of the redox status and heavy metal risk, respectively. Experimental aerobic oxidation results have shown that the sediments of inner sectors of the rías show a higher release of metals to the aqueous phase than those of the middle sector. However, from an environmental point of view, Cu is the only metal released in quantities that may be toxic for the organisms in the area.

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