We are IntechOpen,
the world's leading publisher of
Open Access books
Built by scientists, for scientists

6,900
Open access books available

185,000
International authors and editors

200M
Downloads

154
Countries delivered to

Our authors are among the

TOP 1%
most cited scientists

12.2%
Contributors from top 500 universities

CLARIVATE ANALYTICS
BOOK CITATION INDEX
INDEXED

WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Trace Metals in Shallow Marine Sediments from the Ría de Vigo: Sources, Pollution, Speciation and Early Diagenesis

Paula Álvarez-Iglesias and Belén Rubio
Universidad de Vigo, Vigo (Pontevedra)
Spain

1. Introduction

The maintenance of the environmental quality of coastal environments requires a good knowledge on them, identifying their potential problems and considering the different anthropogenic activities that take place in these settings. A great proportion of the suspended material that arrives to these environments is incorporated to the bottom sediments. Sedimentation is favoured due to the abrupt changes that are produced in the physico-chemical parameters (pH, Eh, salinity, etc.) by the confluence of continental and marine waters. Their sediments constitute environmental archives, recording trace element inputs to the marine environment. Metal concentrations in these sediments usually surpass in several orders of magnitude those existing in the adjacent water column and in the interstitial waters (Tessier & Campbell, 1988). Their analysis allows covering different objectives, such as studying the spatial and temporal history of pollution of a particular place (Zwolsman et al., 1993), detecting pollutant sources (Dassenakis et al., 1996) and evaluating their potential effects to the organisms (Fichet et al., 1998). Sediments can act as a secondary source of pollution by resuspension or dissolution (early diagenesis) processes. Their study needs a multidisciplinary approach, taking into account the different physico-chemical processes operating in the study area and considering the relationships between metal concentration, mineralogy, grain-size and metal sources. All these variables are reviewed in this chapter, showing examples of sediments from a shallow transitional environment: the Ría de Vigo (NW Spain).

The Ría de Vigo is the sourthernmost ría of the Galician Rías Baixas (Fig. 1) with approximately 30 km in length. At its mouth the Cíes Islands are located, which act as a barrier against storms. It can be differentiated the outer and middle ría sectors from the inner sector of the ría (the Bay of San Simón). The central axis of the former runs NE-SW, while the axis of the inner sector is NNE-SSW oriented. This last sector, separated from the rest of the Ría by the Rande Strait (depth > 30 m), is very shallow (average depth of 7 m, in front of ~20 m in the remaining ría). It is a low energy area, where hydrodynamic conditions are ruled by tides, whereas water circulation in the middle and outer ría sectors is conditioned by waves and littoral drift and exhibits a two-layered positive residual circulation pattern (Álvarez-Salgado et al., 2000). Rivers are relatively small and mostly

discharge in the southern margin and in the inner sector (Pérez-Arlucea et al., 2005). They
run on a watershed mainly composed by granites, schist and gneiss (IGME, 1981). Surface
sediment distribution is conditioned by hydrodynamic conditions: coarse-grained particles
of fluvial origin concentrate close to the river inputs, whilst fine-grained particles are located
in the central axis and in the inner sector of the ría, and biogenic sands are located at the
northern margin of the outer ría (Vilas et al., 2005). The area is subjected to seasonal
processes of upwelling/downwelling (Álvarez-Salgado et al., 2000). Upwelling events
contribute to the ecological richness of the ría, where marine organisms (fish, shellfish) are
exploited, some of them in rafts (floating platforms) (Freire & García-Allut, 2000). This high
productivity explains the high organic matter contents observed in the ría sediments (Rubio
et al., 2000a; Vilas et al., 2005), which are maxima toward the inner ría (up to 15%; Álvarez-
Iglesias et al., 2003, 2006, 2007) and are positively correlated with the fine-grained particles
content. Carbonate content is inversely correlated with these variables. Its percentage is
negligible in inner ría sediments (Álvarez-Iglesias et al., 2003) and maximum towards the ría
mouth (Rubio et al., 2000a). The main industrial activities in the ría are shipbuilding,
automobile manufacture, ceramic manufacture and canned food (González-Pérez & Pérez-
González, 2003). The Vigo harbour, which concentrates many of the industrial activities, is
located in the middle ría sector, and the wastewater plant of the city of Vigo (the biggest
settlement in the ría), is located in the middle-outer ría sector, close to the mouth of the
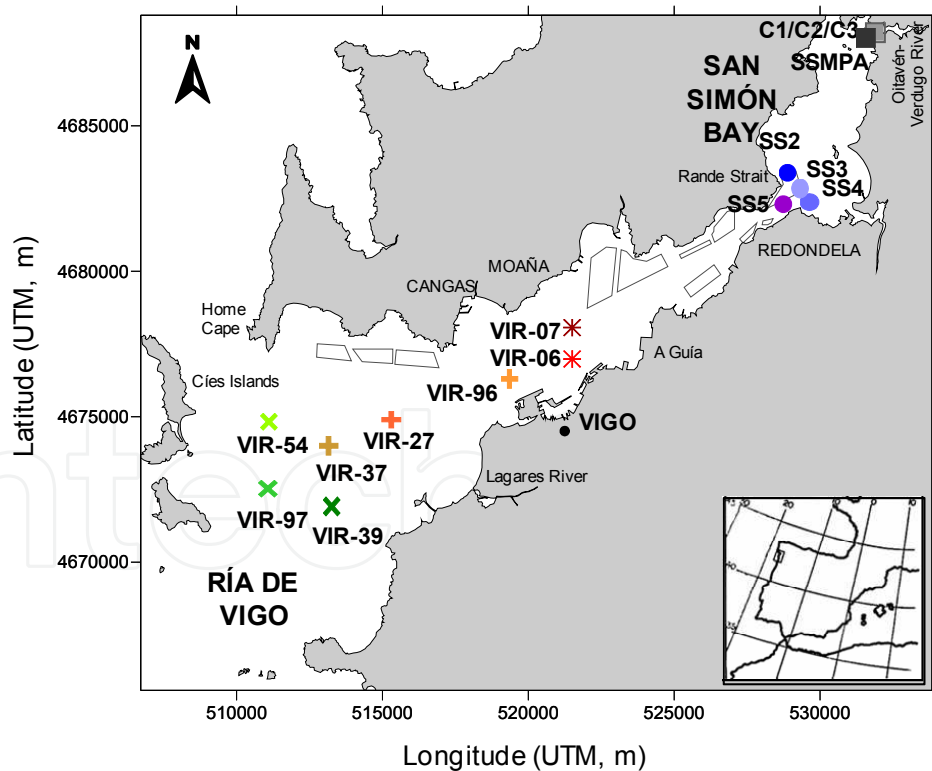Lagares River (Fig. 1).

Fig. 1. Study area. Location of sampling points considered in the present study: inner ría
(squares and circles), middle ría (doble crosses), middle-outer ría (crosses) and outer ría
(vanes) cores. Note that location for intertidal cores C1, C2 and C3 is showed by a single
symbol due to the map scale, although they have been recovered at different points.
Polygonal areas represent current mussel raft areas.

2. Sources of metals to coastal sedimentary environments

Metal content in marine sediments reflects both natural and anthropogenic components. Inputs from weathering of soils, rocks and ores from the watershed, constitutes the lithogenic natural component (background level, see subsection 5.1 for details). The natural component has also inputs from biogenic production, that are going to dilute both lithogenic and anthropogenic inputs. The anthropogenic component is constituted by those metals released to the environment as a consequence of different human activities.

Metal inputs to the marine environment can be direct or indirect. Direct inputs come from urban sewage, industrial wastes (metallic, chemical, building and shipping industries) and metal production and recycling. Indirect inputs come from atmosphere and from rivers as dissolved or suspended load (Salomons & Förstner, 1984). Most of the inputs consist of a group of trace elements (As, Cd, Cu, Co, Fe, Mn, Pb and Zn, among others) usually known as heavy metals. This term, according to Moore (1991) refers to a group of persistent metals and semimetals with relatively high density and that are usually toxic or poisonous at low concentrations. Nevertheless, according to Duffus (2002), the term heavy metal has not a precise deffinition, it is outdated and it should be substituted for another more adequate such as trace element or trace metal depending on the context.

Once trace elements arrive to the marine environment they are going to be distributed between the different compartments by association with dissolved organic and inorganic ligands or with particulate matter, and by ingestion by organisms.

In the particular case of the Ría de Vigo some metal enrichments have been detected for particular areas in several works on surficial sediments: around the harbour area (Cu, Pb, Zn, Fe), the outflow of the Lagares River (Pb, Zn) and the inner ría sector (Pb) (for details see the review by Prego & Cobelo, 2003). Metal ranges of concentrations and metal speciation will be considered in the following sections.

3. Metal concentration *vs* grain size

Trace metals in the marine environment are usually associated to organic-rich fine-grained sediments (Förstner, 1989) related to the good complexation and peptidizing properties of organic matter (Wangersky, 1986) and the high specific surface and surficial charge of clay minerals (Horowitz & Elrick, 1987). The presence of coarse-grained particles in the sediments, that are mostly composed by inert substances (silicates, carbonates, feldspars), usually cause trace metal dilution (Förstner, 1989).

The grain-size effect can be observed in Ría de Vigo sediments, where elements associated with fine-grained fractions, such as Al, V or Ni, are correlated with the mud fraction of sediments (Fig. 2). In opposition, elements such as Si are more abundant in coarse-grained sediments (Fig. 2). Elements such as Ca and Sr, with a biogenic origin are mainly associated with the coarse-grained fractions, and cause a dilution of another elements contents (Fig. 2).

3.1 Normalization procedures

Several normalization methods are generally used in order to correct for grain-size effects (Fig. 3). They are based in different approaches: 1) Indirect approximations (Summers et al., 1996); 2) The physical separation of a specific grain-size fraction –usually that <63 μm

(Förstner, 1989); and/or 3) The normalization of the metal concentrations by the content of a conservative element associated to the fine-grained fraction. In the last case Al, Fe, Li and Rb are usually selected (Ackerman, 1980; Álvarez-Iglesias et al., 2003, 2006; Loring, 1990). Lithium is preferred in front of Al when analyzing sediments from high latitudes (Loring, 1990). Some workers (Prego et al., 2006, among others) have chosen Fe for normalizing because its high abundance in the Earth's crust and its similar behavior and geochemistry to those of many trace elements but this metal shows a high mobility by postdepositional diagenetical processes (Álvarez-Iglesias et al., 2003; Rey et al., 2005) and, furthermore, different coastal areas can show Fe pollution (Rubio et al., 2000a).
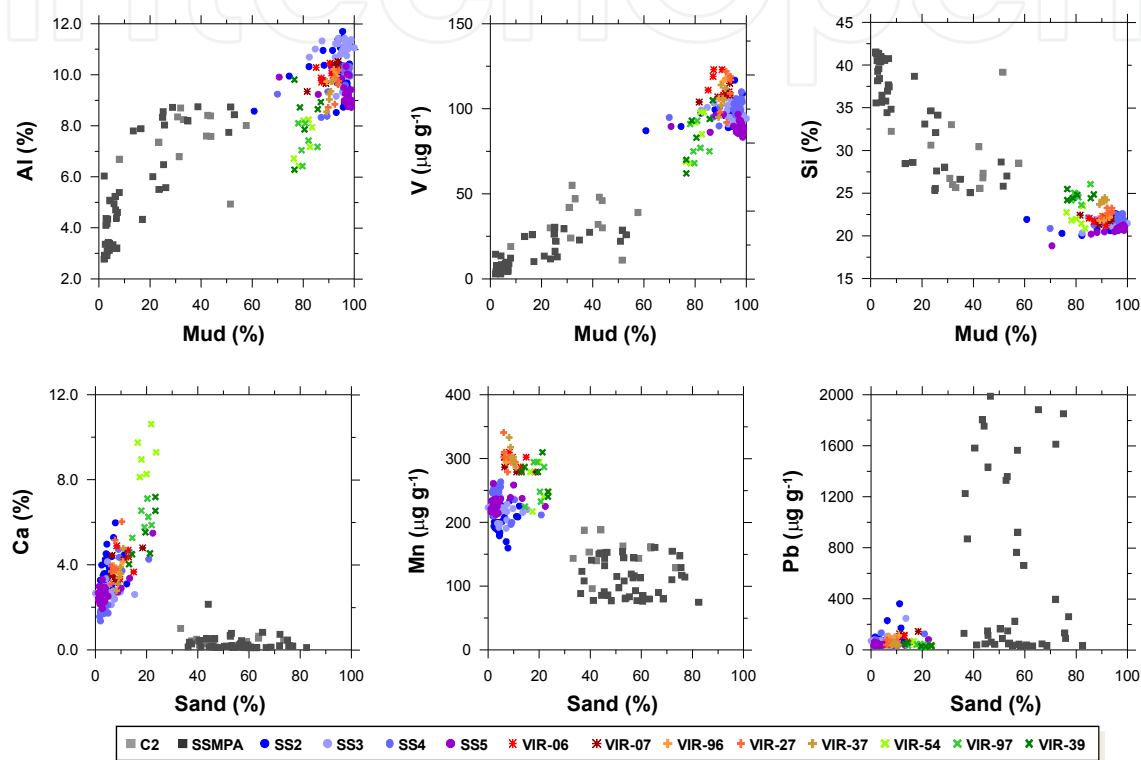

Fig. 2. Scatterplots of element concentrations vs mud (<63 μm) or sand contents in core samples (N = 210) from different sectors of the Ría de Vigo (core depths between 0.24 and 3.10 m): inner ría both intertidal (squares) and subtidal (circles) sediments, middle ría (doble crosses), middle-outer ría (crosses) and outer ría (vanes). Metal concentrations obtained from X-ray fluorescence (XRF) analyses. Note the positive correlation between Al or V vs mud and Ca vs sand, and the negative correlation between Si vs mud and Mn vs sand contents. Note also the extremely high values of Pb in the intertidal sediments. Sample location in Fig. 1.

The approaches 2 and 3 are generally combined (Álvarez-Iglesias et al., 2003) because, even in the grain-size fraction <63 μm, metal contents are not homogeneously distributed (Salomons et al., 1985). Nevertheless, in studies where fine-grained content is very high, normalization is usually accomplished by the use of a normalizer element on bulk sample results. These grain-size effects on metal concentrations can be clearly observed in the scatterplots of Fig. 3, where concentrations of Cr, Cu and Zn in Ría de Vigo sediments increased with the Al content. Note also in Fig. 3 that some samples show metal enrichments lying out of the general trend. This will be discussed in the following sections.
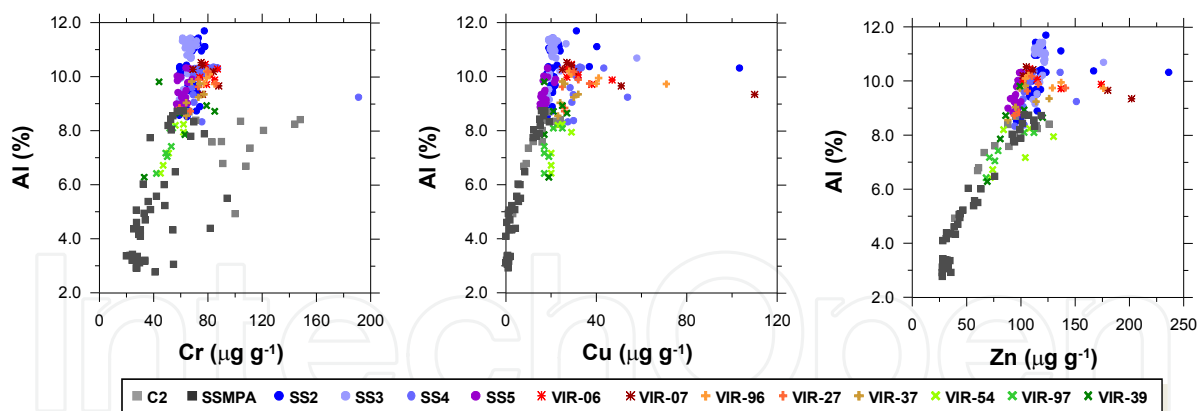
Fig. 3. Scatterplots of Al vs Cr, Al vs Cu and Al vs Zn in core samples (N=210) from different sectors of the Ría de Vigo (sample location in Fig. 1). Metal contents obtained from XRF analyses.

4. Determination of total metal concentration and speciation

The different anthropogenic inputs of metals to the marine environment will cause changes in sediment composition. A detailed study on the sedimentary record will allow evaluating environmental changes both spatially and temporally for a particular coastal area. It is important to consider also metal speciation, to evaluate potential mobility and bioavailability of the different trace metals (Bryan & Langston, 1992).

4.1 Total metal concentration

Total metal concentrations can be determined by XRF or by measuring metal contents, after acid digestion of the sediments, by different techniques such as Atomic Absorption Spectrometry (AAS) or Inductively Coupled Plasma-Mass Spectrometry (ICP-MS), among others.

Advantages of XRF are: 1) easy sample preparation, 2) quickness, 3) relatively low cost of the measurements, and 4) high analytical resolution (Boyle, 2000). Continuous high-resolution XRF core scanner devices allow making a qualitative exploratory analysis very quickly (1.0 m of a core in a few hours) analyzing directly fresh and undisturbed sediments (Rubio et al., 2011). This analysis can be refined by analyzing discrete samples by tradicional XRF techniques (obtaining quatitative data).

Total metal concentrations can be also determined by digestion of the samples in open or closed systems with heating. The different workers usually utilize the following reactants, alone or in combination: HCl, HNO_3, H_2O_2, H_2SO_4, $HClO_4$ and HF (Álvarez-Iglesias et al., 2003; Belzunce-Segarra et al., 1997; Varekamp, 1991). Traditionally samples were acid digested applying dry (oven, hot plate) or humid (water bath) heat, but in the last decades the use of microwave ovens has been extended (Álvarez-Iglesias et al., 2003; Izquierdo et al., 1997; Rubio et al., 2001). The use of a closed system has several advantages: 1) the attack is effective, 2) the analytical results are similar to those traditional (Mahan et al., 1987), 3) the human errors are minimized, 4) the analytical contamination problems are reduced, 5) the losses by volatilization are minimal, 6) the efficiency of destruction under pressure is high (Uhrberg, 1982), and 7) the time for analysis is reduced.

If acids such as HCl, HNO$_3$ or HClO$_4$ are used alone or in combination but not HF, the obtained metal contents do not represent total metal but pseudo-total metal concentrations (Barreiro Lozano, 1991). Then, the selection of one or another analytical technique for determining metal concentration will depend on the objective of the study.

In order to check for accuracy and precission of the results of metal concentration it must be analyzed reference materials by the same techniques that those applied in the sediments under study (Table 1). Furthermore, the reference materials should have similar characteristics than those of the target sediments to avoid the matrix effect (Boyle, 2000). In the case of the Ría de Vigo the reference materials usually analyzed have been MESS-1, MESS-3 and PACS-1 (Álvarez-Iglesias et al., 2003, 2006; Prego et al., 2006; Vega et al., 2008).

	MESS-1			PACS-1	PACS-1	MESS-3	MESS-3
	CV	Measured[1a]	Measured[2b]	CV	Measured[3]	CV	Measured[4d]
Al (%)	5.84±0.20	3.71±2.14	6.09	-	-	-	-
Fe (%)	3.05±0.17	2.47±0.12	2.99	4.87±0.08	5.11±0.09[a]	-	-
Co (µg g^{-1})	10.8±1.9	-	9.4	-	-	-	-
Cr (µg g^{-1})	71±11		74.7	113±8	99±10[c]	-	-
Cu (µg g^{-1})	25.1±3.8	23.84±2.17	24.9	452±16	424±37[c]	33.9±1.6	31±5
Mn (µg g^{-1})	513±25	403.5±35.2	451	-	-	-	-
Ni (µg g^{-1})	29.5±2.7	-	29.2	-	-	-	-
Pb (µg g^{-1})	34.0±6.1	36.50±7.24	38	404±20	409±24[c]	21.1±0.7	23.6±2.5
V (µg g^{-1})	72.4±17	-	101.3	-	-	-	-
Zn (µg g^{-1})	191.0±17.0	161.5±15.4	190.9	-	-	159±8	161±5

[1]Álvarez-Iglesias et al. (2003); [2]Álvarez-Iglesias et al. (2006); [3] Prego et al., 2006; [4]Vega et al. (2008)
[a]AAS; [b]XRF; [c]ET-AAS; [d]ICP-OES.

Table 1. Comparison of certified values and measured values for several reference materials obtained in different studies. CV: Certified value. Measured values were obtained by different techniques: analysis of sediment extracts from total acid digestion in microwave oven by AAS, analysis of bulk sediments by XRF, Electrothermal atomic absorption spectrometry (ET-AAS) and Inductively coupled plasma-optical emission (ICP-OES). Note the differences in metal concentrations obtained by different techniques for the reference material MESS-1.

4.2 Speciation

The bioavailability, toxicity and mobility of a particular trace element depends on the sedimentary phase to which is bound to, that is, on metal speciation. It is necessary to distinguish and quantify the different metal species to study current and potential impacts of polluted sediments, to identify metal sources, and to understand the geochemical processes that take place in a particular environment. Metal association to the sediments can be diverse: adsorbed onto surfaces of clay-particles, Fe-Mn oxyhydroxides and organic matter; occluded in amorphous materials, such as Fe-Mn oxyhydroxides, Fe sulphides or remanents of biological organisms; or being part of the mineral structure. Direct determination of each single chemical form of a metal is not practical, and indirect methods are preferred such as: statistical correlations, thermodynamical calculations based on models of chemical equilibrium, computer simulations, and more commonly chemical extraction methods (Luoma & Bryan, 1981; Luoma, 1986; Tessier et al., 1979; Tessier & Campbell, 1988).

Chemical methods can be selective or non-selective. Non-selective methods extract operationally defined metal fractions that are not directly identifiable with an specific phase in the sediment (Loring, 1981). Although they do not correspond to one isolated chemical form, they suppose a better estimation of reactivity instead of total metal content. These methods can be one-single step or sequentials. The first ones can be grouped in three categories depending on the selected reactant: 1) diluted solutions from strong acids; 2) weak acids; and 3) solutions from strong reducing or complexing agents (Bryan & Langston, 1992; Imperato et al., 2003). Advantages of these methods are quickness, simplicity, cost-efficiency relationship, allowance of a better contrast between background values and anomalous values, and the non-utilization of dangerous acids such as $HClO_4$ or HF. The main inconvenient is the difficulty of finding a single reactant with the capacity of extracting the labile metal fraction (or any other target fraction) without attacking the residual fraction.

Operationally defined fractions					Reference
A	B	C	D	E	Tessier et al., 1979
A+B		C+D		E*	Salomons & Föstner, 1984
A	B	C1	C2	D	E*	Salomons & Föstner, 1984
A	B	C1	C2	D	-	Kersten & Föstner, 1987
A+B+C			D1	D2	E*	Huerta-Díaz & Morse, 1990
A+B		C	D	-	Ure et al., 1993
A	B	C1	C2	D	E*	Borovec, 1996
A*	B+C*		D*	E	Dassenakis et al., 1996
A	B	C1	C2	D	-	Howard & Shu, 1996
A	B	C1	C2	D	E*	Izquierdo et al., 1997
A*	B′	C1′	C2′	D	-	Flyhammamar, 1998
A+B		C	D	E	Gómez-Ariza et al., 2000
A+B		C	D	E*	Stephens et al., 2001

A: exchangeable   C1: Mn oxides(easily reducible)
B: bound to carbonates   C2: Fe oxides (moderatelly reducible)
C: bound to Fe-Mn oxyhydroxides (reducible)   B′: metals non-extracted in A* and bound to carbonates
D: bound to organic matter-sulphides (oxidizable)   C1′: Mn oxides and amorphous Fe oxides
E: residual   C2′: amorphous and poor-cristalyzed Fe
                                                        oxyhydroxides
A*: easily interchangeable   D1: bound to organic matter
B + C*: non-exchangeable inorganic fraction   D2: bound to sulphides
D*: organic fraction   E*: bound to silicates (but without using HF)

Table 2. Comparison between the different metal fractions obtained with different sequential extraction methods.

Sequential methods consist of extracting the same sediment sample with a sequence of reactants, usually among 3 and 8, with increasing reactivity in the disolution process or with different nature regarding the previous one. The application of these methods results in a series of operationally-defined phases. Reactants are diverse and can be grouped in: concentrated inert electrolytes, weak acids, reducing agents, complexing agents, oxidizing agents and strong mineral acids. There are different extraction techniques (Table 2). The lack of uniformity between the different sequential extraction methods prevents comparison of

the results among different techniques. The most applied sequential procedure is that of Tessier et al. (1979), directly applied, or with small modifications (Álvarez-Iglesias et al., 2003; Mahan et al., 1987).

The main inconvenients of sequential extraction methods are the non-specificity of the reactants, the redistribution of trace elements between phases and the overload of the chemical system if the metal content is too high. Furthermore, it has to be beard in mind that some speciation changes could occur because of sample preparation, and also, the lack of reference materials suitable for most of the utilized methods (Quevauviller et al., 1997).

Several complementary analysis can be performed to check for efficiency and selectivity of the extraction procedure: to analyze total organic and inorganic carbon and sulphide contents in the extracts or in the sediments that remains after the different extractions; to study the solids that remain after the different steps by XRF or Scanning Electron Microscopy (SEM); to extract pure samples of geochemically known phases; or to statistically analyze the metals extracted from the sediments and the main sedimentary components that can bind them (Luoma & Bryan, 1981; Rapin & Förstner, 1983).

Metal redistribution or readsorption between the remaining sedimentary phases during the sequential procedure is an inconvenient very difficult to avoid, this is due to the partial selectivity of the extractants (Tessier & Campbell, 1987). One example could be the existence of free sulphides that would cause precipitation of metals previously released from the sediments; another one would be sulphides oxidation (Ngiam & Lim, 2001). Several workers have shown that readsorption happens after the extraction (Guy et al., 1978; Rendell et al., 1980) but they have not agreed if this problem is significant or not.

The problems related to the overload of the chemical system can be solved repeating the same step several times. When metal content is high the quantity of reactant used can be insufficient to completely extract all the metal bound to a certain specific fraction, then, some of the metal would be still retained and would be extracted in the following step.

Regarding to the problems related to the possible changes in especiation because of sample preparation, several workers pointed out that this is more important in anoxic samples than in oxic samples, because most of the extraction procedures have been designed for oxic sediments (Tessier & Campbell, 1988). Techniques of sample preservation before analysis, frozen or keeping at low temperature are better preferred than drying.

In spite of the indicated inconvenients of sequential extraction procedures, these methods are useful to evaluate bioavailability and potential mobility, and to study early diagenetical processes. Among them, the usually applied methods are those proposed by Tessier et al. (1979), Ure et al. (1993) and Huerta-Díaz & Morse (1990). In the Tessier et al. (1979) method (called in the following Tessier's method) the parameters involved in the solubilization of the extracted metals are carefully controled, and five operationally-defined fractions are obtained (Table 2; Fig. 4). The Ure et al. (1993) method, usually known as the BCR method separates three fractions (Table 2), whereas the Huerta-Díaz & Morse (1990) method (called in the following H&M's method) separates four fractions (Table 2, Fig. 4). One important difference is that with the last method metals bound to organic matter are differentiated from those metals bound to sulphides. Nevertheless, the Tessier´s method allows differentiating between interchangeable, bound to carbonates and bound to Fe-Mn

oxyhydroxides metal fractions, whereas all together represents one single fraction together with acid-volatile sulphides in the H&M's method and they are considered as two fractions in the BCR procedure (Table 2).
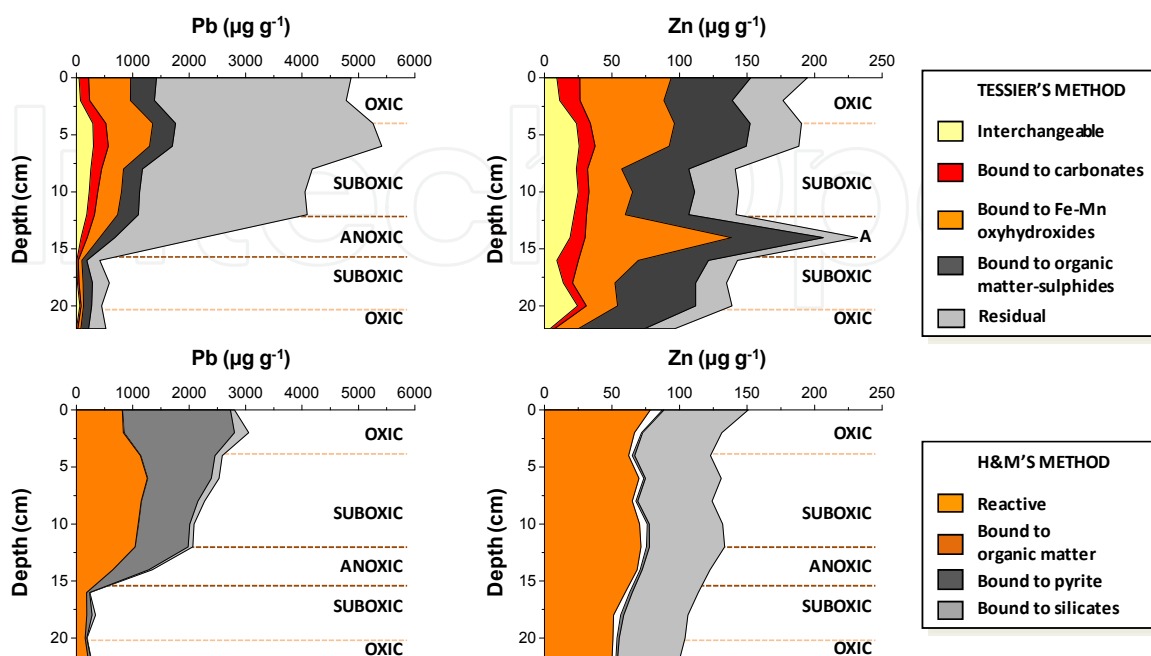

Fig. 4. Metal speciation distribution ($\mu g\ g^{-1}$) according to the sequential extraction methods of Tessier et al. (1979) and Huerta-Díaz & Morse (1990) for Pb and Zn in the fine-grained fraction of muddy sandy sediments (core C2) from inner Ría de Vigo. Note the different fraction recovery obtained for the same metal by the two procedures. Differences in the metal content in the silicate fraction or residual are due to the non-total leaching of silicates with the Huerta-Díaz & Morse method. Redox conditions (oxic, suboxic, anoxic-non sulphidic) in these sediments have been inferred according to DOP values (Álvarez-Iglesias et al., 2003).

The interchangeable fraction corresponds to those metals bound to low energy adsorption places and it is the most active fraction from a biological point of view (Campbell et al., 1988). In the fine-grained fraction of inner Ría de Vigo sediments it represents a relatively low content (average ~50 $\mu g\ g^{-1}$ for Pb and ~10 $\mu g\ g^{-1}$ for Zn, N=34), being more or less abundant depending on the grain-size distribution, the muddier the sediments, the higher the metal contents. The fraction bound to carbonates represents those metals bound or adsorbed into carbonates. In the fine-grained fraction of inner ría sediments it represents a relatively low content (average ~77 $\mu g\ g^{-1}$ for Pb and ~12 $\mu g\ g^{-1}$ for Zn, N=34). These two fractions together are more or less equivalent to the labile fraction of the BCR method. The labile fraction also represents a very low contribution in middle and outer ría sediments (<1.1 $\mu g\ g^{-1}$ for Cu, non-detected for Pb and ~4.1 $\mu g\ g^{-1}$ for Zn, N=47; Fig. 5).

The fraction bound to Fe-Mn oxyhydroxides corresponds to that metallic fraction bound to reducible Al, Fe and Mn oxides/hydroxides. They are unstable compounds under reducing conditions, which causes the release of associated metals. In the sediments of inner Ría de Vigo this fraction represents a significant percentage of the total concentration: around 20% of total Pb and 36% of total Zn (Fig. 4) decreasing to ~6.9% of total Pb and ~14% of total Zn in middle and outer ría sediments (Fig. 5).
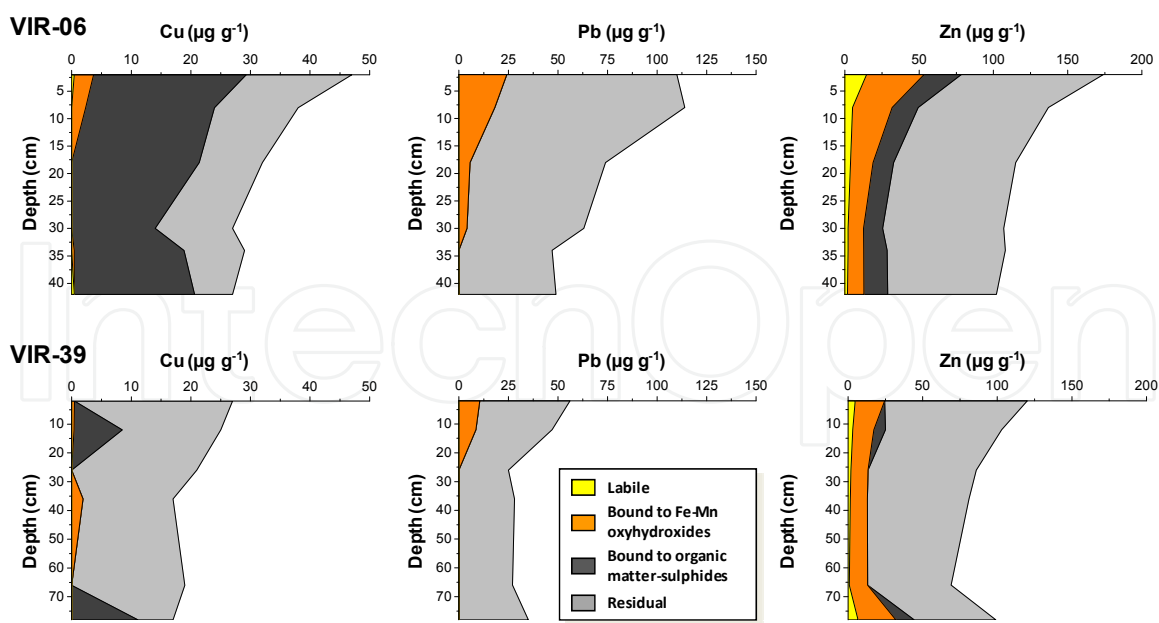
Fig. 5. Depthwise profiles of BCR fractions of Cu, Pb and Zn in cores from middle and outer ría (VIR-06 and VIR-39).

The metal fraction bound to carbonates, to amorphous and cristaline Fe-Mn oxyhydroxides (except goethite) and acid volatile sulphides (AVS) is extracted with the first step of the H&M's method, and then embracing the three fractions formerly discussed. It is called the reactive fraction. This fraction represents 43-75% of total Cu, 27-84% of total Pb and 33-57% of total Zn, in the fine-grained fraction of intertidal inner ría sediments (Fig. 4) and 0.1-51% of total Cu, 54-94% of total Pb and 11-53% of total Zn in subtidal inner ría sediments (Fig. 5).

The metal fraction bound to organic matter can be a significant sink for several metals depending on their relative abundance related to any other sedimentary phases. For example, this fraction represents 1.2-15% of total extracted Cu, 0.2-2.0% of total extracted Pb and 1.7-6.0% of total extracted Zn in intertidal and subtidal oxic sediments (N=20) of inner Ría de Vigo (Fig. 6), being their contribution lower in suboxic and anoxic sediments of the ría. Degradation of organic matter under oxidizing conditions will cause the release of metals bound to this phase.

The metal fraction bound to sulphides is significant in anoxic sediments, where metal sulphides, mainly pyrite, constitute a significant sink for several trace elements, as observed in the Ría de Vigo (Figs. 4, 6). This fraction can represent a high percentage of the total concentration of certain trace elements, such as Cu. For example, this fraction represents 26-94% of total extracted Cu, 5.0-47% of total extracted Pb and 1.2-9.4% of total extracted Zn in anoxic sediments (N=47) of inner Ría de Vigo, with a higher contribution for Cu and Zn in subtidal (Fig. 6) than in intertidal sediments.

These two fractions (bound to organic matter and to sulphides) are obtained as one single fraction, called oxidizable fraction, when applying the Tessier's and the BCR methods. The oxidizable fraction in the fine-grained fraction of intertidal sediments of inner Ría de Vigo according to the Tessier's method represents 7.4-31% of total extracted Pb and 6.1-51% of total extracted Zn (N=34, see examples for particular cores in Fig. 4), whereas this fraction in

middle and outer ría sediments represents, on average, 46% of total extracted Cu, ~1.0% of total extracted Pb and ~11% of total extracted Zn (N=47) in middle and outer ría sediments according to the BCR procedure (see examples for particular cores in Fig. 5).
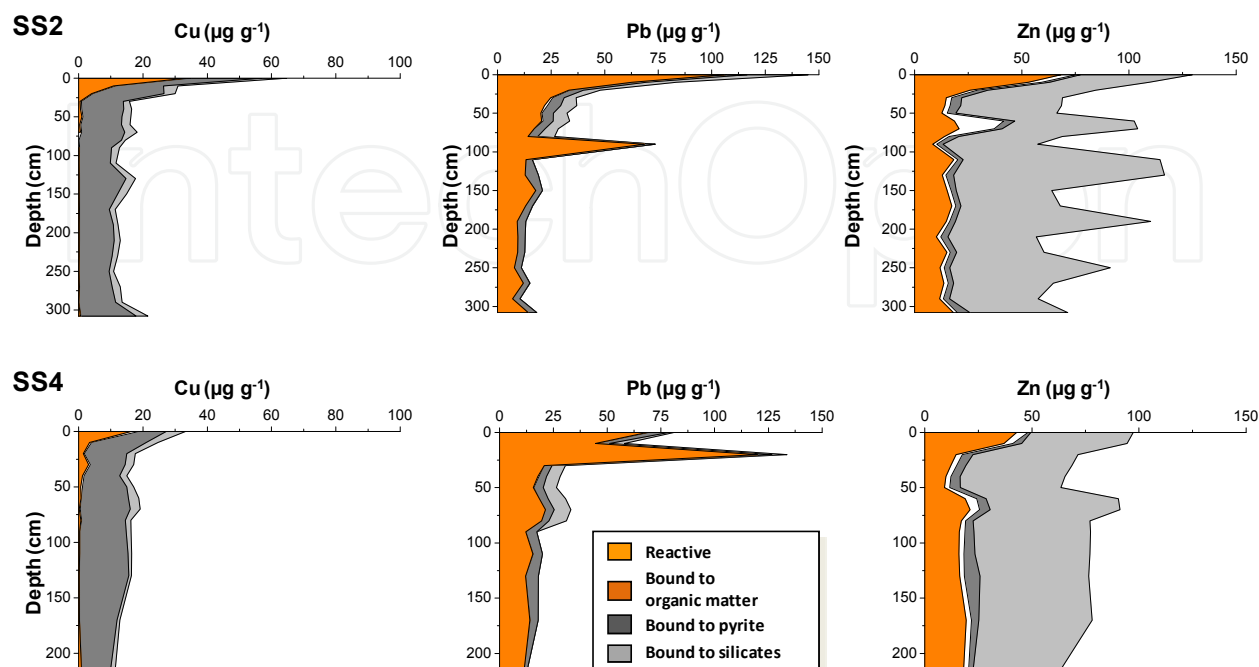

Fig. 6. Metal speciation distribution (µg g^{-1}) for Cu, Pb and Zn according to the Huerta-Díaz & Morse (1990) method for subtidal sediments of inner Ría de Vigo (cores SS2 and SS4).

The residual fraction is composed of primary and secondary detrital silicates that occur naturally and can hold trace elements into their crystal structure, resistant sulphides, and refractory organic matter (Tessier et al., 1979). Under natural conditions trace elements bound to this fraction are not expected to be released to the environment. Metal content in this fraction depends on mineral composition of the watershed, on physical properties that rules transport and deposit (grain-size, density, etc.) and on mineral stability and weathering intensity. This fraction is not obtained by some sequential procedures (Table 2) and then it can be obtained by subtraction. In other sequential methods, a silicate bound fraction is obtained but it does not represent the whole metal bound to this fraction. For example, in Fig. 4 the comparison of total concentrations obtained by the Tessier's and H&M's procedures showed clearly that the recovery for residual Pb was not complete with the second method. The comparison of total metal concentrations with the total recovery after applying these sequential extraction procedures showed differences depending on grain-size and mineralogy (Álvarez-Iglesias & Rubio, 2008, 2009): metal recovery was around 60-100% for Fe, 70-75% for Cu, 46-55% for Pb and 70-100% for Zn in inner ría sediments both subtidal and intertidal (fine-grained fraction). The residual fraction in intertidal sediments of inner Ría de Vigo according to the Tessier´s method represents ~56% of total extracted Pb and ~18% of total extracted Zn (N=34, see examples in Fig. 4), whereas this fraction in middle and outer ría sediments represents on average ~52% of total extracted Cu, ~92% of total extracted Pb and ~71% of total extracted Zn (N=47) in middle and outer ría sediments according to the BCR procedure (see examples in Fig. 5).

5. Assessment of pollution in marine sediments

Establishing the degree of pollution by trace elements in marine sediments allows studying pollutants distribution for a particular area spatially and temporally and identifying pollutant sources (Dassenakis et al., 1996; Zwolsman et al., 1993). This is usually approached by determining several indexes and studying the relationships between metals and sediment characteristics. First, background levels (BLs) have to be considered, and second, the degree of pollution can be evaluated.

5.1 Background levels

Metal BLs correspond to the natural metal concentrations that exist or would exist in sediments without human influence. Several authors have proposed different BLs to global, regional and local scales, summarized in Tables 3 and 4, for major, minor and trace elements, respectively. Global or world-wide BLs correspond to average values calculated for the Earth crust (Taylor, 1964), granites, deep-sea clay sediments or lutites (Turekian & Wedepohl, 1961). Regional and local BLs take into account local geochemical variability (Rubio et al., 2000a). They can be determined in sediments from the target area or from adjacent areas by different methods such as 1) determination of pre-industrial metallic levels in dated cores; 2) application of regresion techniques between a geochemically-stable element without human-influence and the rest of metals; 3) selection of pristine areas; 4) selection of the first-percentile in accumulated distributions of metal concentration; 5) determination of homogenous populations into the target data; 6) a combination of the previous procedure with modal analysis; 7) a direct comparison of polluted and non-polluted sediments from the same study area or an adjacent area; or 8) principal component analysis (Barreiro Lozano, 1991; Carral et al., 1995a, 1995b; Chester & Voutsinou, 1981; Hakanson, 1984; Rubio et al., 2000b; Summers et al., 1996).

The selection of the BL will conditionate the geochemical interpretation of a particular area (Rubio et al., 2000a). The use of local or regional BLs is recommended to take into account local geochemical variability. Even in a local study, BL should be selected considering the watershed composition. It is important to highlight that sediments can be enriched naturally in a particular trace element. For example, Álvarez-Iglesias et al. (2006) showed that sediments in inner Ría de Vigo from a schist-gneiss watershed were enriched in metals such as Fe, Cr and Ni when compared with sediments from a granitic watershed (Fig. 7). Circles in Fig. 7 correspond to a subtidal core of inner ría with relatively high Fe/Al ratios, pointing to a schist-gneiss source, in comparison to another subtidal core samples from inner ría. This can also be deduced for middle and outer Ría de Vigo sediments, with high Fe/Al ratios too. Grain-size and postdepositional physico-chemical processes can also affect to remobilization of some redox-sensitive elements. For example, it can be observed in Fig. 7 that some of the intertidal samples (light squares) showed higher Fe/Al ratios than others from the same area. This can be interpreted as Fe enrichments caused by diagenetic processes. Furthermore, it can be observed that intertidal samples of inner ría (Fig. 7, squares) showed higher coarse-grained particles content and lower concentrations of Fe and Ti than subtidal samples of the ría. Then, it is recommended the use of BLs with similar characteristics (grain size, composition, origin) to those of the sediments of the area under study to avoid misinterpretation of the data. It is also recommended the use of BLs obtained by similar analytical procedures than those applied on the target samples. This will avoid the possible differences in metal concentrations related

only to the efficiency of the followed protocol (Rubio et al., 2000a). For example, Rubio et al. (2000b) established a BL for Cr by XRF higher than that previously established for the same study area by triacid digestion (Rubio et al., 2000a) (Table 4).

Scale	Al	Ca	Fe	K	Mg	P	S	Si	Ti
Global[1,a]	8.00	2.21	4.72	2.66	1.50	0.07	0.24	7.30	0.46
Global[1,b]	8.40	2.90	6.50	2.50	2.10	0.15	0.13	25.00	0.46
Global[1,c]	7.20	0.51	1.42	4.2	0.16	0.06	0.03	34.7	0.12
Global[2,d]	8.89	1.64	4.83	2.82	1.57	-	-	27.11	0.43
Global[3,e]	8.23	4.15	5.63	2.09	2.33	0.105	0.026	28.15	0.57
Global[3,f]	7.70	1.58	2.70	3.34	0.16	0.070	0.027	32.3	0.23
Galicia[4]	-	-	2.69	-	-	-	-	-	-
Galicia[5]	-	-	2.6	-	-	-	-	-	-
Galicia[6, g]	-	-	2.9	-	-	-	-	-	-
Galicia[6, h]	-	-	3.3	-	-	-	-	-	-
RV[7]	6.48	-	3.51	-	-	-	-	-	0.34
RV[8]	6.48	-	3.51	-	-	-	-	-	0.34
SSB[9]	9.82	3.16	3.53	2.59	1.05	0.10	1.06	21.49	0.36
SSB[10, i]	9.91	3.22	3.36	2.56	1.05	0.10	0.94	21.45	0.36
SSB[10, j]	9.36	2.81	4.44	2.75	1.05	0.08	1.69	21.70	0.37

[1] Turekian & Wedepohl (1961); [2]Wedepohl (1971, 1991); [3]Taylor (1964); [4]Barreiro Lozano (1991); [5]Carral et al. (1995a); [6]Carral et al. (1995b); [7]Rubio et al. (2000a); [8]Rubio et al. (2000b); [9]Álvarez-Iglesias et al. (2006); [10]This study.
[a]shales, [b]deep-sea clay sediments, [c]low Calcium granites, [d]average shales, [e]Earth crust, [f]granite average, [g]estuarine sediments from granitic watersheds, [h]estuarine sediments from schist-gneiss watersheds; [i]ría sediments with a granitic source; [j]ría sediments with a schist-gneiss source. RV: Ría de Vigo, SSB: San Simón Bay (inner Ría de Vigo).

Table 3. Global, regional and local background levels for major elements (%).

Scale*	As	Cr	Cu	Mn	Ni	Pb	Rb	V	Zn
Global[1,a]	13	90	45	850	68	20	140	130	95
Global[1,b]	13	90	250	6700	225	80	110	120	165
Global[1,c]	1.5	4.1	10	390	4.5	19	170	44	39
Global[2,d]	-	90	-	-	68	-	-	130	95
Global[3,e]	1.8	100	55	950	75	12.5	90	135	70
Global[3,f]	1.5	4	10	400	0.5	20	150	20	40
Galicia[4]	-	43	25	225	30	25	-	-	100
Galicia[5]	-	32	28	275	32	53	-	-	122
Galicia[6, g]	-	30	20	248	31	78	-	-	136
Galicia[6, h]	-	54	35	395	38	50	-	-	120
RV[7]	-	34	29	244	30	51	-	-	105
RV[8]	-	55	20	244	30	25	-	-	105
SSB[9]	16	65	21	216	33	51	198	94	110
SSB[10, i]	14	64	19	214	33	54	180	93	111
SSB[10, j]	19	70	30	229	35	34	298	99	104

*Uppercase notation similar to that of Table 3.

Table 4. Global, regional and local background levels for minor and trace elements ($\mu g \ g^{-1}$).

The first step for evaluating the degree of pollution of inner Ría de Vigo sediments would be to make the scatterplots of Al-Fe, Al-K, Al-S, Al-Si , Al-Ti and Al-Rb (Fig. 7) in order to decide which background value have to be selected for obtaining reliable data. Those samples out of the general trend in the scatter plots will be identified as enriched samples. In the samples under study, it is neccesary to consider two different background values: one BL for the samples from middle and outer ría together with the samples of one subtidal core (SS4), and another BL for the rest of the subtidal core samples and the intertidal core samples from the inner ría.
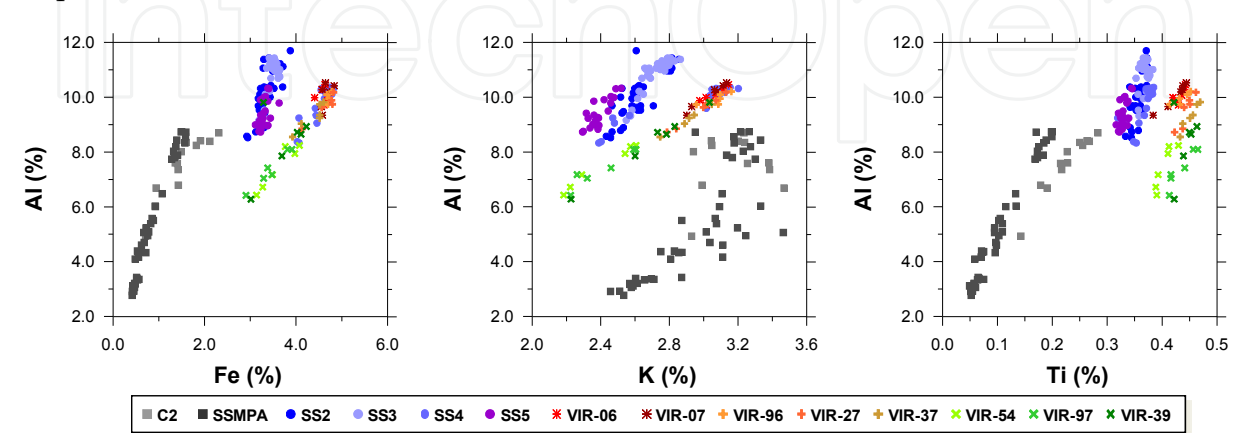
Fig. 7. Scatterplots of Al vs Fe, Al vs K and Al vs Ti in core samples (N=210) from different sectors of the Ría de Vigo (sample location in Fig. 1). Metal contents from XRF analyses. Note the marked differences between intertidal samples (with a higher coarse-grained particles content) and subtidal samples, and the striking differences within subtidal samples, where two populations can be observed, one, with higher Fe/Al ratios (those samples with a schist-gneiss source), the other, with lower Fe/Al ratios (most of the inner ría subtidal cores).

5.2 Degree of pollution

The indexes that are usually applied to evaluate the presence of metal pollution in sediments are the Contamination or Concentration Factor (CF) and the Enrichment Factor (EF) (Barreiro Lozano, 1991; Álvarez-Iglesias et al., 2003; Rubio et al., 2000a).

The CF (Hakanson, 1980) is based on the calculation of the relationship between the concentration of the potential pollutant element measured in the sample $[M]_i$ and the background level for that element $[M]_{BL}$. $FC=[M]_i/[M]_{BL}$. CF value would be close o 1 when there is no metallic enrichment. The degree of contamination can be classified as null or low (CF<1), moderate (CF: 1-3), high (CF: 3-6) or very high (CF>6).

The EF (Zoller et al., 1974) is based on the calculation of the relationship between the concentration of the potential pollutant element and a normalizer element measured in the sample ($[M]_i$ and $[N_e]_i$, respectively), divided by the same relationship considering the previously selected BL ($[M]_{BL}$ and $[N_e]_{BL}$, respectively): $FE=([M]_i/[N_e]_i)/([M]_{BL}/[N_e]_{BL})$. An EF=1 indicates non-enrichment in comparison with the BL. Nevertheless, an EF lower/higher than 1 points to an impoverishment/enrichment, respectively, of the studied trace element. The degree of pollution can be classified in a similar way to that of CF.

Both CF and EF has been calculated for the different cores studied using the new BLs established (Fig. 8). The dispersion among cores considering the deepest samples is higher for CF than for EF depth-profiles, this is explained by the non-consideration of grain-size variability when calculating CF. Furthermore, the high grain-size variability of the intertidal cores, where coarse-grained sediments are very abundant at certain levels, explains the impoverishment observed for the considered trace metals at their bottom. Both CF and EF indexes show a moderate enrichment in Cu and Zn, in general, for the first 0.10-0.20 m of the sedimentary record, in general, for all the cores. Nevertheless, Pb pollution has been detected in the first 0.10-0.80 m, its degree varying from moderate to very high depending on core depth and position. Pollution was classified as high in the first decimeter of inner and middle subtidal cores, whereas the highest EF (up to 40-45) has been detected in the first 0.15-0.20 m of the intertidal core samples. These moderate or high contents of trace metals were explained as anthropogenic inputs, in particular for Cu and Zn from fertilizers and pesticides (Álvarez-Iglesias et al., 2006, 2007) and for Pb both from direct and indirect sources. The main Pb input since the 1970s to the inner ría has been a ceramic factory located at the head of the Ría but previously and nowadays diffuse sources, mainly coal and petrol combustion, have contributed and contribute to Pb inputs to the Ría de Vigo (Álvarez-Iglesias et al., 2003, 2007).
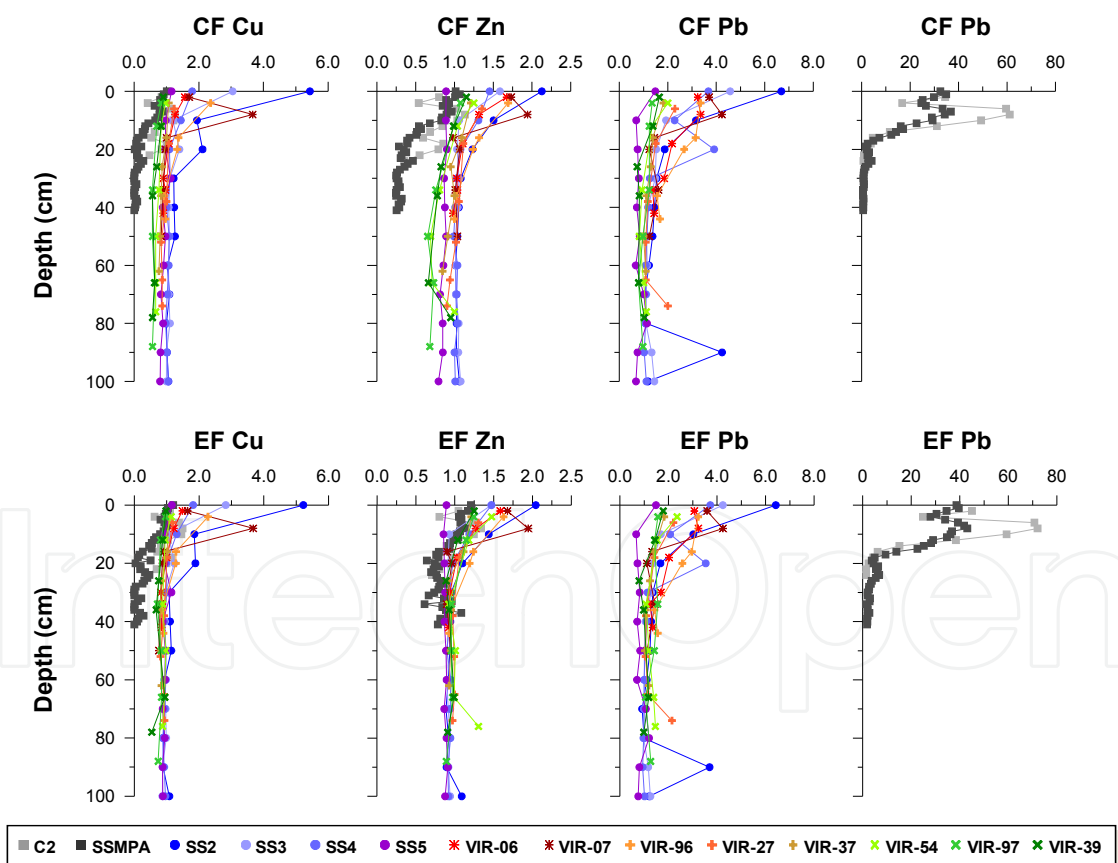

Fig. 8. Evaluation of the degree of pollution according to the CF and EF for Ría de Vigo core samples (sample location in Fig. 1). Note that for the particular case of the subtidal samples of the inner ría it has been only considered those from the first sampled meter in order to allow for a better comparison between cores. CF-Pb and EF-Pb for intertidal cores are showed in a separated graph because of their high pollution factors.

6. Early diagenesis of metals in marine sediments

Early diagenesis processes include all the post-depositional changes that happen in sediments in a short geological time-scale. After sediment deposition, its constituents can suffer chemical modifications, implying a new equilibrium between solid and dissolved species. Then, metal speciation can be modified, and thus, metal mobility and bioavailability too (Shaw et al., 1990). Organic matter degradation fuels early diagenesis processes. Their mineralization is mainly bacterially mediated following an ideal sequence of alternative electron acceptors (Froelich et al., 1979), where the most thermodynamically favoured reaction happens until exhaustion of the corresponding reactant, and then, the next favourable reaction starts. In this way, a diagenetic zonation can be described for the Ría de Vigo sediments.

6.1 Diagenetic zonation

Diagenetic zonation in marine sediments depends on the degree of oxygenation of the water column (Wignall, 1994). According to Berner (1981) different sedimentary environments can be differentiated considering redox potential, electron aceptors and typical mineral associations: oxic, suboxic, anoxic-sulphidic and anoxic-non sulphidic. These four diagenetic zones can be observed in sediments below oxic bottom waters and can be inferred by metal speciation procedures. Considering that sulphate reduction is a significant process in marine sediments, the protocols where the sulphide-bound fraction is independently obtained will be preferred (i.e., H&M's method). One index that is usually used is the degree of pyritization (DOP; Berner, 1970) where the relationship between the pyrite-bound and the reactive fractions is calculated. This index has recently been regarded as an indicator of interstitial water status in coastal sediments (Roychoudhury et al., 2003), with the limits for oxic with DOPs lesser than 42%, suboxic between 42 and 55%, anoxic between 55 and 75% and euxinic higher than 75% (León et al., 2004; Raiswell et al., 1988).

The oxic zone is characterized by the presence of oxygen, which is the first electron acceptor in the organic matter degradation process. Vertical diffusion of dissolved oxygen from the adjacent water column maintains oxygenated the interstitial water of freshly deposited sediments. Nevertheless, oxygen is rapidly consumed with depth because of the high metabolic rates of aerobic bacteria, avoiding vertical diffusion. Organic matter oxidation generates carbon dioxide, nitrate and phosphate (Froelich et al., 1979). CO_2 generation does not usually cause a pH diminution in the interstitial waters, but pH slightly diminishes because of an extensive oxidation of those sulphides migrating toward surface which also causes a carbonate subsaturation. Sediments contains oxides and oxyhydroxides of Fe (hematite, goethite) and Mn, and usually, a low content of organic matter, which is mostly degraded. The extension of the oxic zone is reduced, typically 0.10 m, but controlled by the rate of oxygen comsuption which depends on organic matter abundance and sedimentation rate (Wignall, 1994). Bioturbation by organisms in this zone is significant. In inner Ría de Vigo sediments the oxic zone is extended, as a minimum, along the first 0.25 m of the sedimentary record in intertidal coarse-grained sediments (sediments with about 90% of sand and gravel; Álvarez-Iglesias & Rubio, 2009) but it is restricted to the first 0.06 m in sediment cores with a higher fine-grained particles content (around 37%, core C2). In subtidal inner and middle ría sediments oxic conditions hold only in the top few millimetres (Rubio et al., 2010; Álvarez-Iglesias & Rubio, 2012), whereas the oxic zone is restricted to the top decimetre of outer ría sediments (Rubio et al., 2010).

The suboxic zone is characterized by a very low concentrations of oxygen. Here nitrate reduction, Mn reduction and Fe reduction take place (Froelich et al., 1979). Once interstitial water O_2 is consumed, a narrow denitrification zone appears where nitrate is the oxidant. This process accounts for a small percent of the degradation of organic matter (Canfield & Raiswell, 1991). It is also observed an extensive oxidation of those sulphides migrating towards surface, generating elemental Sulphur and sulphate. Then, interstitial waters in the suboxic zone are slightly acidic, and dissolution of carbonated shells takes place. Sediments show glauconite and other Fe^{+2}-Fe^{+3} silicates, Mn carbonates (rhodocrosite), Fe carbonates (siderite), Fe phosphates (vivianite), non-sulphidic minerals and, usually, a low content of organic matter. In inner Ría de Vigo the suboxic zone is extended approximately from 0.06 to 0.22 m in intertidal sediment cores with a high fine-grained particles content (Álvarez-Iglesias & Rubio, 2009). In subtidal inner and middle ría sediments, the suboxic conditions extend down to 0.10-0.20 m, and in outer ría sediments, down to 0.40 m, excepting those areas of strong turbulent currents (core SS5), where suboxic conditions extend, as a minimum, down to a few meters (Rubio et al., 2010; Álvarez-Iglesias & Rubio, 2012).

Buried Mn oxides below surficial oxic layer are reductively dissolved in the suboxic layer and Mn^{+2} are released to the interstitial waters. These ions diffuse towards surface because of a concentration gradient, reprecipiting as a "second generation", "third generation", etc., of oxides in the bottom of the oxic layer. Then, it can be generated sedimentary layers highly enriched in Mn over the Mn-redox limit as a result of Mn oxidative repreciplitation in the oxic layer (called "Mn trap"). Similarly, Fe^{2+} diffusion towards surface will generate Fe oxyhydroxides repreciplitation. Then, Fe and Mn profiles can be highly affected by redox changes. This has clearly been observed in intertidal sand flat sediments of inner Ría de Vigo, where subsurficial maxima were detected for both elements related to Fe and Mn ions migration and repreciplitation (Álvarez-Iglesias et al., 2003). It has also been detected in middle and outer ría sediments, where it has been observed Mn reducible (BCR method) maxima in the metal content profiles (Rubio et al., 2010). Associated to those maxima it has also been observed Cu, Pb and Zn maxima in the reducible fraction of Ría de Vigo sediments, indicating trace metal coprecipitation with the authigenic oxyhydroxides.

The anoxic-sulphidic zone or sulphate-reduction zone (SRZ) is characterized by metal sulphide generation (Huerta-Díaz & Morse, 1992). Strict anaerobic bacteria run sulphate-reduction, which is a dominant process in marine sediments, in particular, this process accounts for about 50 % of organic matter degradation in coastal sediments (Jørgensen, 1982). When organic matter is degraded by sulphate reduction weak acids are generated (HCO_3^-, HS^-, HPO_4^{2-}), then carbonate subsaturation (coming from the previous zone) is maintained. Most of the generated sulphide ions are oxidized in the redox upper boundary but a significant proportion reacts with iron to form, in the last step, pyrite. The main Fe sources are detrital Fe minerals, in particular fine-grained Fe oxides. Sulphide ions can also react with organic matter and form organosulphur compounds, which represents usually a small fraction in coastal sediments (Berner, 1970, 1981; Fig. 9). While sulphide is removed from dissolution by sulphide generation, interstitial waters pH increase and then, carbonate saturation happens. Then, typical minerals in the SRZ are pyrite, marcasite, rhodocrosite, and alabandite. Different metal ions can coprecipitate with authigenic pyrite or form other sulphides, then, their bioavailability will be limited while environmental reducing conditions maintain. In anoxic sediments from the inner sector of Ría de Vigo it has been

observed that ~28% of Cu, ~34% of Pb and ~1.5% of Zn is retained in the pyrite-bound fraction in intertidal sediments, whereas ~82% of Cu, ~18% of Pb and ~5.1% of Zn in the same fraction of subtidal sediments (Álvarez-Iglesias & Rubio, 2008, 2009). In middle and outer ría sediments it has been observed, in general, an increase with depth in the contents of Cu and Zn in the oxidizable fraction (BCR method) that would probably be related to sulphide generation, taking into account that the organic fraction accounted for ~1.2% of Cu and ~5.2% of Zn in anoxic sediments and ~2.3% of Cu and ~5.1% of Zn in suboxic sediments from the subtidal inner ría sector.
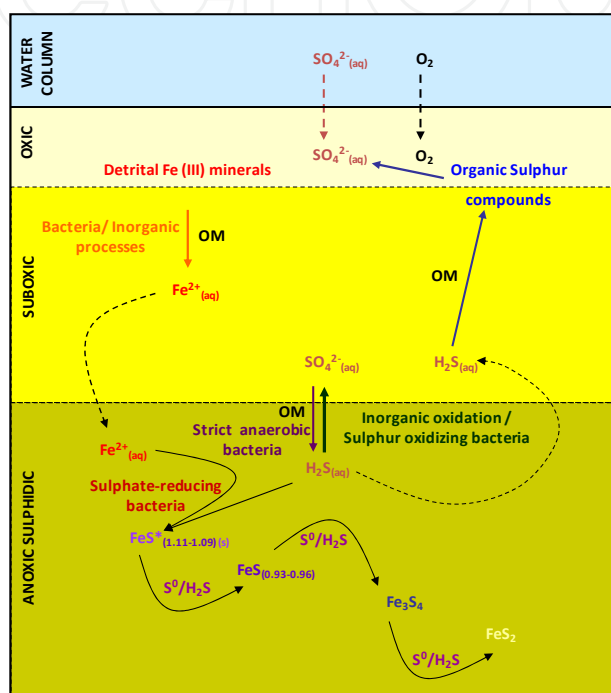
Fig. 9. Schematic representation of pyrite formation in marine sediments (modified from Berner (1970), Rickard et al. (1995) and Schoonen & Barnes (1991). OM= organic matter.

At low temperatures pyrite formation can be conceptually reduced to two steps: a) precipitation of an iron monosulphide precursor (FeS*), and b) pyrite formation by S addition (Berner, 1970; Rickard et al., 1995; Schoonen & Barnes, 1991) (Fig. 9). Nevertheless, direct pyrite precipitation has been described in saltmarsh sediments without intermediate precursors (Giblin & Howard, 1984). The most common pyrite morphologies described in Galician rías sediments, are euhedral and single framboids or polyframboids (Rubio et al., 2001; Álvarez-Iglesias & Rubio, 2012).

In the SRZ it could be observed Mn peaks. Alcalinity genesis in this zone is avoided when organism galleries penetrate actively and regularly. This causes sulphide oxidation. Carbonate dissolution may happen too (Aller, 1982; Canfield & Raiswell, 1991). The limit between the suboxic zone and the SRZ is called redoxcline. It represents a barrier to element transport by diffusion because of the presence of amorphous Fe-Mn oxyhydroxides. It is a dynamic limit, changing its position temporally and spatially. It can be detected de visu in intertidal sediments, such as those of inner Ría de Vigo, by the colour change between the brown-reddish oxidized surficial sediments –which reflects Fe oxides precipitation- and the

dark grey-black reduced sediments-which reflects pyrite precipitation. The anoxic zone develops from 0.14 to 0.18 m in those intertidal sediment cores from the inner ría with a high fine-grained particles content (core C2; Álvarez-Iglesias & Rubio, 2009). In subtidal sediments from inner and middle ría the anoxic zone is extended down the first one-two decimetres of the sedimentary record (with the exception of turbulent areas), whereas in the outer zone, down the first 0.40 m (Rubio et al., 2010; Álvarez-Iglesias & Rubio, 2012). Then, the diagenetic zones all became thicker, as well as lying deeper, as the mouth of the ría was approached.

Finally, the anoxic-non sulphidic zone or methanogenic zone (MZ) is characterized by methane generation by bacterial fermentation (Froelich et al., 1979) which causes a slight pH diminution. Typical minerals in the MZ are siderite, vivianite, rhodocrosite and previously formed sulphides. The MZ only developes if high organic matter quantities have not been degraded in the SRZ. Then, its development is favoured in areas with a high organic carbon flux to the sediments and/or high sedimentation rates, where up to 10% of the sedimentary organic matter is consumed by methanogenesis. When methane solubility is exceeded, gas bubbles accumulate and methane gas will diffuse upwards. In subtidal sediments of the Ría de Vigo it has been described several shallow gas fields, where biogenic methane was detected (García-Gil et al., 2002; Iglesias & García-Gil, 2007) and gas bubbles have been observed in the sediments (Álvarez-Iglesias et al., 2006; García-Gil et al., 2002). The top of the gas fields was located at sediment depths ranging between 11 and 0 m, shallowing towards the ría head (García-Gil et al., 2002; Iglesias & García-Gil, 2007).

7. Conclusion

The study of the sedimentary record allows establishing metal pollution history spatially and temporally for a particular area and needs to be multidisciplinary. First, hydrological, hydrographical, geological and anthropological information (industrial and rural development) on the study area needs to be compiled. Second, adequate analytical techniques, reference materials and background levels have to be selected. Background levels and metal concentrations in target samples should be analyzed by the same analytical protocols.

It has to be considered the relationships between metal concentrations, mineralogy, grain-size and metal sources. Sediments from Ría de Vigo showed that lithogenic elements such as Al, V or Ni were more abundant in fine-grained sediments and elements such as Si, in coarse grained sediments, showing the typical association of trace metals to organic-rich fine-grained sediments. Furthermore, biogenic inputs caused a dilution of detrital metal inputs. For correction of this grain-size effect, the use of normalization techniques is highly recommended.

It is also recommended the use of local or regional background levels to take into account the geological variability of the study area. It is useful for its selection to analyze deep sediments with no-human influence and to use metal-Al scatter-plots to identify outliers (enriched samples). This procedure has shown that in the Ría de Vigo sediments two clear sediment populations can be differentiated influenced by the watersheds composition (metallic natural source) and two different BLs have been considered, depending on the population.

Metal pollution can be identified by the use of pollution indexes, such as the Contamination Factor and the Enrichment Factor. These indexes showed that sediments of Ría de Vigo are moderatelly polluted by Cu and Zn in the first one-two decimeters of the sedimentary record, whereas moderatelly to very highly polluted by Pb, specially in the inner ría sediments.

Metal concentration alone it is not enough to evaluate metal availability and mobility, then, metal speciation protocols have to be considered. The protocols usually followed are those non-selective. In Ría de Vigo sediments, in general, a significant percentage of Cu, Pb and Zn is hosted in the residual fraction, whereas a small content is retained in the interchangeable and bound to carbonates fraction. Metal fraction content bound to Fe-Mn oxyhydroxides is higher in intertidal than subtidal inner ría sediments. Nevertheless, the reactive fraction content contribution is higher in middle and outer ría sediments. Concentrations of Cu, Pb and Zn are very low in the labile fraction of middle and outer ría sediments, and also, the Zn contents in the interchangeable and bound to carbonates fractions. Nevertheless, Pb concentrations in these last two fractions-that are highly bioavailable- in intertidal sediments oversize the background levels established for total concentrations.

The modification of metal speciation patterns by diagenetical processes has been showed for Ría de Vigo sediments, where Mn enrichments were detected, clearly in sandy intertidal sediments. Different sedimentary environments –oxic, suboxic, anoxic-non sulphidic- and their extension has been detected in the studied ría sediments. The boundaries between these diagenetic zones became deeper towards the ría mouth.

8. Acknowledgment

9. References

Ackermann, F. (1980). A procedure for correcting the grain size effect in heavy metal analyses of estuarine and coastal sediments. *Environmental Technology Letters*, Vol. 1, pp. 518-527.

Aller, R.C. (1982). Carbonate dissolution in nearshore terrigenous muds—the role of physical and biological reworking: *Journal of Geology*, Vol. 90, pp. 79-95.

Álvarez-Iglesias, P.; Quintana, B., Rubio, B. & Pérez-Arlucea, M. (2007). Sedimentation rates and trace metal input history in intertidal sediments derived from ^{210}Pb and ^{137}Cs chronology. *Journal of Environmental Radioactivity*, Vol. 98, pp. 229-250.

Álvarez-Iglesias, P. & Rubio, B. (2008). The degree of trace metal pyritization in subtidal sediments of a mariculture area: application to the assessment of toxic risk. *Marine Pollution Bulletin,* Vol. 56, pp. 973–983.

Álvarez-Iglesias, P. & Rubio, B. (2009). Redox status and heavy metal risk in intertidal sediments in NW Spain as inferred from the degrees of pyritization of iron and trace elements. *Marine Pollution Bulletin*, Vol. 58, pp. 542-551.

Álvarez-Iglesias, P. & Rubio, B. (2012). Early diagenesis of organic-matter-rich sediments in a ría environment: Organic matter sources, pyrites morphology and limitation of pyritization at depth. *Estuarine, Coastal and Shelf Science,* Vol. 100, pp. 113-123.

Álvarez-Iglesias, P.; Rubio, B. & Pérez-Arlucea, M. (2006). Reliability of subtidal sediments as "geochemical recorders" of pollution input: San Simón Bay (Ría de Vigo, NW Spain). *Estuarine, Coastal and Shelf Science,* Vol. 70, pp. 507-521.

Álvarez-Iglesias, P.; Rubio, B. & Vilas, F. (2003). Pollution in intertidal sediments of San Simón Bay (Inner Ría de Vigo, NW of Spain): total heavy metal concentrations and speciation. *Marine Pollution Bulletin*, Vol. 46, pp. 491-506.

Álvarez-Salgado, X. A.; Gago, J.; Míguez, B. M.; Gilcoto, M. & Pérez, F. F. (2000). Surface waters of the NW Iberian Margin: upwelling on the shelf versus outwelling of upwelled waters from the Rías Baixas. *Estuarine, Coastal and Shelf Science,* Vol. 51, pp. 821-837.

Barreiro Lozano, R. (1991): *Estudio de metales pesados en medio y organismos de un ecosistema de ría (Pontedeume, A Coruña).* Ph.D. Thesis, Universidad de Santiago de Compostela, 227 p.

Belzunce-Segarra, M.J.; Bacon, J.R.; Prego, R. & Wilson, M.J. (1997). Chemical forms of heavy metals in surface sediments of the San Simon inlet, Ria de Vigo, Galicia. *Journal of Environmental Science and Health*, Vol. A32, pp. 1271-1292.

Berner, R.A. (1970). Sedimentary pyrite formation. *American Journal of Science,* Vol. 268, pp. 1-23.

Berner, R.A. (1981). A new geochemical classification of sedimentary environments. *Journal of Sedimentary Petrology*, Vol. 51, No.2, pp. 359-365.

Borovec, Z. (1996). Evaluation of the concentrations of trace elements in stream sediments by factor and cluster analysis and the sequential extraction procedure. *The Science of the Total Environment*, Vol. 177, pp. 237-250.

Bryan, G.W. & Langston, W.J. (1992). Bioavailability, accumulation and effects of heavy metals in sediments with special reference to United Kingdom Estuaries: a review. *Environmental Pollution,* Vol. 76, pp. 89-131.

Boyle, J.F. (2000). Rapid elemental analysis of sediment samples by isotope source XRF. *Journal of Paleolimnology*, Vol. 23, pp. 213-221.

Campbell, P.G.C.; Lewis, A.G.; Chapman, P.M.; Crowder, A.A.; Fletcher, W.K.; Imber, B.; Luoma, S.N.; Stokes, P.M. & Winfrey, M. (1988). *Biologically available metals in sediments.* NRCC, Division of Chemistry Publication, Otawa, 296 pp.

Canfield, D.E. & Raiswell, R. (1991). Pyrite formation and fossil preservation, *Taphonomy: Releasing the Data Locked in the Fossil Record. Topics in Geobiology.* P.A. Allison & D.E.G. Briggs (Eds.), Vol. 9, 337–387.

Carral, E.; Puente, X.; Villares, E. & Carballeira, A. (1995a). Background heavy metal levels in estuarine sediments and organism in Galicia (Northwest Spain) as determined by modal analysis. *Science of the Total Environment*, Vol. 172, pp. 175-188.

Carral, E.; Villares, R.; Puente, X. & Carballeira, A. (1995b). Influence of watershed lithology on heavy metal levels in estuarine sediments and organisms in Galicia (North-west Spain). *Marine Pollution Bulletin*, Vol. 30, No.9, pp. 604-608.

Chester, R. & Voutsinou, F. G. (1981). The initial assessment of trace metal pollution in coastal sediments. *Marine Pollution Bulletin*, Vol. 12, pp. 84-91.

Dassenakis, M.I.; Kloukiniotou, M.A. & Pavlidou, A.S. (1996). The influence of long existing pollution on trace metal levels in a small tidal Mediterranean Bay. *Marine Pollution Bulletin*, Vol. 32, pp. 275-282.

Duffus, J.H. (2002). "Heavy metals" – A meaningless term? *Pure Applied Chemistry*, Vol. 74, pp. 793-807.

Fichet, D.; Radenac, G. & Miramand, P. (1998). Experimental studies of impacts of harbour sediments resuspension to marine invertebrates larvae: bioavailability of Cd, Cu, Pb and Zn and toxicity. *Marine Pollution Bulletin*, Vol. 36, pp. 509-518.

Flyhammar, P. (1998). Use of sequential extraction on anaerobically degraded municipal solid waste. *The Science of the Total Environment*, Vol. 212, pp. 203-215.

Förstner, U. (1989). *Contaminated Sediments. Lecture notes on Earth Science 21*. Springer-Verlag, London, 157 pp.

Freire, J. & García-Allut, A. (2000). Socioeconomic and biological causes of management failures in European artisanal fisheries: the case of Galicia (NW Spain). *Marine Policy*, Vol. 24, pp. 375-384.

Froelich, P.N.; Klinkhammer, G.P.; Bender, M.L.; Luedtke, N.A.; Heath, G.R.; Cullen, D.; Dauphin P.; Hammond, D. & Hartman, B. (1979). Early oxidation of organic matter in pelagic sediments of the eastern equatorial Atlantic: suboxic diagenesis. *Geochimica et Cosmochimica Acta*, Vol. 43, pp. 1075-1090.

García-Gil, S.; Vilas, F. & García-García, A. (2002). Shallow gas features in incised-valley fills (Ria de Vigo, NW Spain): a case study. *Continental Shelf Research*, Vol. 22, pp. 2303-2315.

Giblin, A.E. & Howarth, R.W. (1984). Porewater evidence for a dynamic sedimentary iron cycle in salt marshes. *Limnology and Oceanography*, Vol. 29, pp. 47-63.

Gómez Ariza, J.L.; Giráldez, I.; Sánchez-Rodas, D. & Morales, E. (2000). Comparison of the feasibility of three extraction procedures for trace metal partitioning in sediments from South-West Spain. *The Science of the Total Environment*, Vol. 246, pp. 271-283.

González-Pérez, J.M. & Pérez González, A. (2003). Demographic dinamycs and urban planning in Vigo since 1960. The impact of industrialization. *Anales de Geografía de la Universidad Complutense*, Vol. 23, pp. 163-185.

Guy, R.D.; Chakrabarti, C.L. & McBain, D.C. (1978). An evaluation of extraction techniques for the fractionation of Copper and Lead in model sediment systems. *Water Research*, Vol. 12, pp. 21-24.

Hakanson, L. (1980). An ecological risk index for aquatic pollution control. A sedimentological approach. *Water Research*, Vol. 14, pp. 975-1001.

Hakanson, L. (1984). Metals in fish and sediments from the River Kolbäcksan water system, Sweden. *Archiv für Hydrobiologie*, Vol. 101, No.3, pp. 373-400.

Horowitz, A.J. & Elrick, K.A. (1987). The relation of stream sediment surface area, grain size, and composition of trace element chemistry. *Applied Geochemistry*, Vol. 2, pp. 437-451.

Howard, J.L & Shu, J. (1996). Sequential extraction analysis of heavy metals using a chelating agent (NTA) to counteract resorption. *Environmental Pollution*, Vol. 91, No. 1, pp. 89-96.

Huerta-Díaz, M.A. & Morse, J.W. (1992). Pyritisation of trace metals in anoxic marine sediments. *Geochimica et Cosmochimica Acta*, Vol. 56, pp. 2681-2702.

Huerta-Díaz, M.A. & Morse, J. (1990). A quantitative method for determination of trace metal concentrations in sedimentary pyrite. *Marine Chemistry*, Vol. 29, pp. 119-144.

IGME (1981). *Mapa Geológico de España*, 1:50000, Servicio de Publicaciones Ministerio de Industria y Energía.

Imperato, M.; Adamo, P.; Naimo, D.; Arienzo, M.; Stanzione, D. & Violante, P. (2003). Spatial distribution of heavy metals in urban soils of Naples city (Italy). *Environmental Pollution*, Vol. 124, pp. 247-256.

Iglesias, J. & García-Gil. S., 2007. High-resolution mapping of shallow gas accumulations and gas seeps in San Simón Bay (Ría de Vigo, NW Spain). *Geo-Marine Letters*, Vol. 27, pp. 103-114.

Izquierdo, C.; Usero, J. & Gracia, I. (1997). Speciation of heavy metals in sediments from salt marshes on the Southern Atlantic Coast of Spain. *Marine Pollution Bulletin*, Vol. 34, No. 2, pp. 123-128.

Jørgensen, B.B. (1982). Mineralization of organic matter in the sea bed- the role of sulphate reduction. *Nature*, Vol. 296, pp. 643-645.

Kersten, M. & Förstner, U. (1987). Effect of sample pretreatment on the reliability of solid speciation data of heavy metals -implications sesfor the study of early diagenetic processes. *Marine Chemistry*, Vol. 22, pp. 99-312.

León, I.; Méndez, G. & Rubio, B. (2004). Geochemical phases of Fe and degree of pyritization in sediments from Ría de Pontevedra (NW Spain): Implications of mussel raft culture. *Ciencias Marinas,* Vol. 30, pp. 585-602.

Loring, D.H. (1981). Potential bioavailability of trace metals in eastern Canadian estuarine sediments. *Rapports et Proces-Verbaux des Reunions, Conseil International pour l'Exploration de la Mer*, Vol. 181, pp. 93-101.

Loring, D.H. (1990). Lithium-a new approach for the granulometric normalization of trace metal data. *Marine Chemistry*, Vol. 29, pp. 155-168.

Luoma S.N. & Bryan, G.W. (1981). A statistical assessment of the form of trace metals in oxidized estuarine sediment employing chemical extractants. *The Science of the Total Environment*, Vol. 17, pp. 165-196.

Luoma, S.N. (1986). A comparison of two methods for determining copper partitioning in oxidized sediments. *Marine Chemistry*, Vol. 20, pp. 45-49.

Mahan, K. I.; Foderaro, T.A.; Garza, T.L.; Martínez, R.M.; Maroney, G.A.; Trivisonno, M.R. & Willging, E.M. (1987). Microwave digestion techniques in the sequential extraction of Calcium, Iron, Chromium, Manganese, Lead and Zinc in sediments. *Analytical Chemistry*, Vol. 59, pp. 938-945.

Moore, H.W. (1991). *Inorganic Contaminants of Surface Water. Research and Monitoring priorities*. Springer-Verlag, New York, 334 pp.

Ngiam, L.-S. & Lim, P.-E. (2001). Speciation patterns of heavy metals in tropical estuarine anoxic and oxidized sediments by different sequential extraction schemes. *The Science of the Total Environment*, Vol. 275, pp. 53-61.

Pérez-Arlucea, M.; Méndez, G.; Clemente, F.; Nombela, M.; Rubio, B. & Filgueira, M. (2005). Hydrology, sediment yield, erosion and sedimentation rates in the estuarine environment of the Ría de Vigo, Galicia, Spain. *Journal of Marine Systems*, Vol. 54, pp. 206-226.

Prego, R. & Cobelo-Garcia, A. (2003). Twentieth century overview of heavy metals in the Galician Rias (NW Iberian Peninsula). *Environmental Pollution,* Vol. 121, pp. 425–452.

Prego, R., Otxotorena, U. & Cobelo-García, A. (2006) Presence of Cr, Cu, Fe and Pb in sediments underlying mussel-culture rafts (Arosa and Vigo rias, NW Spain). Are they metal-contaminated areas? *Ciencias Marinas*, Vol. 32, No.2B, pp. 339-349.

Quevauviller, Ph.; Rauret, G.; López-Sánchez, J-F.; Rubio, R.; Ure, A. & Muntau, H. (1997). Certification of trace metal extractable contents in a sediment reference material (CMR 601) following a three-step sequential extraction procedure. *The Science of the Total Environment*, Vol. 205, pp. 223-234.

Raiswell, R.; Buckley, F.; Berner, R. & Anderson, T. (1988). Degree of pyritization of iron as a paleoenvironmental indicator of bottom-water oxygenation. *Journal of Sedimentary Petrology*, Vol. 58, pp. 812-819.

Rapin, F. & Förstner, U. (1983). Sequential leaching techniques for particulate metal speciation: the selectivity of various extractants, In: *Proceedings of the 4th Conference on Heavy Metals and the Environment* (Heidelberg, Germany), 1074-1077.

Rendell, P.S.; Bately, G.E. & Cameron, A.J. (1980). Adsorption as a control of metal concentrations in sediment extracts. *Environmental Technology Letters*, Vol. 14, pp. 314-318.

Rey, D.; Mohamed, K.J.; Bernabeu, A.; Rubio, B. & Vilas, F. (2005). Early diagenesis of magnetic minerals in marine transitional environments: geochemical signatures of hydrodynamic forcing. *Marine Geology*, Vol. 215, pp. 215-236.

Rickard, D.; Schoonen, M.A.A. & Luther III, G.W. (1995). Chemistry of iron sulfides in sedimentary environments, In: *Geochemical Transformations of Sedimentary Sulfur*, M.A. Vairavamurthy & M.A.A. Schoonen (Eds.), Vol. 612, 168-193. American Chemical Society Symposium Series.

Roychoudhury, A.N.; Kostka, J.E. & Van Capellen, P. (2003). Pyritization: a palaeoenvironmental and redox proxy reevaluated. *Estuarine, Coastal and Shelf Science,* Vol. 57, pp. 1183-1193.

Rubio, B.; Álvarez-Iglesias, P. & Vilas, F. (2010). Diagenesis and anthropogenesis of metals in the recent Holocene sedimentary record of the Ría de Vigo (NW Spain). *Marine Pollution Bulletin*, Vol. 60, pp. 1122-1129.

Rubio, B.; Nombela M.A. & Vilas F. (2000a). Geochemistry of major and trace elements in sediments of the Ría de Vigo (NW Spain): An assessment of metal pollution. *Marine Pollution Bulletin*, Vol. 40, pp. 968-980.

Rubio, B.; Nombela M.A. & Vilas F. (2000b): La contaminación por metales pesados en las Rías Baixas gallegas: nuevos valores de fondo para la Ría de Vigo (NO de España). *Journal of Iberian Geology*, Vol. 26, pp. 121-149.

Rubio, B.; Pye, K.; Rae, J. & Rey, D. (2001). Sedimentological characteristics, heavy metal distribution and magnetic properties in subtidal sediments, Ría de Pontevedra, NW Spain. *Sedimentology,* Vol. 48 No.6, pp. 1277-1296.

Rubio, B.; Rey, D.; Bernabeu, A.; Vilas, F. & Rodríguez-Germade, I. (2011). Nuevas técnicas de obtención de datos geoquímicos de alta resolución en testigos sedimentarios, el XRF core scanner, In: *Métodos y técnicas en investigación marina*. Editorial TECNOS, Madrid (Spain), 383-393.

Salomons, W. & Förstner, U. (1984). *Metals in the hydrocycle*. Springer-Verlag, Berlin, 349 p.

Salomons, W.; Kerdiijk, H.; Van Pagee, H. & Schreur, A. (1985). Behaviour and impact assessment of heavy metals in estuarine and coastal zones, In: *Metals in Coastal Environments of Latin America*. U. Seeliger; L.D. de Lacerda & S.R. Patchineelam (Eds.), 157-198.

Schoonen, M.A.A. & Barnes, H.L. (1991). Reactions forming pyrite and marcasite from solution: II. Via FeS precursors below 100°C. *Geochimica et Cosmochimica Acta*, Vol. 55, pp. 1505-1514.

Shaw, T.J.; Gieskes, J.M. & Jahnke, R.A. (1990). Early diagenesis in differing depositional environments: the response of transition metals in pore water. *Geochimica et Cosmochimica Acta*, Vol. 54, pp. 1233-1246.

Stephens, S.R.; Alloway, B.J.; Parker, A.; Carter, J.E. & Hodson, M.E. (2001). Changes in the leachability of metals from dredged canal sediments during drying and oxidation. *Environmental Pollution*, Vol. 114, pp. 407-413.

Summers, J.K.; Wade, T.L. & Engle, V.D. (1996). Normalization of metal concentrations in estuarine sediments from the Gulf of Mexico. *Estuaries*, Vol. 19, No.3, pp. 581-594.

Taylor, S.R. (1964). Abundance of chemical elements in the continental crust: a new table. *Geochimica et Cosmochimica Acta*, Vol. 28, pp. 1273-1285.

Tessier, A. & Campbell, P.G.C. (1987). Partitioning of trace metals in sediments: relationships with bioavailability. *Hydrobiologia*, Vol. 149, pp. 43-52.

Tessier, A. & Campbell, P.G.C. (1988). Partitioning of trace metals in sediments, In: *Metal Speciation: Theory, Analysis and Application*, J.R. Kramer & H.E. Allen (Eds.), 183-199, Lewis Publishers, Inc.

Tessier, A., Campbell P.G.C. & Bisson, M. (1979). Sequential extraction procedure for the speciation of particulate trace metals. *Analytical Chemistry*, Vol. 51, pp. 844-851.

Turekian, K.K. & Wedepohl, K.H. (1961). Distribution of the elements in some major units of the Earth's Crust. *Geological Society of America Bulletin*, Vol. 72, pp. 175-192.

Uhrberg, R. (1982). Acid digestion bomb for biological samples. *Analytical Chemistry*, Vol. 54, pp. 1906-1908.

Ure, A.M.; Quevauviller, P.; Muntau, H. & Griepink, B. (1993). Speciation of heavy metals in soils and sediments: an account of the improvement and harmonization of extraction techniques undertaken under the auspices of the BCR of the Commission of the European Communities. *International Journal of Environmental Analytical Chemistry*, Vol. 51, pp. 135–151.

Varekamp, J.C. (1991). Trace element geochemistry and pollution history of mud flats and marsh sediments from the Connecticut River estuary. *Journal of Coastal Research*, Vol. SI11, pp. 105-124.

Vega, F.A.; Covelo, E.F & Andrade, M.L. (2008). Impact of industrial and urban waste on the heavy metal content of salt marsh soils in the southwest of the province of Pontevedra (Galicia, Spain). *Journal of Geochemical Exploration*, Vol. 96, pp. 148-160.

Vilas, F.; Bernabeu, A. M. & Méndez, G. (2005). Sediment distribution pattern in the Rías Baixas (NW Spain): main facies and hydrodynamic dependence. *Journal of Marine Systems*, Vol. 54, pp. 261-276.

Wangersky, P.J. (1986). Biological control of trace metal residence time and speciation: A review and synthesis. *Marine Chemistry*, Vol. 18, pp. 269-297.

Wedepohl, K.H. (1971). Environmental influences on the chemical composition of shales and clays, In: *Physics and chemistry of the Earth*, L.H. Ahrens; F. Press; S.K. Runcorn & H.C. Urey, (Eds.), 307-331, Oxford, Pergamon.

Wedepohl, K.H. (1991). The composition of the upper Earth's crust and the natural cycles of selected metals: metals in natural raw materials; natural resources, In: *Metals and Their Compounds in the Natural Environment*, E. Merian (Ed.), 3-17, Weinheim: VCH.

Wignall, P.B. (1994). *Black shales and their controversies*, Oxford University Press, 124 p.

Zoller, W.H.; Gladney, E.S.; Gordon, G.E. & Bors, J.J. (1974). Emissions of trace elements from coal fired power plants, In: *Trace Substances in Environmental Health*, D.D. Hemphill (Ed.), Vol. 8, 167-172, Rolla, University of Missouri, Columbia.

Zwolsman, J.J.G; Berger, G.W. & Van Eck, G.T.M. (1993). Sediment accumulation rates, historical input, postdepositional mobility and retention of major elements and trace metals in salt marsh sediments of the Scheldt Estuary, SW Netherlands. *Marine Chemistry*, Vol. 44, pp. 73-94.
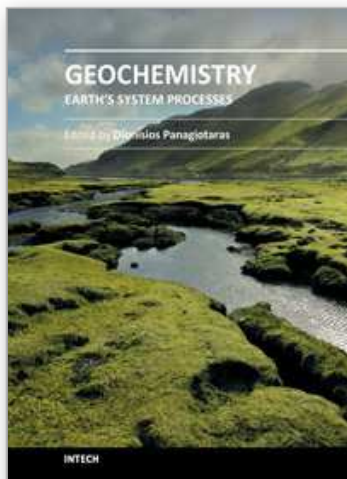
Geochemistry - Earth's System Processes

Edited by Dr. Dionisios Panagiotaras

This book brings together the knowledge from a variety of topics within the field of geochemistry. The audience for this book consists of a multitude of scientists such as physicists, geologists, technologists, petroleum engineers, volcanologists, geochemists and government agencies. The topics represented facilitate as establishing a starting point for new ideas and further contributions. An effective management of geological and environmental issues requires the understanding of recent research in minerals, soil, ores, rocks, water, sediments. The use of geostatistical and geochemical methods relies heavily on the extraction of this book. The research presented was carried out by experts and is therefore highly recommended to scientists, under- and post-graduate students who want to gain knowledge about the recent developments in geochemistry and benefit from an enhanced understanding of the dynamics of the earth's system processes.

How to reference

In order to correctly reference this scholarly work, feel free to copy and paste the following:

INTECH

open science | open minds