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Geochemistry of Major and Trace Elements in Sediments of the Ria de Vigo (NW Spain): an Assessment of Metal Pollution☆

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Ria de Vigo is a funnel-shaped, fault-bounded coastal embayment in Galicia, NW Spain. There are a number of important centres of population and industrial activity along its margins, which serve as sources of pollution. Sixty-six subtidal sediment samples have been collected in the Ria. The samples have been subjected to a total digestion technique and analysed for major and trace elements (Al, Fe,Ti, Mn, Cu, Pb, Cr, Zn, Co, As, Ni, Cd and Sr). Variations of absolute metal concentrations reflected variations in textural and/or carbonate and organic matter content. Geoaccumulation indexes and enrichment factors have been calculated to assess whether the concentrations observed represent background or contaminated levels. It is proved that the choice of the background plays an important role in the interpretation of the geochemical data. PCA was a very useful tool to define background values for metals in the Ria de Vigo area. These values were similar to regional values given by other authors. It is concluded that the Ria is slightly to moderately polluted for some of the studied metals. The spatial extent of pollution was examined, and it was found that the most polluted area is located in the inner and southern parts of the Ria. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: heavy metals; Ria de Vigo; pollution; subtidal sediments; normalization; principal component analysis.

Introduction

In Galicia, 40% of the population live in or near Rias, and the principal industrialized areas are also located nearby, thus leading to a high risk of contamination. The city of Vigo is the biggest human settlement in Galicia (287000 inhabitants, INE, Padrón, 1996) and also one of the most important harbours. The Rias of north-west Spain are coastal ecosystems of high biological productivity and great economic importance. They are intensively exploited by man for fish and shellfish. Mariculture represents the most significant human impact in the past 20 years or so and has undoubtedly changed the nature of sedimentation in some parts of the Rias (Nombela *et al.*, 1995). Filter feeding mussels have led to a dramatic increase in biological production of sediment, changes to sediment type and increased sedimentation rates. Over the last 5–7 years, construction of hotels, urban and recreation areas has also produced changes to coastal sedimentary processes. However, the industrial waste reaching the sea through atmospheric precipitation and dumping of urban and rural waste is mostly responsible for the input of trace metals into the marine environment which are subsequently incorporated into the sediments.

In recent years, increasing interest has been shown in the level of heavy metals in sediments of the Galician Rias (Barreiro *et al.*, 1988; Carral *et al.*, 1992, 1995; Carballeira *et al.*, 1997). Most of these papers have only concerned intertidal sediments, probably due to the simplicity of collecting the samples. Although in some of these studies (e.g., Carballeira *et al.*, 1997), sampling distribution was extensive and appropriate for tidal flats and intertidal areas, there is a scarcity of data for subtidal areas.

The main objectives of the study reported here were:

1. To determine the total content of heavy metals in surface sediments of the Ria de Vigo, and to produce geochemical maps for the Ria, based on an appropiate sampling density (1 km^2), that can be used by other disciplines.
2. To evaluate the sedimentological and geochemical factors that control the distribution pattern of major and trace elements.
3. To estimate the anthropogenic input and to assess the pollution status on the area.

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Study Area

The Ria de Vigo constitutes the southermost Ria of the Rias Bajas (Fig. 1). The general shape in plan view is that of a funnel axially centred along N75E. The whole complex occupies an area of 176 km^2 with an axial length of 33 km and a maximum width of 10 km (at its mouth). Water depths are generally less than 50 m. The Ria becomes progressively narrower towards its head (Rande Strait) after which it widens to form a well-differentiated basin (San Simón Bay) which is notably smaller and generally shallower than the rest of the complex (Nombela *et al.*, 1995).

Two large islands (the Isles Cíes) located at the mouth of the Ria provide a natural protection from Atlantic swell. The almost north–south orientation of these islands leaves two relatively narrow corridors at the north and south entrances of the Ria. These two corridors constitute the natural connection between the Ria and the shelf and have water depths of 27 and 51 m, respectively.

The mean tidal range of the Ria de Vigo is 2.2 m. Water circulation belongs to the type of a partly stratified estuary (Prego and Fraga, 1992). The geology of the area is dominated by igneous and metamorphic rocks of Precambrian–Paleozoic age. The only younger rocks comprise Miocene–Quaternary continental sediments.

The Rias are characterized by seasonal upwelling and sharply contrasted boundary conditions at their seaward and landward margins (upwelling and estuarine, respectively) mean that they incorporate processes normally associated with both continental margin and coastal boundary zones. Both, water depth and salinity increase towards the Ria mouth and a positive residual circulation is normally present. However, only the landward margins (i.e., inner Rias) are properly estuarine, with density stratification produced by freshwater input.

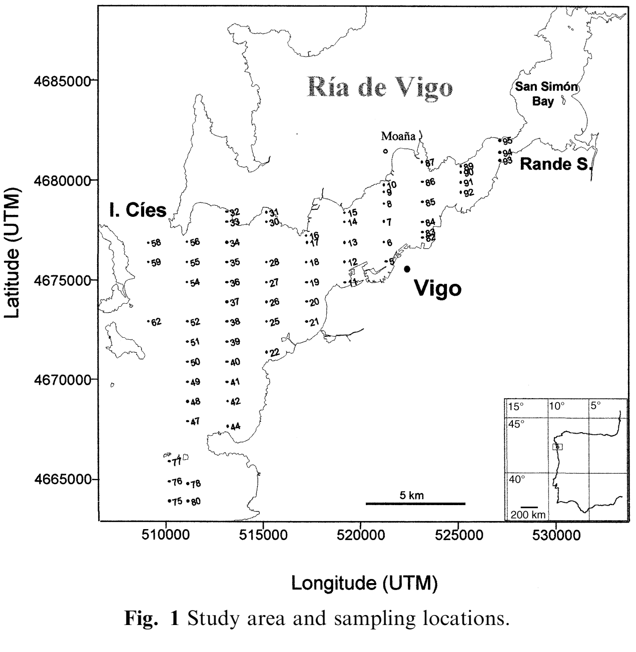

Fig. 1 Study area and sampling locations.

The sediments reflect the general character of the material transported by rivers from adjacent land areas, derived from shoreline erosion, carried by marine currents from external sources, produced in situ by organisms, and contributed by human activities. Recent sediments of the Ria de Vigo consist of terrigenous and biogenic deposits. The reconnaisance studies of the Ria de Vigo indicate a heterogeneous distribution of both terrigenous and carbonate sediments with a major axial deposit of cohesive sediments (Vilas *et al.*, 1995). The fine sediments are relatively rich in organic matter, particularly in the inner part of the Ria. The carbonate-rich sediments show a large proportion of bioclastic material in the sand fraction, but an important proportion is in the mud fraction. Carbonate material is concentrated near the Ria mouth, falling off rapidly into the inner Ria and more slowly offshore. The biogenic deposits, almost exclusively composed of carbonates, are produced by benthic organisms. The bioclasts are composed of calcareous algae and fragments of molluscs, echinoderms and crustacea, which are all abundant in the Ria de Vigo. Terrigenous sediments are supplied by the main river system (Oitabén-Verdugo) at the head of the Ria and by several small rivers and streams along the coast. These rivers do not carry large loads of suspended sediment into the Ria. Oitabén-Verdugo constitutes about 57.3% of the total catchment areas and thus the principal source of freshwater into the Ria. There is some evidence that sediment supply to the Ria de Vigo has been recently altered (Pazos and Nombela, 1996) by anthropogenic factors such as land use, agricultural activities and forest fires.

Material and Methods

Surface sediments were collected from 66 stations (Fig. 1) by using a Shipek drag sampler.

A representative portion of each sample was used for the determination of gravel, sand and mud ratios using the standard dry and wet sieving techniques (Folk, 1974). A second portion of each sample was finely powdered using an agate mortar and used for chemical analysis.

Organic carbon was determined by wet digestion and calcium carbonate by using a Bernald calcimeter. These determinations were performed as per Guitián and Carballas (1976). Analyses of metals were carried out using inductively coupled plasma atomic emission spectrophotometry ICP/AES, after triacid total digestion (HNO_3, HF and $HClO_4$). ICP has the advantage of simultaneously analysing all the metals in a single sample at low detection levels. The detection limits for trace elements were 0.1 μg ml^{-1} for Pb and As; 0.025 μg ml^{-1} for Zn, Ni, Co and Cr; 0.02 μg ml^{-1} for Cd and 0.05 μg ml^{-1} for Cu. Analytical blanks were run in the same way as the samples and concentrations were determined using standard solutions prepared in the same acid matrix. Suspensions were duplicated with results as mean values. Results are expressed in μg g^{-1} dry sediment. The accuracy and precision of our results were checked by analysing sediment reference material (CRM 277). The results indicate good agreement between the certified and the analytical values (Table 1), the recovery of elements being practically complete for most of them. Only in the case of Ni the recovery was approx. 83%.

Results and Discussion

Sediment type

Fig. 2 shows a box and wisker plot for the more relevant textural and other properties of the samples. The great variability range is noted in the figure where the horizontal bar in the box refers to the median value, the ends of the wiskers to the maximum and minimum values and the top and bottom of the boxes include half of the data between the median and the extremes of the range. Sediment properties are in concordance with the sedimentological setting described previously (Vilas *et al.*, 1995). Distribution patterns of percentage of organic matter and calcium carbonate are shown in Fig. 3, together with the less than 63 μm fraction. The organic matter content in the study area (Fig. 3(b)) ranges between 0.00% and 9.65% with maximum values in the inner and axial parts of the Ria. This is associated with the areas where fine-grained sediments are predominant, as seen in Fig. 3(a). Calcium carbonate content ranged between 1.37 and 94.26%, and contrary to organic matter, is highest in the external and outer parts of the Ria (Fig. 3(c)).

Spatial distribution patterns of elements

Spatial contour maps of surface metal concentrations provide a simple and effective manner of presenting results in contamination investigations (Chester and Voutsinou, 1981; Baker and Harris, 1991, Mackey and Hodgkinson, 1995; Steiger *et al.*, 1996). In this paper, contour maps were constructed using SURFER (Golden Software, 1993–1996). The interpolation method used was kriging and it was done following the recommended application for a uniformly spaced numerical data set given by Shan and Stephens (1994).

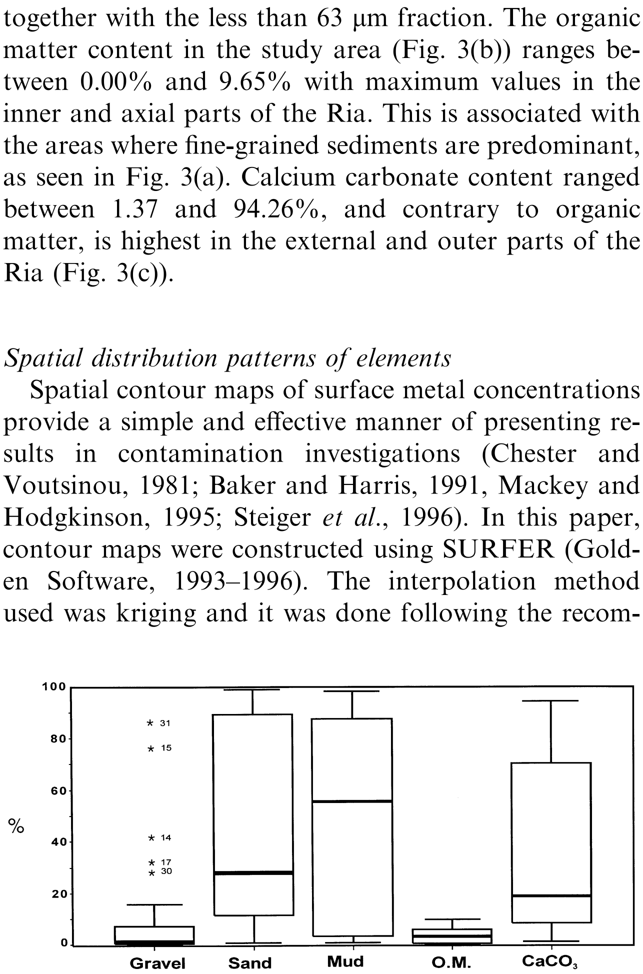

Fig. 2 General properties of the samples.

In general terms, heavy metal distribution in the Ria de Vigo exhibits three trends. Maximum values were detected in the innermost area close to the Rande Strait, in the surroundings of Vigo harbour and in the axial areas. Major elements (Al, Ti and Fe) best reflect these trends (Fig. 4). Iron content has a peak (7–8%) in the transect between Vigo-Moaña. On the contrary, the distribution of the majority of the trace elements follows only one or two of these trends. For example, Pb and Cu show highest values towards the inner parts and the southern margin of the Ria (Fig. 5). Chromium is distributed in a similar way (Fig. 5), with the exception of three sampling stations near the harbour where the values are very low (less than 9 μg g^{-1}).

The Zn content showed a very high value in the inner part of Vigo harbour (567 μg g^{-1}), but, excluding this value, mean values are approximately 90 μg g^{-1} (Fig. 6). By contrast, Co content (Fig. 6) shows high values in the axial part of the Ria with a minimum close to the Rande Strait (1.8 μg g^{-1}). Ni distribution (Fig. 6) shows a similar pattern as Co. For Mn, maximum concentrations (1170, 671 and 318 μg g^{-1}) are located around the southern entrance to the Ria, between the southern part of the Isles Cies and the mainland, corresponding to sandy areas (Fig. 7). Other authors (Shrader *et al.*, 1977) have found highest concentrations of Mn in the sand fractions. This phenomenon is most probably attributable to Mn oxide coatings on the sand grains. In our samples, the shells showed a reddish coating, although Mn oxides were not detected by X-ray diffraction (XRD). Nevertheless, in two of them (samples 42 and 48) was detected rhodocrosite ($MnCO_3$) by the reflection at 0.284 nm. Although a more representative mineral in the sediments of the Ria de Vigo is probably glauconite (Pazos *et al.*, 1997), rhodocrosite is a typical mineral in post-oxic sediments characterized by low concentrations of organic carbon (Berner, 1981). In any case, the presence of Mn inside the calcite in the sediments indicates the accumulation of these sediments under oxic conditions (Calvert and Pedersen, 1993). Ward *et al.* (1995) have also found this type of association Ca–Mn, and they suggest a co-precipitation of a calcite-manganese phase. This phase could also be present in some of these samples with high values of Mn, where rhodocrosite was not detected by XRD.

Sr, related to the biogenic carbonates, has, in general terms, an opposite distribution (Fig. 7) to the major elements, i.e., with a clear decrease in content towards the inner and axial part of the Ria.

Finally, Cd shows high values in the southern entrance to the Ria (close to 6 μg g^{-1}). However, a high percentage (77.6%) of the samples had no detectable values by ICP. The anomalous distribution of Cd is attributed to its occurrence close to the instrumental limit. The most frequently applied analytical method for cadmium is atomic absorption spectrometry (AAS)

TABLE 1

Comparison of the analytical results of the reference estuarine material (CRM 277) with the certified data.[a]

Metal	As (mg kg^{-1})	Cd (mg kg^{-1})	Cr (mg kg^{-1})	Cu (mg kg^{-1})	Ni (mg kg^{-1})	Pb (mg kg^{-1})	Zn (mg kg^{-1})	Al (mg g^{-1})	Co (µg g^{-1})	Fe (mg g^{-1})	Mn (mg g^{-1})	Sr (mg g^{-1})
Certified value	47.3 ± 1.6	11.9 ± 0.4	192 ± 7	101.7 ± 1.6	43.4 ± 1.6	146 ± 3	547 ± 12	(48)	(17)	(45.5)	1.5	–
Measured value	53.9 ± 1.2	10.85 ± 2.5	188 ± 0.62	99.08 ± 0.49	36.16 ± 2.1	160.1 ± 1.2	546 ± 1.6	–	23.04 ± 0.94	–	–	310.8 ± 0.5

[a] Values in parentheses are not certified.

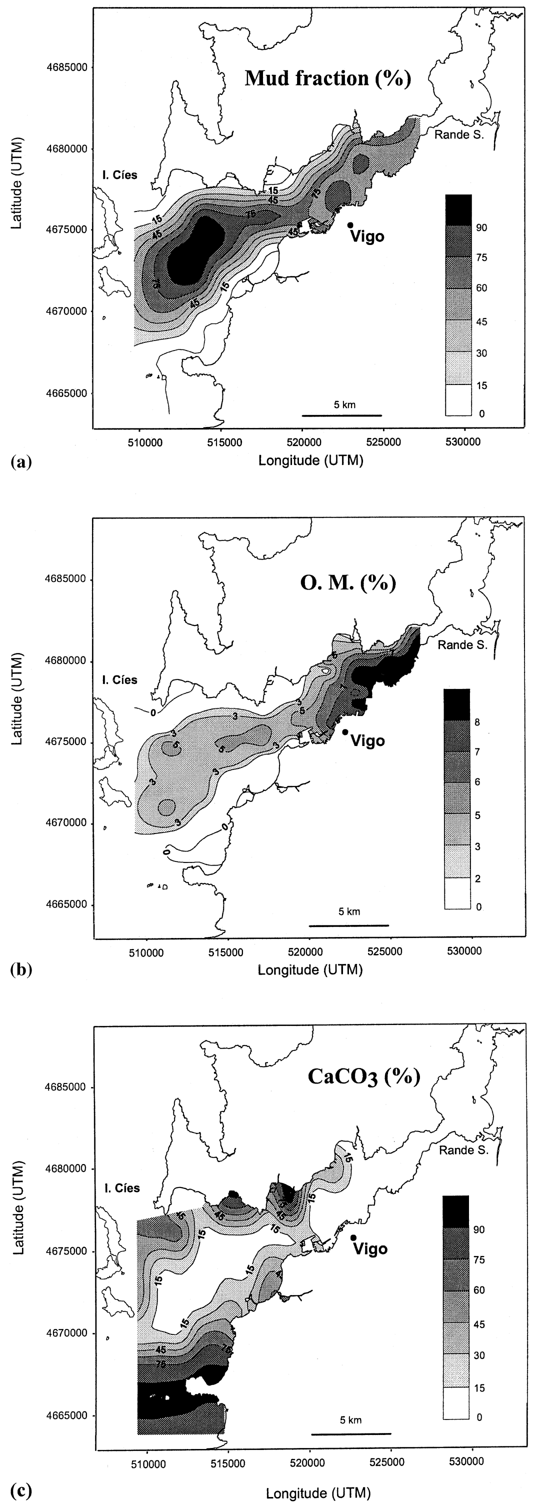

Fig. 3 Distribution of mud fraction (< 63 µm) (a), organic matter (OM) (b) and carbonate contents (c) in surficial sediments of the Ria de Vigo.

using flame and graphite furnace (Stoeppler, 1992). Other researchers have also criticized the efficiency of ICP for the determination of this element (Schramel *et al.*, 1982). Also, As was not detected in 58.2% of the samples and maximum concentrations were located in the surroundings of the harbour area.

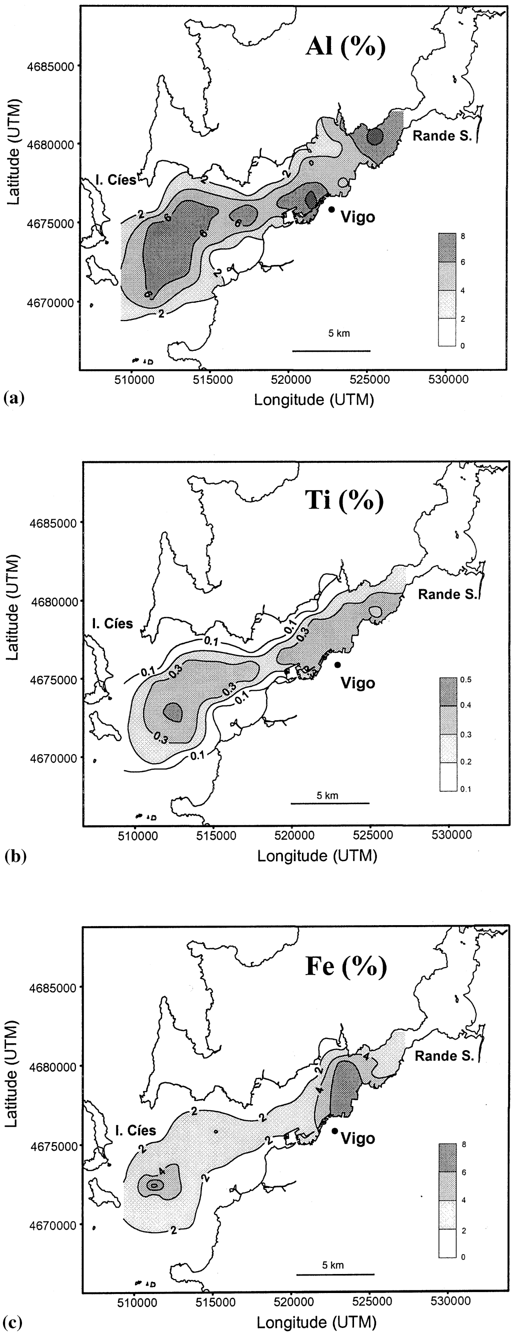

Fig. 4 Distribution of Al, Ti and Fe (%) in surficial sediments of the Ria de Vigo.

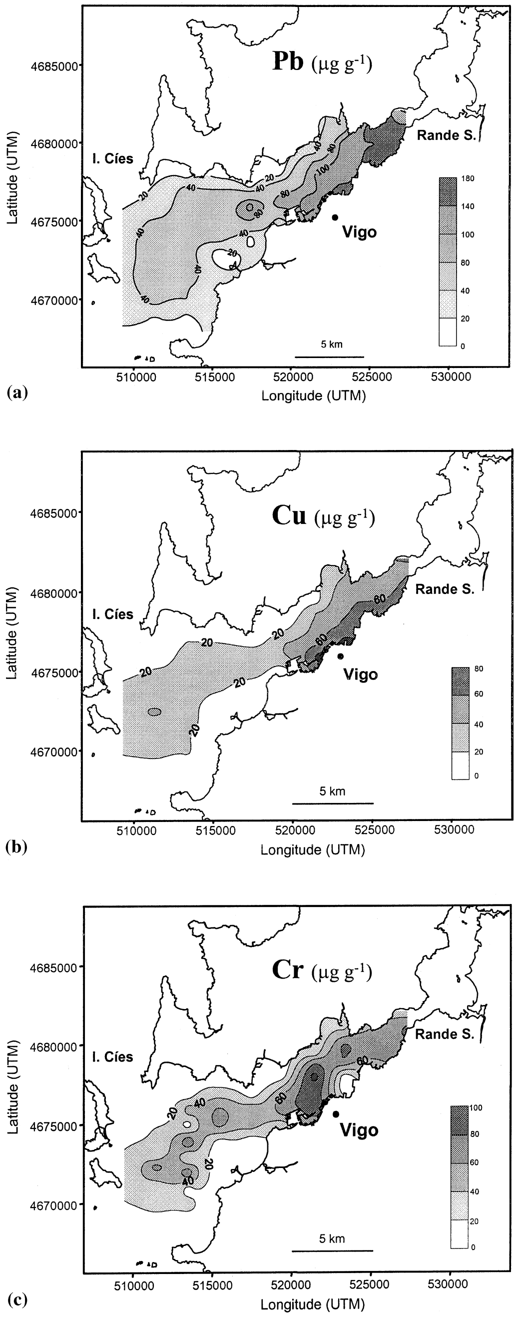

Fig. 5 Distribution of Pb, Cu and Cr (μg g^{-1}) in surficial sediments of the Ria de Vigo.

Effects of grain size on metal concentrations

The wide range of variation in the element concentrations in the sediments of the Ria de Vigo area, could be, at least partly, related to the presence of different sediment types (Table 2). Samples were divided in two clearly differentiated groups: (1) sandy sediments which comprise samples with less than 10% of mud and include sand and gravel-rich samples; (2) muddy sediments correspond to samples with high contents of mud, i.e., samples in the axial part of the Ria. The average concentration of Al, Fe, Ti, Cu and Zn in the muddy sediments is five to almost seven times their average concentration in the sandy sediments. Pb and Cr are almost four times higher in the muddy sediments, while, Ni, Co and As are only approximately doubled. Surprisingly, mean Mn values in muddy sediments are only 1.33 times higher than in sandy sediments, but there is a high standard deviation in these sandy sediments. This was due to extreme values of 1170 and 671 μg g^{-1} for carbonate-rich samples 48 and 42, respectively, due to the presence of rhodocrosite in these samples, mentioned before. The high standard deviation in sandy sediments is also found for Al, Fe, Ti, Cu, Zn and Ni. The presence of relatively high Sr concentrations is indicative of the presence of important proportions of aragonite

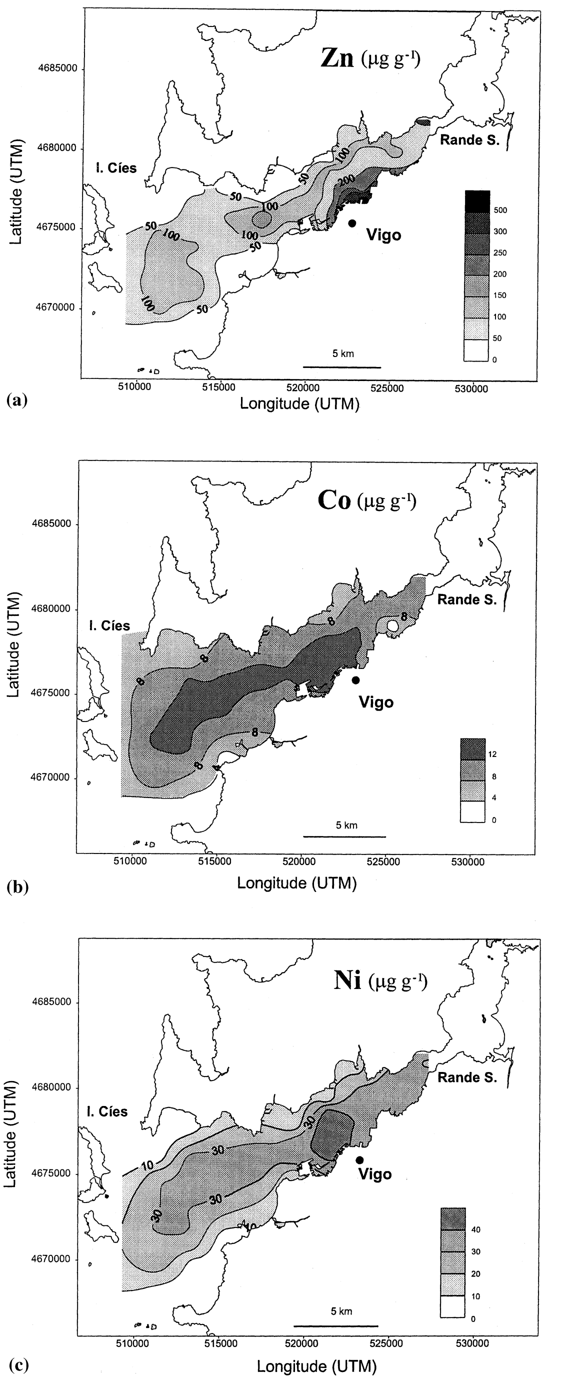

Fig. 6 Distribution of Zn, Co and Ni (μg g^{-1}) in surficial sediments of the Ria de Vigo.

(Fernández-Bastero *et al.*, 1998). This is in good agreement with the biogenic origin of most of the carbonate deposits. Carbonates have certainly a diluting effect on this group of elements which are of terrigenous origin. Finally, Cd has similar average values (approximately 3 μg g^{-1}) in both groups of sediments. This behaviour of cadmium is not surprising and has been reported before (Daskalakis and O'Connor, 1995; Lee *et al.*, 1998).

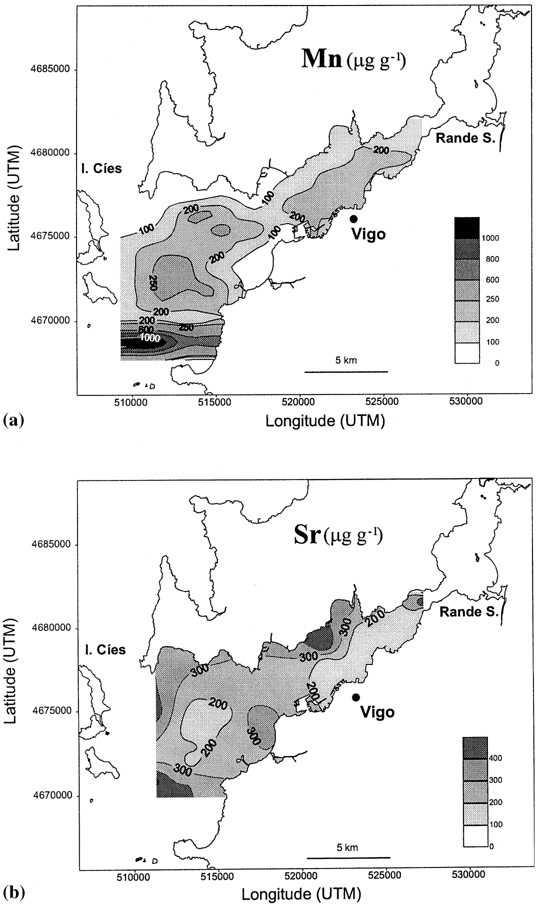

Fig. 7 Distribution of Mn and Sr (μg g^{-1}) in surficial sediments of the Ria de Vigo.

Data were subjected to simple statistical analysis in order to explore the possible associations existing between different variables. Table 3(a) shows a correlation matrix for the metals. Most metals are well-correlated ($p < 0.001$), the most noticeable positive correlations were Cu vs Pb ($r = 0.917$); Cu vs Zn ($r = 0.857$); Co vs Ti ($r = 0.888$) and Co vs Ni ($r = 0.818$). The significant correlation between Al and the other elements (except Cd, Mn and Sr) confirms that these elements are associated with aluminosilicate minerals.

It is well-established that granulometry, carbonate and also organic matter contents are important controlling factors in the abundance of trace metals. Fine-grained sediments tend to have relatively high metal contents, due in part to the high specific surface of the smaller particles. This enrichment is mainly due to surface adsorption and ionic attraction (McCave, 1984; Horowitz and Elrick, 1987). Also, coatings of organic matter are prevalent in fine-grained sediments, and these coatings bind a variety of trace elements (Wangersky, 1986). On the other hand, high carbonate contents are associated with low concentrations of trace metals. These relationships are clearly evident in Table 3(b) where variations in absolute metal concentrations are linked clearly with variations in grain size or carbonate content. Bivariate correlations between elements and sediment properties are positive and sta-

TABLE 2

The average concentrations of major and trace elements in the two main sediment types.

Sediment type	Al	Fe	Ti	Cu	Zn	Pb	Cr	Mn	Ni	Co	As	Cd	Sr
		(%)						(μg g^{-1})					
Sandy sediments	1.14	0.57	0.05	7.93	30.68	23.23	11.72	168.67	10.72	4.43	19.09	3.43	1387.47
$(n = 32)$[a]	±1.24	±0.62	±0.09	±9.07	±36.17	±13.12	±9.17	±219.60	±13.76	±1.21	±6.06	±1.68	±413.98
Muddy sediments	6.24	4.03	0.33	42.44	158.38	89.09	52.58	224.29	33.77	11.51	37.20	3.03	240.08
$(n = 34)$[b]	±1.37	±1.54	±0.04	±17.07	±86.34	±40.95	±29.51	± 24.52	±5.86	±2.07	±14.42	±1.74	±122.91

[a] n is less than 32, due to the values below detection limits, for the following elements: Cu $(n = 29)$; Cr $(n = 26)$; Pb $(n = 23)$; Ni $(n = 22)$; Co $(n = 7)$; As $(n = 8)$ and Cd $(n = 4)$.

[b] n is less than 34 , due to the values below detection limits, for the following elements: As $(n = 20)$; Cd $(n = 11)$.

tistically significant with organic matter content and the finest fractions. Metal concentrations, except Sr, show significant negative correlation with calcium carbonate and coarsest fractions. Although not statistically significant, Cd shows a positive correlation with carbonate content and Sr. This could suggest a preferential association of this element with carbonates as it has previously been reported (Daskalakis and O'Connor, 1995; WHO, 1992).

In general terms, the spatial distribution of metals in sediments of Ria de Vigo is controlled primarily by the association of metals with a fine-grained, organic-rich phase which has accumulated in areas of low turbulence, i.e., inner parts of the Ria. In addition, these patterns reflect the main anthropogenic discharges to the Ria that constitute a source for several heavy metals, being Vigo harbour the most noticeable point for these discharges.

Evaluation of sediment pollution

This evaluation was focused on the muddy sediments of the axial part of the Ria due to the dependence of metal levels on grain size, resulting from the association of metals with the finer particles. It is difficult to make an overall assessment of the degree of metal contamination in estuarine and marine sediments. This is a consequence of variations in analytical procedures between studies and the presence of an unknown natural background in the sediment. Measurement of total (rather than extractable) metal and normalization of concentrations as ratios to an element, associated with clays, provides a solution to the first difficulty. Some workers circumvent this by separating the finer particles for analysis, but there is no general agreement on procedures for this (Förstner and Wittmann, 1981; Ackerman *et al.*, 1983, Klamer *et al.*, 1990) and to do so increases sample preparation time. Expressing these

TABLE 3

(a) Pearson correlation matrix for the metals

	Al	Fe	Mn	Ti	Zn	Cu	Pb	Cr	Ni	Co	As	Sr	Cd
Al	1.000	0.709^{**}	0.164	0.863^{**}	0.571^{**}	0.742^{**}	0.619^{**}	0.709^{**}	0.677^{**}	0.615^{**}	0.542^{*}	-0.883^{**}	−0.322
Fe		1.000	0.168	0.760^{**}	0.733^{**}	0.831^{**}	0.655^{**}	0.511^{**}	0.626^{**}	0.572^{**}	0.476^{*}	-0.761^{**}	−0.257
Mn			1.000	0.178	0.108	0.120	0.031	0.043	−0.008	−0.300	−0.124	−0.055	−0.371
Ti				1.000	0.633^{**}	0.786^{**}	0.592^{**}	0.644^{**}	0.704^{**}	0.888^{**}	0.642^{**}	-0.840^{**}	−0.236
Zn					1.000	0.587^{**}	0.796^{**}	0.426^{*}	0.633^{**}	0.410^{*}	0.469^{*}	-0.696^{**}	−0.339
Cu						1.000	0.917^{**}	0.629^{**}	0.668^{**}	0.438^{*}	0.651^{**}	-0.783^{**}	−0.368
Pb							1.000	0.582^{**}	0.604^{**}	0.317	0.485	-0.693^{**}	−0.393
Cr								1.000	0.559^{**}	0.415^{*}	0.573^{*}	-0.667^{**}	−0.377
Ni									1.000	0.818^{**}	0.664^{**}	-0.667^{**}	−0.381
Co										1.000	0.611^{*}	-0.709^{**}	0.165
As											1.000	-0.547^{*}	−0.308
Sr												1.000	0.436
Cd													1.000

(b) Bivariate correlations between concentrations of heavy metals and sediment properties

Property (%)	Al	Fe	Mn	Ti	Zn	Cu	Pb	Cr	Ni	Co	As	Sr	Cd
O.M.	0.713^{**}	0.694^{**}	0.091	0.764^{**}	0.726^{**}	0.852^{**}	0.869^{**}	0.622^{**}	0.692^{**}	0.432^{*}	0.469^{*}	-0.754^{**}	−0.447
CaCO3	-0.875^{**}	-0.735^{**}	−0.058	-0.835^{**}	-0.641^{**}	-0.765^{**}	-0.674^{**}	-0.625^{**}	-0.621^{**}	-0.699^{**}	-0.491^{*}	0.976^{**}	0.462
Gravel	-0.443^{**}	-0.382^{*}	−0.155	-0.466^{**}	-0.310^{*}	-0.342^{*}	-0.327^{*}	−0.329	−0.098	-0.499^{**}	−0.432	0.557^{**}	0.076
Sand	-0.776^{**}	-0.755^{**}	−0.099	-0.862^{**}	-0.596^{**}	-0.724^{**}	-0.660^{**}	-0.567^{**}	-0.821^{**}	-0.846^{**}	-0.531^{**}	0.697^{**}	−0.277
Silt	0.603^{**}	0.329	0.757^{**}	0.867^{**}	0.165	0.071	−0.007	0.055	0.537^{**}	0.637^{**}	0.123	-0.711^{**}	0.380
Clay	0.555^{**}	0.633^{**}	0.455^{*}	0.765^{**}	0.483^{*}	0.619^{**}	0.661^{**}	0.503^{**}	0.869^{**}	0.660^{**}	0.537	-0.848^{**}	−0.576

[*] $p < 0.01$.

[**] $p < 0.001$.

values as geoaccumulation indexes (Igeo) or enrichment factors (EF), relative to pre-industrial sediments from the same environment, solves the second; although it is not always easy to reach these pre-industrial sediments data. Many authors (Angelidis and Aloupi, 1995) use these kinds of approaches, however, their calculation poses several problems. Both, Igeo and EF, depend on the 'background' data used. For the total metal content of the sediments, these data can be provided by the average metal concentration of texturally and mineralogically equivalent sediments, either reported in the literature or measured by the authors in a known pristine region (Loring and Rantala, 1992). The world average shale and the world average soil are among the materials often used to provide background metal levels. However, these metal levels tend to be very general and may mislead in a specific coastal area (Gibbs, 1993). The latest author recommends the use of regional background values. We suspect that the obtained information of pollution status can be more dependent on the background used than the index/factor chosen.

Index of geoaccumulation. The geoaccumulation index (Igeo) was originally defined by Müller (1979) for metal concentrations in the <2 μm fraction and developed for the global standard shale values, which is expressed as follows:

$$\mathrm{Igeo} = \log_2 \frac{C_n}{1.5 \cdot B_n},$$

where C_n is the measured concentration in the sediment for the metal n, B_n the background value for the metal n and the factor 1.5 is used because of possible variations of the background data due to lithological variations.

However, several researchers (Subramanian and Mohanachandran, 1990; Barreiro, 1991; Sahu and Bhosale, 1991) have used the previous expression using regional backgrounds and on the less than 63–65 μm sediment fraction.

In this paper, Igeo has been calculated using three background values, two of them regional values and the third the global average shale data from Turekian and Wedepohl, 1961 (Igeo Sh). For the regional background values we have taken the data from Carral *et al.* (1995) – Igeo Ca – and the data from Barreiro (1991) – Igeo Ba – Carral *et al.* (1995) determined (by modal analysis) background metal levels in intertidal sediments of Galician estuaries for watersheds over granite and/or over schist/gneiss. We have calculated the percent of the surface of the watershed Ria de Vigo that is granite (83.5%) and schist/gneiss (16.7%) and we have recalculated the background values having account of this lithology (Table 4). Barreiro (1991) established a background value for Galician Rias, obtained from Ria sediments, using similar digestion procedures to those used in our study.

The index of geoaccumulation consists of seven grades or classes, with Igeo of 6 indicating almost a 100-fold enrichment above background values (Müller, 1979) (Table 5). In Fig. 8, the histograms represent the percent of samples for each metal in Classes 3, 2, 1 and 0 for the three background values used. The figure reflects that, independent of the background used, 100% of the samples fall in Class 0 (background concentrations) for the metals Mn, Co and practically Ni, i.e., it leads us to conclude that the Ria de Vigo is not polluted for any of these metals. The same could be infered for Cr if we use the Igeo Sh. However, if we use the background regional values, different inferences can be made. Approximately 50% of the samples fall in Class 1 (up to double the background values) using background values from Barreiro (Igeo Ba) and more than a 50% using the values from Carral *et al.* (Igeo Ca). A small percentage of the samples is included in Class 2 for this element, using the regional background values. Similar behaviour was found for Cu, i.e., practically 90% of the samples fall in Class 0 for Igeo Sh, whereas for Igeo Ba and Igeo Ca, more than 50% of the samples are indicative of a moderate pollution status. For Fe, the three background values used gave similar information, a small number of samples are moderately polluted. These samples are mainly corresponding to the transect Vigo-Moaña. Pb presented the highest values of Igeo, about 25% of the samples are in Class 3 using background values for average shale (Igeo Sh), and close to 12% for Igeo Ba. Also, Pb was the metal more significant in Class 2 for these two backgrounds (approximately 40% of the samples), and none of the samples were in Class 0. A significant difference was found for this element using Igeo Ca. This difference between backgrounds was also noted for Zn, mainly in % of samples in Class 1 (less than 10% for Igeo Ca, vs approximately 40% for Igeo Ba and Igeo Sh).

This index allows us to deduce that, in general terms, the Ria de Vigo is moderately polluted for some of the studied metals. In order to synthesize the data set and to assess the areal extension of this pollution, superimposed maps has been prepared (Fig. 9) for the Igeos > 0 for each metal and background. In general terms, the inner and southern parts of the Ria are generally the

TABLE 4

Background concentrations of heavy metals from Carral *et al.* (1995), modified according the lithology for the Ria de Vigo watershed.

	Lithology		
Metal (μg g^{-1})	Granite	Schist-gneiss	Ria de Vigo[a]
Fe	29000	33000	29500
Mn	248	395	272.6
Co	12	13	12.2
Pb	78	50	73.3
Ni	31	38	32.17
Zn	136	120	133.3
Cu	20	35	22.5
Cr	30	54	34

[a] Recalculated according the lithology of the watershed.

TABLE 5

Geoaccumulation indexes (after Müller, 1979).

Igeo	Class	Pollution intensity
>5	6	Very strong polluted
4–5	5	Strong to very strong
3–4	4	Strongly polluted
2–3	3	Moderately to strongly
1–2	2	Moderatelly polluted
0–1	1	Unpolluted to mod. polluted
0	0	Unpolluted

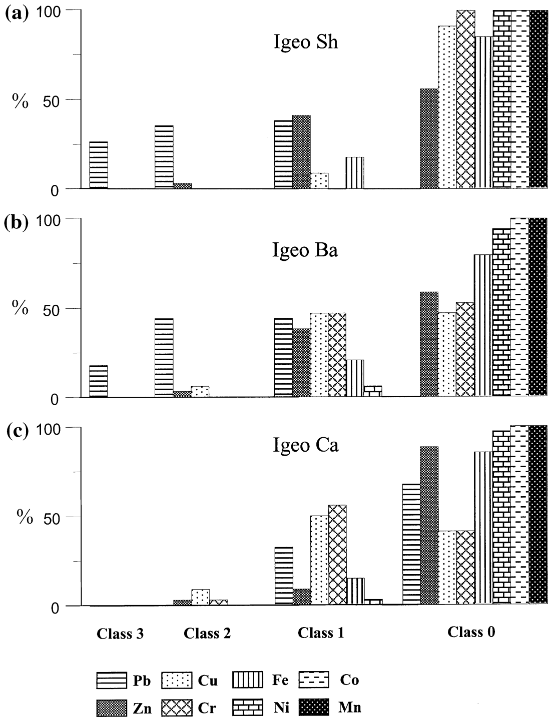

Fig. 8 Percentage of samples in Müller (1979) Igeo classes 3, 2, 1 and 0 for each metal using three different backgrounds values: (a) background values from average shale – Igeo Sh, (b) background values from Barreiro (1991) – Igeo Ba, (c) background values from Carral *et al.* (1995) – Igeo Ca.

areas most affected by pollution. However, there are significant differences between backgrounds used, for Cr, Pb and Cu. For Cr, with Igeo Sh, there were no values with Igeo bigger than 0, whereas with Igeo Ca and Igeo Ba, an important part of the Ria is moderatelly polluted by this element. For Igeo Ba, the inner part and some isolated samples in the outer part are mainly polluted with Cr (Fig. 9(b)). For Igeo Ca, the area polluted by Cr is extended towards the outer part of the Ria (Fig. 9(c)). This can be attributed to the different mobility that presents this element in its forms. Cr^{+6} is soluble in water and can be displaced from the discharge places. But also it is probable that the background values from Carral *et al.* (1995) are underestimated for Cr.

For Pb, a similar distribution is observed for Igeo Sh and Igeo Ba (Fig. 9(a) and (b)), whereas, considering Igeo Ca, only the innermost part of the Ria is polluted by Pb (Fig. 9(c)). Also, in this case it is probable that the background values from Carral *et al.* (1995) are over-estimated for this element.

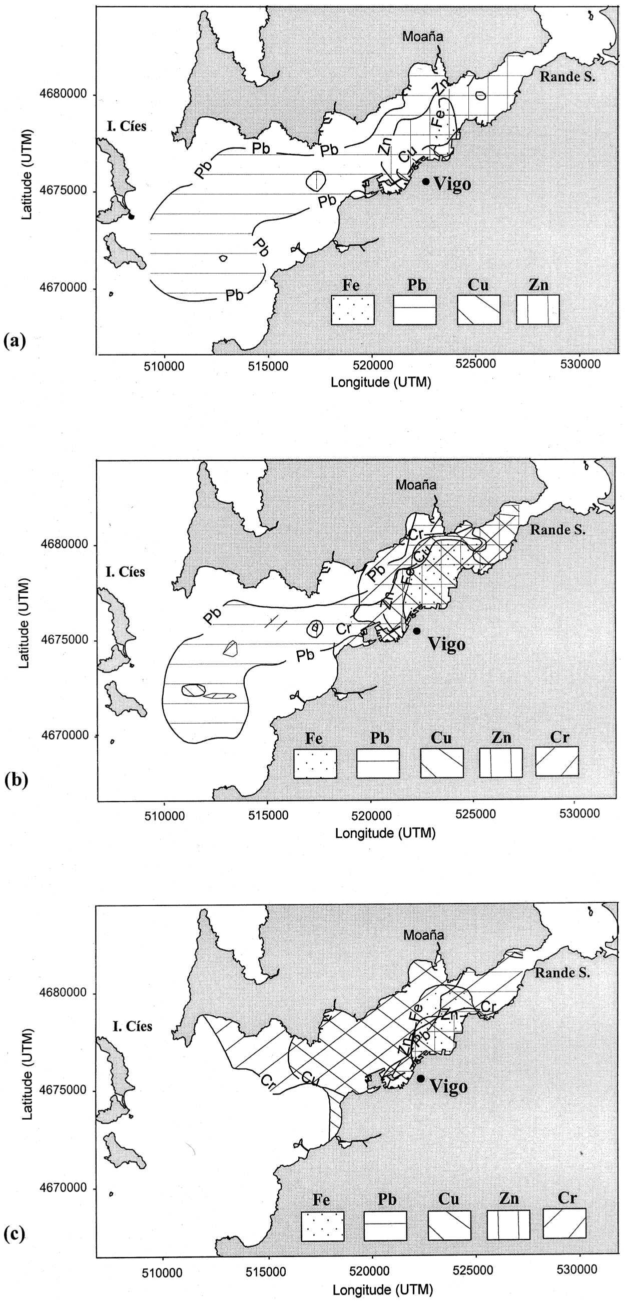

Fig. 9 Superimposed maps for the Igeos > 0 for each metal and the three background values used: (a) background values from average shale Igeo Sh, (b) background values from Barreiro (1991) Igeo Ba, (c) background values from Carral *et al.* (1995) Igeo Ca.

Finally, Cu, was also another element with very different behaviour among backgrounds. With Igeo Sh a very small area close to the harbour is polluted. This polluted area is slightly increased and strongly increased towards the north and west, with Igeo Ba and Igeo Ca, respectively (Fig. 9(b) and (c)).

Determination of background values. It is difficult to draw a definite conclusion about the pollution status of the Ria de Vigo because different backgrounds employed give different results. In general terms, they point out that there are natural concentrations of Mn, Ni and Co, and some signs of pollution for Cu, Cr, Fe, Zn and Pb. Nevertheless, depending on the background used the grade and the extension of pollution are very different, especially for Cr, Pb and Cu.

In order to obtain a global view of the obtained results, principal component analysis (PCA) was applied. A large number of researchers (Zitko, 1994; Soares *et al.*, 1999, *inter alia*) have used PCA in the evaluation of environmental data, obtaining interesting conclusions that are not inmediately obvious. PCA was performed on the entire data set (except As and Cd due to the non-availability of values for some of the samples) in order to identify the major processes that determine the sediment trace metal content. Three principal components (PC) have been identified, explaining c. 70% of the total variance. The plot of loadings of these three components gives a distribution of variables in three groups (Fig. 10) interpreted as different origins of the metals. The first group includes a correlation of sand, calcium carbonate, gravel and Sr. This association is strongly controlled by the biogenic carbonates, and plays an important role as a dilutant material of the heavy metals in the samples. A second group is formed by Fe, Cu, Zn, Pb and organic matter. They are mainly related to anthropogenic inputs and reflect the complexing nature of the organic matter. The remaining elements, except Cr, constitute a third group that represents the lithological input in the area. Cr cannot be clearly included in any of these groups. This metal is interpreted as an anthropogenic element that is not forming part of organo-metallic compounds.

The application of PCA only to the metals normalized by Al increased to more than 90% the percentage of the explained variance (Table 6), explaining only the first two components more than 80% of the data variance. PC1 is interpreted as the lithogenic component, most of the metals have high loadings for this component because an important fraction of all the metals is lithogenic. PC2 shows the polluted signal of the elements Cu, Pb, Zn and in lesser grade Fe and finally PC3 gives the signal of pollution by Cr. A plot of scores (factor score 1 vs 2 and 1 vs 3), which give the positions of the samples in the coordinates of the principal components, isolated 9 samples not affected by pollution and interpreted as natural or background levels. Mean values of the concentrations of metals for these samples were defined as background values for Ria de Vigo. They are presented in Table 7 and compared with the previous background used. These background values are much more closer to regional than global ones. In the table equal or similar values to other authors are indicated in bold. This is the case for Cr and Co, practically the same values as the background values from Carral. Ni, Zn and Cu background values were very similar to Barreiro's, although the two latest elements were slightly higher. The most noticeable differences were for Mn, Pb and Fe. For the first two elements, calculated background is intermediate between Barreiro's and Carral's. Calculated background value for Fe was higher than the regional ones and lower than the global one, previously used. These differences can be seen in Fig. 11, where the superimposed map for Igeo is drawn using the new background values defined for the Ria de Vigo. This map represents a more realistic picture of the pollution status of the Ria. The overestimation of background values for Pb and Cr from Carral *et al.* (1995) and Barreiro (1991) respectively, is also confirmed.

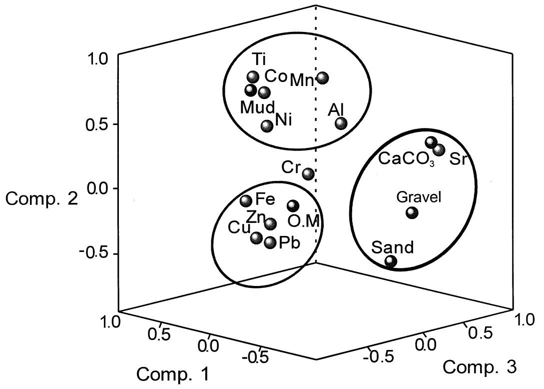

Fig. 10 PCA results: plot of loadings of the three first components obtained in the analysis.

TABLE 6

PCA results applied to metal normalized by Al.

Component	Eigenvalues	Explained variance (%)	Accumulated variance (%)
1	6.12	67.96	67.96
2	1.17	13.01	80.97
3	1.08	11.99	92.96

Component loadings

	Component 1	Component 2	Component 3
Zn	0.831	−0.427	−0.086
Co	0.867	0.390	−0.121
Ni	0.912	0.218	0.163
Ti	0.887	0.385	−0.134
Mn	0.836	0.337	−0.315
Fe	0.934	−0.093	−0.054
Cu	0.886	−0.420	0.125
Cr	0.178	0.319	0.918
Pb	0.818	−0.491	0.229

Normalization and enrichment factors. Several authors (Covelli and Fontolan, 1997, among others) have criticized the use of Igeo for evaluation of status pollution and they propose the use of normalized values. Several methods of normalization are possible, ranging from the use of simple metal/ normalizer ratios to more complex methods based on regression analysis (Rowlatt and Lovell, 1994). We have chosen to normalize metal concentrations as ratios to another constituent of the sediment. There is no consensus about the most appropiate

TABLE 7

Comparison between background values for heavy metals given by other authors and calculated for the Ria de Vigo sediments.

Metal	Barreiro	Carral recalculated	Average shale	Ría de Vigo (this paper)
Al	–	–	8.0	6.48
Fe	2.69	2.95	4.72	3.51
Ti	–	–	0.46	0.34
Mn	225	272.6	850	244.33
Zn	**100**	133.3	95	**105.34**
Cu	**25**	22.5	45	**29.41**
Pb	25	73.3	20	51.29
Cr	43	**34**	90	**34.04**
Ni	**30**	32.17	68	**30.32**
Co	16	**12.2**	19	**11.66**

sediment constituent to be used for normalization. Among those used have been Al, Fe, total organic carbon and grain size. The constituent chosen for this purpose should also be associated with finer particles (related to grain size) and its concentration should not be anthropogenically altered (Ackerman, 1980). Al is a conservative element and a major constituent of clay minerals, and has been used successfully by several workers (Ryan and Windom, 1988; Sinex and Wright, 1988; Balls *et al.*, 1997). In addition, its distribution in the Ria de Vigo shows no evidence of anthropogenic enrichment (Fig. 3). After Al, the next most consistent candidates are Fe and total organic carbon, although other elements such as Cs, Rb and Li have been used (Ackerman, 1980; Allen and Rae, 1987; Loring, 1990; Loring *et al.*, 1995).

Normalization to Fe has been used previously as a grain size proxy by a number of authors working on marine and estuarine sediments (Ackerman, 1980; Emmerson *et al.*, 1997; Lee *et al.*, 1998). Iron is not a matrix element, like aluminium, but is like trace elements in being associated with surfaces. Iron geochemistry is similar to that of many trace metals both in oxic and anoxic environments. This association argues for its use as a normalizer. A potential difficulty with using Fe is that in certain circumstances this element can be mobile during diagenesis (Finney and Huh, 1989). A very real difficulty with using Fe in this case is that the Ria de Vigo is presumably contaminated with this element (Fig. 3). Other authors (Din, 1992) have cited accumulation of Fe compounds in coastal sediments.

Organic carbon has also been used (Daskalakis and O'Connor, 1995; Zwolsman *et al.*, 1996). However, organic carbon itself can be considered as a contaminant and the normalization approach has no geochemical basis (Kersten *et al.*, 1994).

For the exposed reasons, in this study, we have chosen to normalize metal concentration using aluminium as a grain-size proxy. The method employed was calculating EF as follows:

$$\mathrm{EF} = \frac{(\mathrm{Metal/Al})\ \mathrm{Sediment}}{(\mathrm{Metal/Al})\ \mathrm{Background}}.$$

As we have seen previously with the Igeo index an objective evaluation on the degree of heavy-metal contamination depends on the choice of an appropriate background as a reference level. EF was calculated using the previous background values defined for the Ria (Table 7). The EF gives similar information as Igeo. On average, no enrichment is noted for Mn, Ni, Co and Fe. Nevertheless, for Fe the samples located along the transect Vigo-Moaña are clearly enriched in this element as was reported in previous paragraphs. On the contrary, clear signs of enrichment are present for Pb, Cu, Cr and Zn, with maximum values of EF close to 5 (Fig. 12). On drawing the superimposed maps for the EF > 1 (Fig. 13) and comparing with the distribution map for the Igeo (Fig. 11) we can say that the obtained results with both indexes are quite similar between them and they show the pollution status for the Ria. They confirm that inner and southern parts of the Ria are the most affected areas of pollution by Zn, Cu, Cr, Pb and Fe. The transect Vigo-Moaña is clearly the most affected area by pollution for these five metals. The urban effect of other small villages, such as Cangas, is also noted for Zn, Cr and Pb. In comparison with other estuarine systems (Balls *et al.*, 1997) grade of pollution in Ria de Vigo is not very high.

This approach leads us to classify the Ria de Vigo as being in a moderate state of contamination for Pb, Cu, Cr, Zn and Fe, especially in the area near Rande Strait and in the surroundings of Vigo harbour. These results are consistent with the studies recently carried out by Gómez-Gesteira *et al.* (1999). In a study of pollution dispersion in the Ria de Vigo, these authors found that the particles coming from the river tend to accumulate around the Rande Strait despite the existence of strong tidal currents in that area. This is due to low river discharge and to the narrowing of the Rande Strait, which prevents the creation of large gyres in the area. In this area flocculation processes must be important and therefore heavy metal accumulation occurs in the sedi-

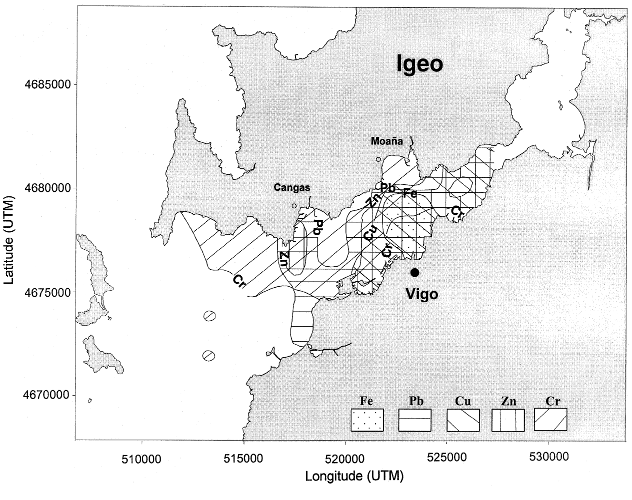

Fig. 11 Igeo > 0 distribution superimposed maps calculated using the background values defined for Ria de Vigo sediments.

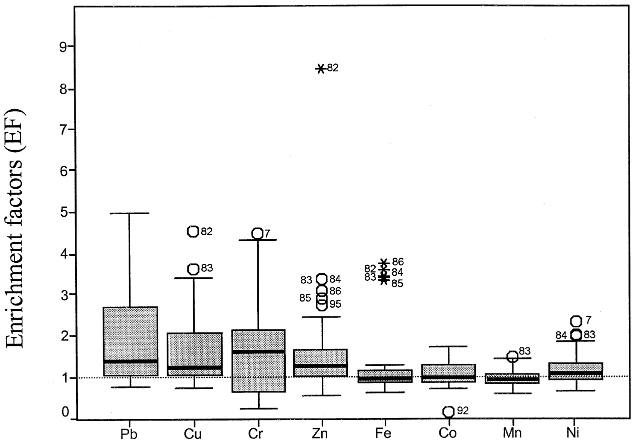

Fig. 12 Box and whisker plots for the EF for each metal using the background values defined for Ria de Vigo sediments.

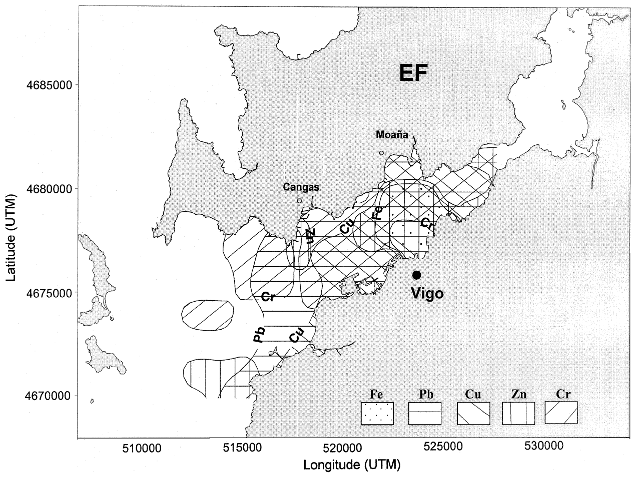

Fig. 13 EF > 1 distribution superimposed maps calculated using the background values defined for Ria de Vigo sediments.

ments. Near the Vigo harbour area, these authors found by particle tracking that there is a movement towards the north.

Conclusions

This study shows the importance of adjusting for particle size when studying metal contamination. Normalization using ratios to an element associated with fine particles is a considerably easier process than using methods which involve an initial separation of fine particles. Several approaches to the study of pollution were employed (Igeo and EF), and they lead us to conclude that the interpretation of the pollution status in Ria de Vigo is more dependent on the background values than on the index/factor used.

PCA was a useful tool to determine the relationships between elements and properties of the sediments. Also PCA allowed us to establish background values for Ria de Vigo, which were similar to regional values given by other authors.

Based on these calculated backgrounds, pollution status was determined for the Ria and the spatial extent of pollution was examined. It is concluded that Ria de Vigo is slightly to moderately polluted for Pb, Zn, Cu, Cr and Fe. The maximum grade of pollution is located near Vigo harbour as a consequence of the anthropogenic activity. Continuous monitoring and further studies of the area are recommended to ascertain long-term effects.

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