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ORIGINAL ARTICLE

# Historical analysis of heavy metal pollution in three estuaries on the north coast of Galicia (NW Spain)

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**Abstract** This research focuses on the development of metal pollution in sediment cores from three estuaries in Northwest Spain: Viveiro, Ortigueira and Barqueiro. Pb, Cu, Co, Cr, Cd and Zn and total organic carbon were assessed using principal component analysis (PCA) in order to obtain background values, measure pollution levels and identify pollution sources. Results were interpreted by considering the local industrial history, grain size and C/N relationship. The pollution levels obtained bear a strong resemblance to those documented for of a moderately industrialised area. PCA identifies factors that reflect mainly temporal associations with metals. Sedimentation rates between 0.9 and 1.1 cm/year were determined. In Viveiro core levels of Cr pollution are associated with tanneries. In Ortigueira, high core levels of Cu and Co are linked to mining, and Cr levels to adjacent ultramafic rocks. Erosion of Holocene sediment causes high values of Co and Cr in the Barqueiro core. Cu increase in the three estuaries is related to fungicide use since 1910. Sea level rise appears to be affecting the marine characteristics of the sediments in Barqueiro. In Viveiro, the nature of the sediment reflects engineering work and land reclamation.

**Keywords** Metals · Cores · PCA · Background values · Estuaries · NW Spain

## Introduction

Estuaries are sensitive zones, especially with respect to contamination because they are sediment traps and because of their historical role in urban, port and industrial development. Thus, a large number of authors have worked on the distribution of heavy metals in estuarine sediment cores as indicators of past and present pollution events (Hornberger et al. 1999; Tuncer et al. 2001; Abrahim and Parker 2002; Cundy et al. 2003).

Some studies in Spain have dealt with the highly contaminated estuaries at Bilbao in the north (Cearreta et al. 2000) and Rio Tinto in the south (Davis et al. 2000). At Galicia in the northwest only the Ferrol estuary (Cobelo and Prego 2003) has had its historical data studied, and the estuaries of this region have barely been documented. Carballeira et al. (2000) included the area in their general study on heavy metal pollution affecting all the estuaries of Galicia, and Otero et al. (2000) studied the contamination of the upper 35 cm of sediments of the Ortigueira estuary. This paper provides the first detailed description of historical metal levels and how they have been influenced by human activity in the area.

Erosion (Spencer 2002; Daesslé et al. 2004) and dredging (Cearreta et al. 2000) of historically contaminated sediments may provide a contemporary source

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of pollution input to the estuarine system. Dyke construction and dredging activity can erode Holocene sediments (Lesueur et al. 2003). In contrast, sea-level rise can enhance sedimentation rates in intertidal estuary regions (Plater and Appleby 2004). General erosive trends along the northern coast of Galicia have been identified, affecting beaches, cliffs and archaeological sites. Engineering work is the main cause of erosion. Sea-level rise of about 2.5 mm/year could also be an influence (Lorenzo et al. 2006). This paper tries to determine how engineering work, industrial activity and sea-level change affect marine sediments and whether or not they are acting as sources of pollution in the estuaries.

Principal component analysis (PCA) allows for a description of a multidimensional system with the need for the analysis of only a small number of variables. PCA has been used to define the natural or anthropogenic origin of metal-polluted samples (Banerjee 2003; Landajo et al. 2004; Spencer 2002) and to determine pollution distribution (Ausili et al. 1998). The majority of research has focused on metal-pollution sources for the superficial sediments in estuaries (Filgueiras et al. 2004) and rivers (Chang et al. 1998; Yu et al. 2000), soils (Slavkovic et al. 2004) and estuarine sediment cores (Alvarez-Iglesias et al. 2003). Loska and Wiechula (2003) analysed the spatial and temporal variabilities of sediments. In this paper we use PCA to discriminate between non-polluted and polluted samples, in order to establish the background levels of contaminants.

The present study is focused on the evolution of heavy metal contamination in the estuaries of the Viveiro, Barqueiro and Ortigueira rias on the northwest coast of Spain. They are examples of locations with a short history of industrialisation and varying degrees of human impact in this area. The objectives of the paper are (1) evaluation of the historical levels and sources of Pb, Cd, Cu, Cr, Co and Zn pollution in the estuaries of north Galicia, (2) evaluation of the effects of engineering work and sea-level rise upon the sediments and (3) determination of the background values of pollutants and the identification of non-polluted samples using PCA.

## Study area

The studied estuaries form the interior parts of the rias of Ortigueira, Barqueiro and Viveiro. Rias are deep, funnel-like incised, tidal valleys characteristic of a relatively submergent coastline, here open to the north (Fig. 1). The Landro River flows into the Viveiro estuary (a fluvial basin of 270 km$^2$, with an average discharge of 10.5 m$^3$/s), the river Sor into the Barqueiro estuary (202 km$^2$, 6.0 m$^3$/s) and the rivers Mera and Baleo into the Ortigueira estuary (177 and 72 km$^2$, respectively, with average discharges of 5.8 and 6.3 m$^3$/s) (Rio and Rodriguez 1992). The estuaries lie on a mesotidal coast with a mean tidal range of 3.5 m and a NW swell, although, because of the rias' morphology, waves got diffracted and enter the estuaries from the NE. All of them have an entrance dominated by marine processes and an interior hosting partially enclosed estuaries with well-developed beach barriers forming mouth complexes.

The Viveiro estuary has undergone considerable morphodynamic alteration because of significant

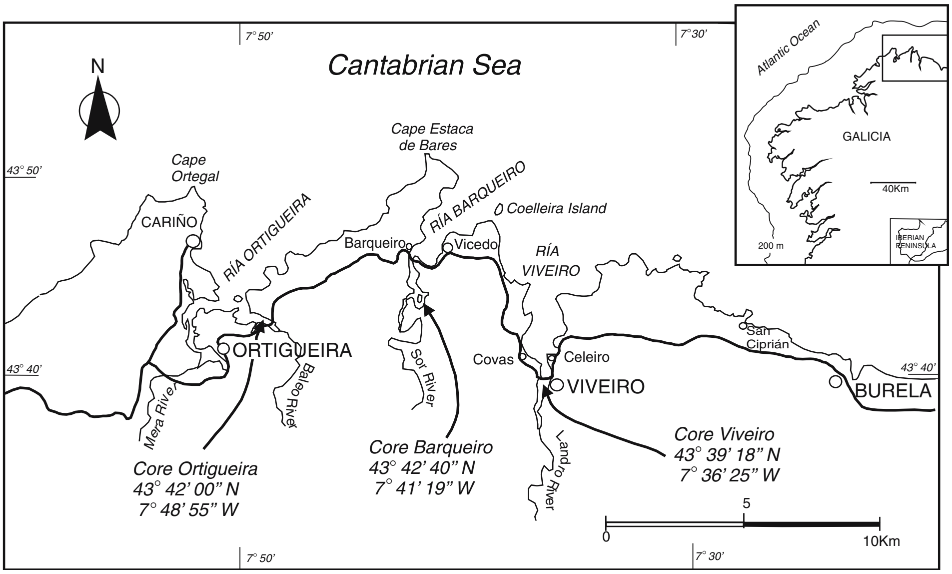


**Fig. 1** Geographical location of the studied estuaries and sites of the boreholes sampled

human occupancy, evidenced by the development of ports, residential settlements and reclaimed marshes. There is a fair-sized local population in an estuary who supports the important fishing port of Celeiro with its surrounding canning factories, shipyards and metal works. New roads cross the waterway and a considerable area where all marshes have been reclaimed. As a result, the dynamic of the entire fluviomarine system has been greatly modified and the changes have considerably diminished the energy of entering waves (Lorenzo et al. 2003).

The Barqueiro estuary has always been sparsely populated, having two little villages with their respective small ports in the entrance. In the second half of the twentieth century, there were also a canning factory and a kaolin plant, both currently abandoned. A few houses and farms are scattered along the coast and only one little village is situated on the river bank about 1 km upstream of the river entry into the estuary. Port improvements in the 1990s, which included dredging, have substantially modified the dynamics of the mouth complex, mainly provoking an intense and accelerated erosion of the beach at Arealonga. The salt marshes are, however, fully preserved.

The Ortigueira estuary has suffered very limited morphodynamic alteration. There are two villages, Ortigueira in the estuary and Cariño at the entrance to the ria, the latter being a fairly important fishing port. In the twentieth century it developed a canning industry. Nowadays, quarrying of slate for construction is an increasing economic activity that constitutes a source of solid waste to the rivers flowing into the estuary. The mouth complex has a double spit that separates the Baleo and Mera estuaries, and this extends towards both the east and west. The Mera estuary is wide and very shallow with a single channel navigable at high tide. The Baleo estuary is narrow and is very dynamic with large sand bars. The entire system of marshes, beaches and dunes has been very well preserved.

The estuaries are located in different geological domains, which are the Cabo Ortegal Complex, with the Ollo de Sapo and Manto de Mondoñedo domains. These are tectono-sedimentary units progressively thrusted from west to east (Fig. 2).

The Viveiro estuary is located across a thrust in which gneisses and metasediments of the Ollo de Sapo Domain overlay the granites and metasediments of the Manto de Mondoñedo Domain. The basin of the River Landro shows a predominance of two-mica granites, and to a lesser degree, a variety of metasediments that have given rise to economically important mining for sedimentary iron ore. Veins of pegmatite and quartz with feldspar and kaolin are also common.

In the Barqueiro Estuary, intrusive rocks containing biotite, amphibolite and very deformed two-mica granite predominate. One striking feature of the rocks surrounding this estuary is an abundance of large white

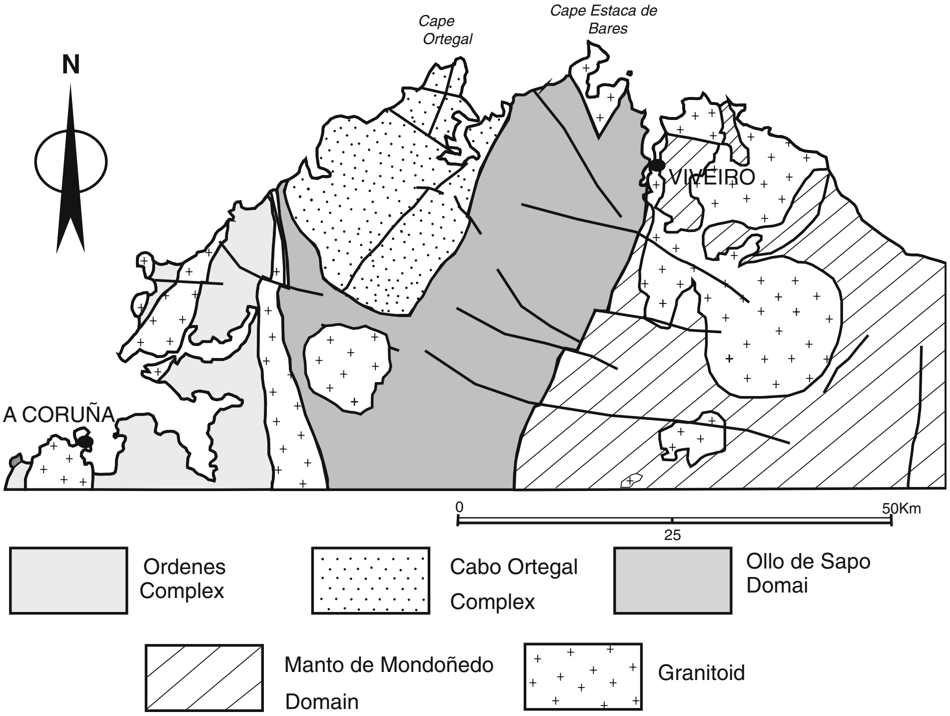


**Fig. 2** Simplified sketch map showing the main geological units in the area

quartz veins. The basin of the Sor River is made up of pre-Cambrian gneisses and quartzite flanked by metasediments of the Lower Palaeozoic. There are small abandoned mining operations for sedimentary iron ore in the Ordovician strata.

The river basin that feeds into the Ortigueira estuary displays a varied lithology of gneiss, amphibolite, eclogite and basic serpentinite, which form a part of the Cabo Ortegal Complex, and metasediments from the Ollo de Sapo Domain. The ultrabasic rocks include chromite, $Cr_2O_4$ Fe mineralisation, a mineral that resists chemical weathering and is incorporated into the estuarine sediment. Although this mineralisation has led to mining operations from time to time, the small size of the individual deposits has prevented a complete and continuous exploitation. Nevertheless, it is pertinent to observe that alluvial chromite in the estuarine sediments was documented at the Mining Council in 1945. The basin of the River Mera has old pyrite and chalcopyrite mines with a mineral paragenesis that includes sphalerite. Within the zone there are also three areas where these minerals have been exploited. In the most recent mining phase, 250,000 tons of pyrite and chalcopyrite were mined between 1950 and the early 1960s (Monterrubio 1992).

## Materials and methods

A sampling station was selected in the intertidal mudflat of each estuary (Fig. 1). In June 2002, sediment cores were extracted by a PVC suction corer TESS-1 (Méndez et al. 2003) at the Baleo river estuary in Ortigueira (220 cm length, 3.5 cm diameter core) and at the Landro River estuary in Viveiro (155 cm length, 3.5 cm diameter core). In September of 2002 at the Sor River estuary in Barqueiro, a manual corer was used (150 cm length, 3.0 cm diameter core).

The sediment cores were kept in PVC tubes, sealed with polyethylene and transported horizontally to the laboratory where they were kept at a temperature of 4°C. The cores were divided into 10-cm subsamples. The samples were handled with a plastic spatula and were homogenised before storing in vials of the same material previously washed with 10% $HNO_3$ and Milli-Q water, hermetically sealed and stored at 4°C until dried in an oven without exceeding 50°C. In order to homogenise the results for comparison (Luoma et al. 1990), the finer fraction (<63 μm) was then separated to determine the metals.

The metal content for Cd, Co, Cr, Cu and Pb was determined by analysis at the Institute of Marine Research (CSIC, Vigo) by direct injection of sediment suspension (Bermejo-Barrera et al. 1994) using atomic absorption spectrometry with electrothermal atomisation in a 220 Varian instrument with Zeeman background correction.

To determine Zn, the samples were previously digested in Teflon bombs with a 3:1 mixture of $HNO_3$ and HF in a Milestone 1200 Mega microwave oven in accordance with the EPA 3052 (EPA 1996) standard. The Zn analyses were carried out with Varian 220FS atomic absorption spectrometry with air–acetylene flame. The procedure was verified by Canadian reference material (PACS-2). Agreement with the certified values was Al 85%, Cd 96%, Co 96%, Cr 99%, Cu 104%, Pb 101%, Zn 105%.

Total organic carbon (TOC) and N were analysed in the raw samples using a CNH Flash EA elemental analyser at the SXAIN Laboratory of the University of A Coruña. Ten samples of 10 g from each core were sent to the geology laboratory at the University of Bordeaux, where $^{210}Pb$ in excess was measured in an Intertechnique EGSP 2200-25 gamma spectrometer equipped with a germanium detector. Background noise was noted. A constant flux and constant sedimentation rate (CFCS) model was used. Finally, the <63 μm fraction was sieved for use as an indicator of the sedimentation regime (Helland 2001).

The PCA is a powerful tool for the characterisation of anthropogenic and geogenetic loads, the identification of substantial discharges and the detection of interactions between components (Filgueiras et al. 2004). The use of this analysis makes it possible to reduce the number of studied variables and facilitates the interpretation of a large volume of data (Álvarez-Iglesias et al. 2003). Rough metal concentrations were studied by the principal components method (Tuncer 2001; Spencer 2002) together with TOC with the software package SPSS for Windows in order to obtain the factors responsible for the data variance. We also gathered data on the industrial history of the areas studied, including the types of industry and periods of activity.

## Results

For sediments to provide an accurate history of pollution caused by human activity, the sediment cores should be mainly fine grained, rich in clays and dateable. The samples should present reasonable rates of sedimentation, be reasonably undisturbed and should not display a significant redistribution of elements because of mixing or early diagenesis (Cundy et al. 1997). The results obtained in the three cores differ considerably with respect to suitability.

## $^{210}$Pb analysis

The use of $^{210}$Pb to date coastal sediments is problematic given the fact that sedimentary records are often incomplete, and are subjected to deposition, erosion and resedimentation (Kirchner and Ehlers 1998; Cundy et al. 2003). The corresponding analyses of the samples taken in the three estuaries presented serious difficulties and the results were equivocal; therefore they are only briefly considered.

The core taken in the Viveiro estuary (Fig. 3) presents some difficulties attributed mainly to the high percentage of fine sand making up the samples. The only assumption that can be made is that the upper 60 cm is younger than 100 years in age, given the absence of $^{210}$Pb activity below this depth.

In the Barqueiro core, the $^{210}$Pb activity was very erratic even though the core granulometry was satisfactory. The results may not be consistent due to sediment remobilisation. Moreover, the type of core used at this site could in part be responsible for the anomalies detected, given that the lower levels could be contaminated by the upper ones.

The profile of the Ortigueira core showed a consistent decrease in activity, which ceased below 80 cm depth.

## Metal content

The differing granulometry of the cores demands a standardisation in order to assess the content of heavy metals using the <63 μm fraction, as suggested by Luoma et al. (1990). In Ortigueira, we could only determine the metal concentration levels of the nine upper samples due to the arenaceous core. We could not determine the Al and Zn content in samples 7, 8 and 9 because of their small size. The results of the analysis are shown in Fig. 4. The metal levels in the three estuaries fall within the following ranges: 0–1 μg g$^{-1}$ for Ca, 5–25 μg g$^{-1}$ for Co, 82–248 μg g$^{-1}$ for Cr, 14–44 μg g$^{-1}$ for Cu, 15–134 μg g$^{-1}$ for Pb, and 62–161 μg g$^{-1}$ for Zn.

These concentrations fall within the values generally measured in the Galician estuaries (Prego and Cobelo-Garcia 2003). Compared with other examples, the levels of pollution obtained resemble those of a moderately industrialised area such as the Tamaki estuary in Auckland, New Zealand, but differ considerably from those of highly polluted areas such as the Bilbao estuary in Spain or the Golden Horn in Istanbul, Turkey (Table 1).

In general, a standard element is used to offset the effects due to the texture so that if the concentrations of the analysed metals do not reveal an association with the standard, their enrichment through the sediment column will not result from an increase in the clay content (Cearreta et al. 2000). Aluminium was selected for the study area following the recommendation of Carral et al. (1995). Figure 3 gives the values of Al for each estuary and shows that the values at Viveiro and Barqueiro are fairly constant. Even though there is an increase in Al concentration in the upper samples from Ortigueira, their association with the metal concentration is not significant except for that of Zn.

## TOC, the C/N ratio and the <63 μm fraction content

We have used TOC, C/N and the <63 μm fraction to determine the origin and evolution of the sediments from a physical point of view. A number of authors have used the C/N ratio to identify the origin of the sediment (Muller 1997; Thornton and Mc Manus 1994; Helland 2001; Silva and Prego 2002). The variation in TOC can be used to indicate ground erosion and the dilution with mineral particles (Pereira et al. 1999), and the <63 μm fraction can be used to indicate the energy of the sedimentary environment (Helland 2001).

According to Muller (1997), sediment from marine material has a relation to C/N of approximately six, while vascular plants, rich in cellulose and with little protein, provide sedimentary material with relations of 20 or greater (Meyers and Teranes 2001). Pereira et al. (1999) identify C/N values between 7.8 and 8.9 in sediment columns characterised as having mixed marine or continental origins.

Diagenetic processes could modify the C/N relation in sediment columns after sedimentation (Pereira et al. 1999), thus limiting its usefulness if the carbon source initial signal is changed by a previous biochemical alteration and/or later sedimentation. Furthermore, the impact of the diagenetic processes in relation to the C/N relation is related to the type of decomposing material and the susceptibility to decomposition (Thornton and McManus 1994). Therefore, the thicker sediments present greater TOC and C/N values and in wood-derived materials the degradation of selected sugars and rich lipids in the carbon diminishes the C/N relation with time, whereas the C/N relation increases in algae-derived substances due to the nitrogen-rich proteins (Meyers and Teranes 2001). The same authors suggest that the change in the composition of sedimentary organic material is generally insufficient to mask its origin.

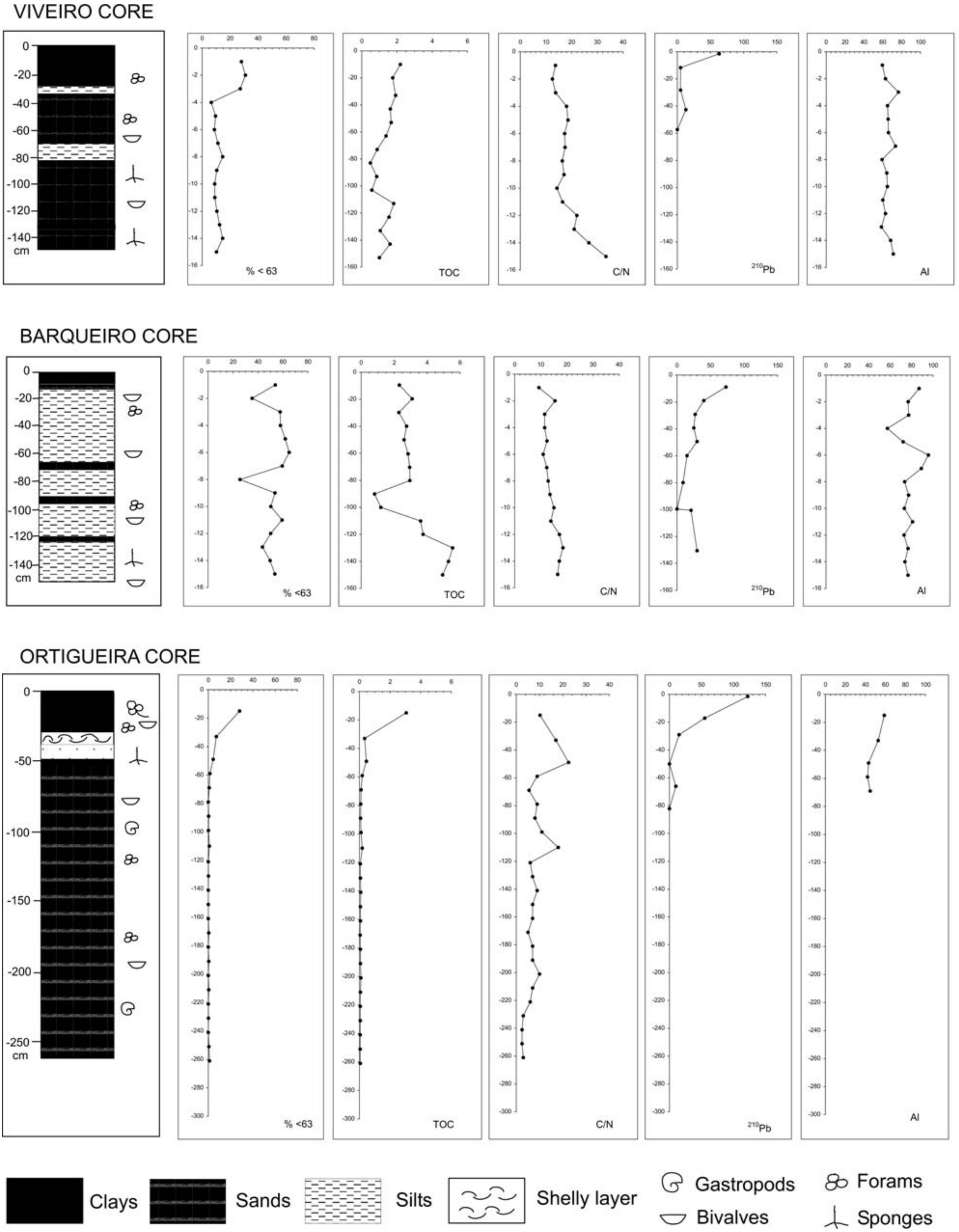


**Fig. 3** Lithological description of the cores, and variations in the organic content, C/N ratio, $^{210}$Pb, A1 and the <63 μm fraction

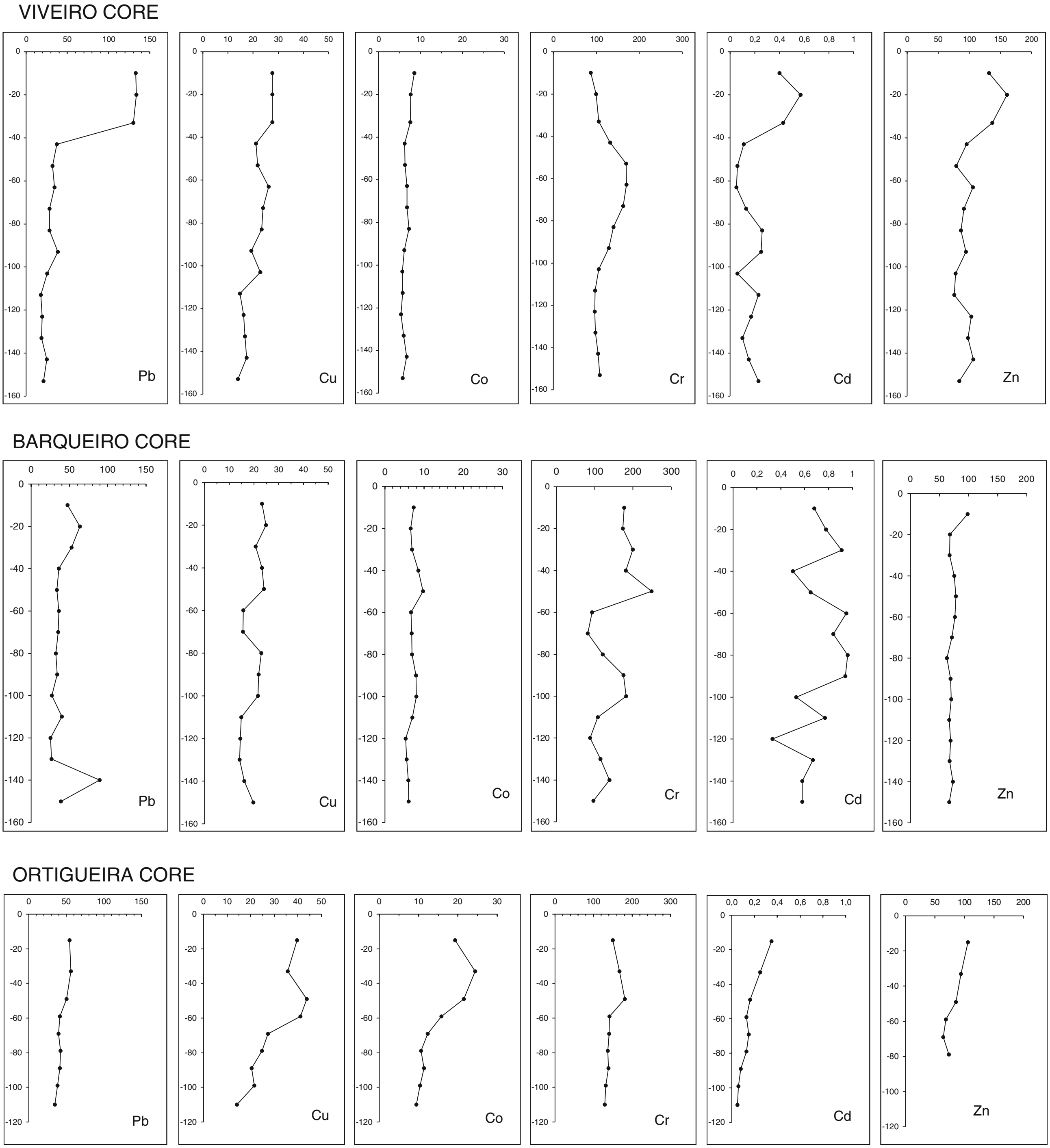


**Fig. 4** Variations in the concentrations of metals (μg/g) measured in the cores

In the interior parts of the Galician estuaries, distant from the oceanic influence, the C/N relation has an average value of 11, suggesting the importance of the continental organic material supply (Carballeira et al. 1997), whereas in superficial open waters, fronting the coast, a C/N value of 6.8 was obtained (IEO 1993). In this paper, the C/N values in the three cores show that the organic matter content is basically of terrestrial origin (Fig. 3).

Some differences detected are as follows:

In the Viveiro core, the TOC values range from 1 to 2% except in the central samples, 7–10, where the value is lower (Fig. 3). The C/N ratio decreases from base to top from 33 to 13, which indicates an increase

**Table 1** Content of heavy metal compared with that from samples in highly contaminated areas

| | | Pb | Cd | Zn | Cu | Co | Cr |
|---|---|---|---|---|---|---|---|
| Present work (<63 micras) | Top | 32.2–133.9 | 0.11–0.57 | 64.1–160.8 | 20.7–43.7 | 6.19–24.4 | 87–284.2 |
| | Bottom | 15–55.6 | 0.05–0.23 | 67.4–106.3 | 14.2–24.8 | 5.25–11.4 | 83.6–162.6 |
| Tamaki Estuary New Zealand (<63 micras) | Top | 74–200 | 0.14–1.49 | 138–365 | 23–60.35 | | |
| | Bottom | 9–27 | 0.02–0.09 | 14–121 | 1–22 | | |
| Bilbao (Spain)—heavily polluted | Top | 75–2,566 | | 167–7,687 | 41–1,949 | | 76–350 |
| | Bottom | 21 | | 63 | 20 | | 85 |
| Golden Horn (Turkey)—heavily polluted | Top | 510 | 6 | 890 | 194 | 24.5 | 390 |
| | Bottom | 420 | 1.25 | 128 | 274 | 20 | 84 |

Units are in μg/g. Data from Tuncer et al. (2001), Cundy et al. (2003) and Abrahim and Parker (2002)

in the marine character of the sediment. The <6.3 μm fraction remains approximately 10% in value except in the three upper samples, where it attains 30%, indicating a diminution of energy at the sampling site.

The Barqueiro core shows a constant diminution of the C/N value between 16 and 9 (Fig. 3). The TOC shows a decreasing tendency with basal values of 5.5%, and 2.3% at the top, with the exception of the two central samples, which show a marked dilution with values of 1%. The <63 μm fraction remains within a mean value of 50%, which indicates an area of very low energy throughout the period represented by the core.

The Ortigueira core reveals very low values for the <63 μm fraction with the exception of the upper 30 cm, reflecting an energy decrease at the sample point. The TOC values are very low <1% except for the upper sample, reflecting a lack of fine sediments, and there are important oscillations in the C/N ratio (Fig. 3).

## PCA

The PCA was applied separately to all samples from each estuary. Eigen values >1 were selected. To interpret a group of variables as associated in a particular factor, loadings greater than 0.6 were selected (Filgueiras et al. 2004). The factor loadings in the samples were then plotted in order to identify clusters.

For the Viveiro estuary, the results in Tables 2, 3 show that two eigen values are >1, which explains approximately 82.4% of the variance. PC1 includes the greater amount of variance (61.8%) and is highly loaded with Pb, Cd, Cu, Co and Zn (Table 4), and to a lesser extent with TOC, suggesting anthropogenic inputs. PC2, 20.6% of variance, includes Cr and Cu and it is considered as the second pollution factor because of an old industrial source of Cr. The influence of the PC1 on the samples slightly increases in sample 9 and jumps up in sample 3 (Fig. 5).

In the Barqueiro core, Cd was eliminated from the analysis because its anomalous values were attributed to the possible contamination of the samples. Two factors explain 72.3% of the variance in the Barqueiro estuary. PC1 of 51.4% shows a high loading of Cu, Co and positive Cr and is interpreted as sediment remobilisation because of the lack of industrial sources of Cr, whereas the strong negative load of TOC indicates an opposite relationship to these metals. The PC1 increasingly influences the core presenting an abrupt increase in sample 7 (Fig. 5); this jump is very clear in the Cr profile. Pb alone (Table 4) is explained by PC2 of 20, 9%, which may be of industrial origin. The clustering of samples clearly differs between the top and bottom of the core.

For the Ortigueira core, Zn was not considered in the analysis given that its value was not available for all samples. The two identified factors account for 92.2% of the variance. PC1 of 74.8% shows an influence of all the metals; and samples show increasing influence of this factor (Fig. 5) so it is interpreted as general pollution. PC2 (17, 4%) is loaded with just TOC and influences the three upper samples; it reflects changes in the physical composition of the sediment.

## Discussion

We found that the lowest samples in all three estuaries had low PC1 values, which can be considered a priori as a result of human influence. The PC1 content has been used as the criterion for obtaining the background value such that a sample not showing a positive PC1 charge was considered to be uncontaminated (Table 4). This is the first time that pre-industrialisation sediment deposit samples from this area have been found, so the background values herein can thus be considered more representative than those obtained by Carral et al. (1995) and Carballeira et al. (1997), who only analysed superficial samples.

Each estuary is assessed keeping in mind the above results and the industrial history of the area.

**Table 2** PCA results

| | Factor | Eigen value | Explained variance (%) | Accumulated variance (%) |
|---|---|---|---|---|
| Viveiro | 1 | 4.326 | 61.793 | 61.793 |
| | 2 | 1.439 | 20.557 | 82.351 |
| Barqueiro | 1 | 3.087 | 51.447 | 51.447 |
| | 2 | 1.252 | 20.873 | 72.320 |
| Ortigueira | 1 | 4.487 | 74.789 | 74.789 |
| | 2 | 1.042 | 17.364 | 92.153 |

**Table 3** Content of heavy metal in baseline (un-contaminated) samples of the estuaries studied

| Area | Pb | Cd | Cu | Co | Cr | Zn |
|---|---|---|---|---|---|---|
| Viveiro | 20 ± 2.8 | 0.18 ± 0.06 | 15.8 ± 1.4 | 5.9 ± 0.5 | 100.7 ± 5.2 | 93.4 ± 13.1 |
| Barqueiro | 29.7 ± 5.5 | | 16.3 ± 3.3 | 6.4 ± 0.7 | 96 ± 15.6 | 68.9 ± 4.6 |
| Ortigueira | 39.6 ± 2.8 | 0.1 ± 0.4 | 24.9 ± 9.1 | 11.6 ± 2.2 | 136.5 ± 4.9 | |
| Galicia[a] | 50 | | 35 | 13 | 54 | 20 |

Units are in µg/g

[a] Values given by Carballeira (1977) for Galicia, based on the analysis of surficial samples

**Table 4** Component matrix

| Metal | Viveiro | | Barqueiro | | Ortigueira | |
|---|---|---|---|---|---|---|
| | Component | | | | | |
| | 1 | 2 | 1 | 2 | 1 | 2 |
| Pb | 0.982 | 0.014 | –0.067 | 0.919 | 0.964 | 0.001 |
| Cd | 0.857 | –0.258 | – | – | 0.895 | 0.389 |
| Cu | 0.723 | 0.631 | 0.861 | 0.138 | 0.872 | –0.180 |
| Co | 0.868 | 0.335 | 0.900 | –0.141 | 0.945 | –0.264 |
| Cr | –0.330 | 0.875 | 0.885 | 0.229 | 0.828 | –0.501 |
| Zn | 0.927 | –0.071 | 0.395 | 0.411 | – | – |
| TOC | 0.619 | –0.300 | –0.770 | 0.384 | 0.646 | 0.733 |

## The Viveiro Ria

The grain size in the Viveiro core decreases upwards; this is indicative of a fall in energy at this point in recent decades. It is possible that the construction of a large breakwater in the port of Celeiro during the 1970s has had some influence. This structure has produced a marked reduction in wave energy with respect to the open sea waves, from 50 to 10% (Lorenzo et al. 2003).

The reduction in TOC of the sediments is often attributed to the dilution of these with inorganic components from mining operations (Pereira et al. 1999). In Viveiro, a reduction in the levels from 90 to 100 cm could be ascribed to the construction between 1921 and 1935 of the railway bridge over the Landro River (Gómez 1991), which involved large amounts of sediment remobilisation.

We can differentiate two inflection points (samples 3 and 11) in the decrease of the C/N profile. The increase of the marine character could correspond with an enlargement of the tidal prism that can be enhanced by engineering, dredging (Cox et al. 2003) and land reclamation (Plater and Appleby 2004). The key periods of the latter in the estuary are 1880, the 1930s and the 1970s (Fig. 6)

Three groups of samples were identified in the PCA and are interpreted as high, low and non-polluted (Fig. 5). The group formed by the three upper samples, which is strongly influenced by PC1, shows a parallel increase in the values of all the metals with the exception of Cr. Thus, it seems reasonable to attribute this factor to pollution due to human activity such as port improvements and the construction of shipyards in the Viveiro estuary in the 1970s. Although the values of Pb are high in the three estuaries, they are highest in the Viveiro estuary (Fig. 4), suggesting an additional local source of contamination, probably associated with the shipyards and ancillary industries at the port of Celeiro. Paint residues from these activities would

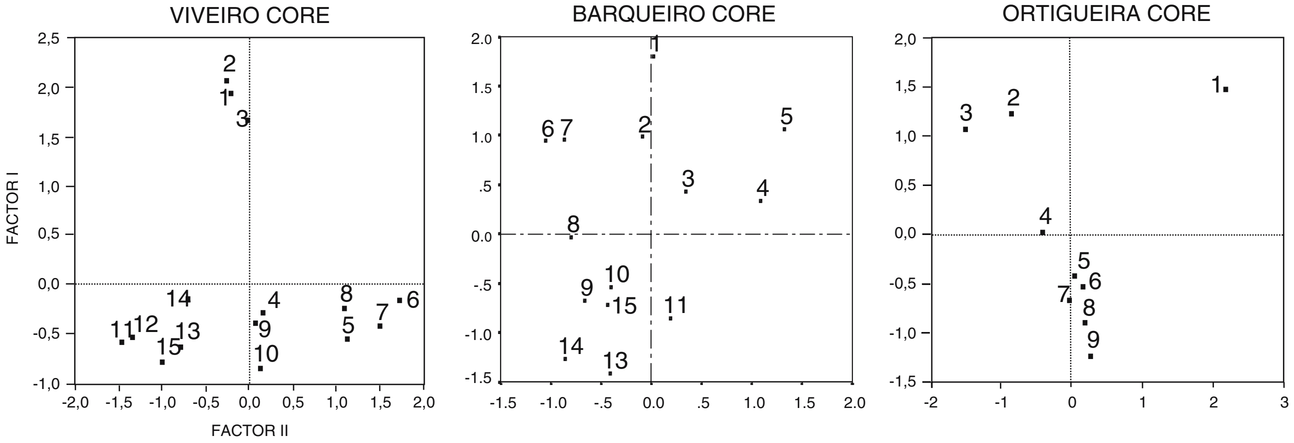


**Fig. 5** PCA loading plots for the samples

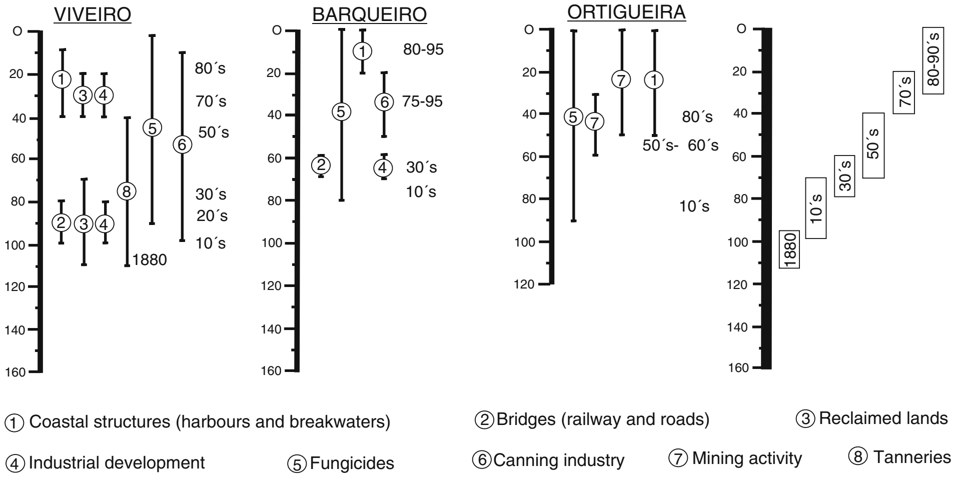
account not only for the high values of Pb but also for those of Cd and Co.

Group samples 4–10 show contamination due to Cu and Cr (PC2). The bell-curve distribution of Cr (Fig. 4) can be attributed to industrial pollution. Chromium sulphate has been used as a tanning agent since 1860, and tanneries were installed in Viveiro at the end of the nineteenth century (Fernandez 2002); in 1900, the village had three of these that ceased to operate by the 1950s. Cu, which is ubiquitous in Galicia, increases concentration in the upper 100 cm. Actual sources of Cu are power plants, industrial areas, the use of copper sulphate as a fungicide in vineyards (Fernandez 2000) and the use of slurry as a fertiliser, given the occurrence of Cu in cattle feed (Lopez Alonso 2002). Another possible source of Cu could be the anti-fouling products present in boat paints. Fernandez Prieto (1988, 1992) and Rosende (1988) considered 1910 as the date when the use of Cu sulphate in local agriculture became general practice. With this in mind, it may be considered that the upper 100 cm of sediment was deposited after this date.

Pb, Cd, Co and Zn show a peak at 90 cm, which suggests a common origin. The peak of Co is unnoticeable in the graphic representation because of the scale used, which was chosen to best compare the three estuaries. In 1912, there was an important automobile industry incorporating the use of metal, upholstery, paint, electrical workshops, and foundries (Chao 1988). This collapsed in 1930. The first canning industries in the area were first installed in 1908, and peaked in the1950s.

The correlation between the metals showing PCA seems to show a temporal association such that the different contaminating sources appear at the same time as the increase in industrial development, with samples 3 and 10 as the inflection points. Sample 3 (30 cm) corresponds to the construction of the port in the 1970s, and sample 10 coincides with the onset of zonal development in the decade between 1910 and

**Fig. 6** Chronology derived from the indicators of anthropogenic activity



1920 of canning, automobile industry and use of agrochemicals. These dates are further substantiated by the estimates obtained from the TOC, C/N, <63 μm and individual metal profiles.

Samples 11–15 are considered as non-contaminated, and their metal concentration corresponds to a background level before industrial growth. Sedimentation rates calculated on the basis of estimated ages are a maximum of 1 cm/year between 1970 and 2000 and 1.1 cm/year between 1910 and 2000.

### The Barqueiro Ria

In the Barqueiro estuary, the composition of the sediment core suggests a low-energy sedimentary environment. The organic matter content is higher than in the other estuaries, showing a dilution at 60–70 cm depth. This bears a strong resemblance to the situation in the Viveiro estuary, which could also be ascribed to the construction of the railway bridge near the mouth between 1930 and 1934 (Gomez 1991). This construction would be represented in the level of 70 cm and place the upper 70 cm later than 1930 (Fig. 6). The high TOC values at the base of the core could be due to the widespread deforestation that occurred in Galicia in the nineteenth century; this event is only factored into this estuary because the core gives the oldest representation. The gradual decrease of C/N could reflect sea-level rise that augmented the marine character of the sediment with an increase of the tidal prism.

Plotting of the sample loads identified two groups of samples interpreted as polluted and non-polluted. The sample group 8–14 is considered non-polluted and was used to calculate the background levels, while the group 1–7 is affected by PC1 (Fig. 5) that involves Cu, Co and Cr and is considered polluted. The possibility of an industrial origin for Cr may be ruled out given the absence of such activity. The nearest source of Cr is the Ortigueira estuary, which is underlain by basic and ultrabasic rocks containing high levels of Cr (Carballeira et al. 1997; Otero et al. 2000). Ultramafic rocks are also cited as a Cr source by Hornberger et al. (1999) for San Francisco Bay, California. During the low Last Glacial sea-level stage, sediments containing chromite could have been transported to the offshore platform by the rivers. During the Holocene marine transgression they entered the estuaries, which acted as sedimentary traps (Komar 1998; Bird 2000).

The levels of Cr could reflect the remobilisation of these sediments due to engineering works, the construction of a bridge across the River Sor from 1930 to 1934 and the construction of the port at O Vicedo between 1980 and 1995. This last event led to intensive erosion of the estuary beach-barrier (Lorenzo et al. 2003). The tidal flat immediately fronting any structure is often characterised by marked disturbance and eventual adjustment via erosion and sediment accretion (Plater and Appleby 2004). These works justify the existence of peaks in the Cr concentration, but not its sustained elevation, which is explained by the continual dredging of the estuary mouth. Co is highly concentrated in ultramafic rocks, and could have a similar origin to that of Cr even though the mobility is different. Sediment remobilisation could explain the low values of $^{210}$Pb in the upper core.

The profile distribution of Cu is similar to that in the Viveiro estuary. The base shows 15 ppm, reaches 20 ppm above, then decreases, followed by another jump in the upper samples (Fig. 4). This similarity could indicate a common source for the first jump as the use of Cu sulphate in agriculture around 1910. This would place the upper 80 cm of the core as later than 1910.

There are two peaks of Pb pollution; the upper one could correspond to recent industrial activity in the estuary. The only important installations were a canning factory from 1975 to 1995 and a kaolin washery from 1930 to 1980. No historical record of industrial activity accounting for this metal was found, with the exception of some old iron works.

The association presented by the PC1 appears to be only temporary. There is a jump at 70–80 cm that could coincide with the development of the estuary in the 1930s, at the time of installation of the kaolin washery and construction activity, and another jump in the upper 10–20 cm corresponding to the major thrust of port improvements in the 1980s.

Using Cu as reference, we interpret the upper 80 cm of sediment in the Barqueiro estuary as having been deposited since 1910 (Fig. 6). The TOC concentration shows a dilution at 70 cm and could correspond to the construction of the railway bridge between 1930 and 1934, as in the Viveiro estuary. PC1 suggests that the upper 70 cm was deposited after 1930. Using these dates, sedimentation rates of 0.9 cm/year between 1910 and 2000 and 1 cm/year between 1930 and 2000 may be derived.

### The Ortigueira Ria

This core had an arenaceous granulometry except in the argilaceous upper 30 cm, which indicates that the core represents the evolution of an active estuary channel into an intertidal mudflat. The latter is less affected by tides and has a greater biological activity.

Furthermore, the core shows large oscillations in its C/N relations, showing us alternations in the source. The change in the upper 30 cm is reflected in the PC2 (Table 4) that is rich in TOC and a noticeable negative charge of Cu, Co and Cr, three metals that are closely linked to the mineral assemblage within the deposits of this estuary. There is also a dilution of the mineral fraction caused by the organic matter. The dynamic character of the sediment that makes up this core is not generally representative of the estuary characteristics.

Clustering clearly differentiates samples 1, 2 and 3 from the others (Fig. 5). All samples are arranged in ascending order by PC1. The inclusion of all metals suggests increased human activity. Sample 9 (90 cm), the deepest sample analysed, contrasts with the others because of its lower values and is probably the only one from here that could be regarded as non-contaminated. Considering the PC1, the three upper samples are clearly polluted. Current industrial development is represented by a slate factory and mine in 1983 and the Cariño port enlargement during the 1980s. Consequently, the level of 50 cm of core represents the 1980s.

The levels of Cu and Co are much higher than those seen in the other estuaries (Fig. 4). These levels increase upward from 60 cm depth, reach a peak and then diminish to the surface. They are attributed to copper-mining operations in the Mera River basin, where diverse mineralisation of pyrite and chalcopyrite with other Cu sulphides including sphalerite-containing Co were exploited. The increase in concentration could be related to recent exploitation in the 1950s and 1960s. The upper 60 cm would be above the level of 1950 (Fig. 6).

The background values obtained (Table 4) are generally higher than those of the other two estuaries. This could be attributed to a lithological factor in the case of Co and Cr (Carballeira et al. 1997; Otero et al. 2000). Cu levels could be due to the mining operations and Pb to the old metal workshops that were common in the nineteenth century. These levels could also result from the use of recent, more contaminated samples for the background values. For example, if we view sample 9 (90 cm) as non-polluted, the background values would be similar. Cu reaches values of 15 ppm in sample 9 only; the increase, as in the other estuaries, could be related to the use of Cu sulphate in agriculture since 1910.

The sedimentation rates calculated with respect to the estimates of age according to the use of Cu sulphate in agriculture, mining of Cu and Co and the results of the PC1 are 1.2 cm/year between 1910–2000 and 1960–2000, and 2.5 cm/year between 1980 and 2000.

## Conclusions

The levels of pollution detected bear a marked similarity to those documented as occurring in association with a moderately industrialised area. The pollution in the Viveiro estuary is associated with progressive industrialisation of the area, including port improvement, industrial development and associated population growth. Cr in the sediment can be linked to the establishment and later collapse of the tanneries. In the Barqueiro estuary, the low level of industrialisation cannot account for the fairly high values of Co and Cr with respect to the baseline values. Erosion of Holocene marine sediments seems to be the source. In the Ortigueira estuary the high concentrations of Cr are associated with the Cabo Ortegal ultramafic rocks, and the high levels of Cu and Co are connected with discontinued mining activity. In the sediment of all the three estuaries, a part of the increase in the level of Cu may be ascribed to fungicides used since 1910 in local agriculture, and this can be used as a marker horizon.

The three estuaries present evidence of active sediment deposition. The sedimentation rate is around 1 cm/year.

In Viveiro the sediment composition reflects engineering work and land reclamation.

In Barqueiro there is evidence that the Holocene sediments act as the source of metals following engineering work. Sea-level rise seems to be affecting the marine character of the estuarine deposits at Barqueiro by enhancing sedimentation; more research is necessary to determine how this is affecting the sedimentation rate.

At Ortigueira the dynamic character of the sediments mask the detailed characteristics of metal pollution in the estuary.

Principal component analysis undertaken within the historical and geological setting of the pollutants has proven to be a very useful tool to differentiate polluted samples from those unaffected by anthropogenic impact in areas of medium to low human activity such as that which has taken place in and around the estuaries analysed here. The factors identified mainly reflect temporal associations with periodically available metallic sources.

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