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Industrial supply of trace elements during the "Anthropocene": a record in estuarine sediments from the Ria of Ferrol (NW Iberian Peninsula)

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Abstract

This work addresses the study of a sediment core retrieved in the estuary of the Grande-de-Xubia River (Ria of Ferrol), which is among the first industrialized areas in the Iberian Peninsula and has links to the shipbuilding industry since 1750. The chemical analysis of trace elements (i.e. As, Cd, Co, Cr, Cu, Hg, Mo, Ni, Pb, V, and Zn) was coupled with ^{210}Pb dating. The results span a period of about 130 years and cover the whole of the 20th century. Trace element anthropogenic fluxes accumulating in the sediments were calculated and show that human inputs are the most important sources for Cu, Cd, Hg and Zn, being, on average, well over the

natural loads. The temporal variation in the anthropogenic contaminants allows the identification of four main phases describing the human-natural input interactions, which in chronological order, are: (i) early industrialization, (ii) industrial acceleration or first industrial transition, (iii) industrial collapse, and (iv) an industrial maturity or a second industrial transition.

Keywords: chemostratigraphy, Industrial Revolution, risk elements, Pb-210 dating

Highlights

- Trace element anthropogenic fluxes were calculated.
- Copper, Cd, Hg and Zn are indicators of the historical human pressure in the area.
- True industrialization in the study area begins around 1945.
- The Great Acceleration in the industrial record was detected as between 1945 and 1973.

1. Introduction

Since humans entered the global industrial stage, "human activities have also grown to become significant geological forces" (Crutzen, 2002). The classification of a new chronostratigraphic epoch named "Anthropocene" is currently under evaluation by the International Commission on Stratigraphy (Zalasiewicz et al., 2017). Regardless of its formal definition (or not), the term is now widely used, being a cultural "zeitgeist" (Malhi, 2017) as a framework for a time marked by an exponential population growth, important alterations in natural dynamics, and an unprecedented quantity of anthropogenic materials entering the environment (Gaillardet et al., 2003; Lewis and Maslim, 2015). One of the most suitable environmental indicators highlighting human-nature interactions are sediments: they hold a memory of the current global alteration of geochemical cycles. Some trace elements such as Pb or Hg are recognized as chemostratigraphic markers with enough distinctiveness to leave reliable signals in sediments (Zalasiewicz et al., 2011). Their study promotes the necessity of high resolution temporal signals such as annual accumulation rates of geochemical indicators, coupled with the use of radiometric dating techniques such as those based on ^{210}Pb-^{226}Ra with an accuracy of years to decades (Waters et al., 2018).

Trace elements, hereinafter TEs, are defined as any element presenting an average concentration below 100 parts per million atoms, or under 100 mg kg^{-1} (IUPAC, 2014), in a given matrix. Some of them (i.e. Cu, Ni, Pb, Zn) are intimately linked to human activities, being common contaminants and elements of concern, and regarded as potentially toxic elements (Thornton et al., 2001) due to their possible harm to human health or ecosystem functioning. Rivers and coastal areas host many human activities such that estuaries are nowadays often the most impacted systems on the Earth (Brich et al., 2015) due to their being the ultimate end-point of anthropogenic waste materials, particularly during the industrial era. In this way, the Ria of Ferrol is linked to the beginnings of the Industrial Revolution in Spain through the development of the shipbuilding industry (Ocampo Suárez-Valdés and Ruiz García, 2017) and its establishment in 1750 as one of the most important naval headquarters in Spain, together with Cádiz and Cartagena. Two long cores previously retrieved from the middle part of the ria (Cobelo-García and Prego, 2003), showed a noticeable metal enrichment, mainly by Cu, Pb and Zn deposited during the industrial era. Other works on surficial sediments pointed to a higher impact in the middle part of this ria due to urban settlements and industrial activities (Cobelo-García et al., 2005), favored by a “restricted water exchange between the ria and the shelf” (Cobelo-García and Prego,. 2004a). Nevertheless, the estuarine area was barely addressed.

The work herein presents the analysis and interpretation of the anthropogenic TEs inputs to the estuary of the Grande-de-Xubia River, developed in the head of the Ria of Ferrol. Using TEs as indicators of human pressure, the aim is to characterize the human and natural processes interacting during the industrial era through the quantification of their anthropogenic fluxes recorded in estuarine sedimentary sequences.

2. Study area

Rias are particular coastal features, they are former fluvial valleys flooded by the sea after the last glacial maximum due to sea level rise. Their geomorphology is the result of glacioeustatic dynamics, tectonic structure and fluvial processes (Vidal Romaní, 1984; Méndez and Rey, 2000). Rias were first described in a scientific context by the geographer Ferdinand Von Richtofen in 1886 (Méndez and Vilas, 2005). A defining feature is that a ria has at least one small inner estuary which can move in response to climatic changes (Evans and Prego, 2003). The Artabro Gulf (NW Iberian Peninsula, see Fig. 1) is featured by the confluence of four rias (i.e. Ferrol, Ares, Betanzos and Coruña; sometimes a 5thria is also included, that of Cedeira, located northward), formed by fluvial incision (incised valleys) during the Neogene (Vidal Romaní, 2018). Between them, the Ria of Ferrol is a 15 km long valley covering a surface of 21 km^2 and containing about 0.25 km^3 of water (deCastro et al., 2004). The main continental watercourse is the Grande-de-Xubia River (or Xubia River), which drains into the innermost part of the ria featuring a small estuary. This river has a watershed of 182 km^2 and an average flow of 5.77 m^3 s^{-1} (Augas de Galicia, 2019). The lithology of the basin is composed of schist with paragneiss, siltstones, amphibolites and graywackes, and alkaline and calcoalkaline granites (DHGC, 2016). It also contains two points identified as mineral deposits (i.e. one with mineral associations of Cu, Fe, Au and Zn; and another with Fe, Cr, Ni and Pt; IGME, 2019; see location in Fig. 1). Land uses are highly modified, a 41 % of the basin is dedicated to eucalyptus plantations, and a 35 % corresponds to cultivation fields, while around 9 % are artificial surfaces (IET, 2015). Population density is low in this basin, about 163 inhab km^{-2}, being more concentrated on the ria shore with an estimated 612 inhab km^{-2} (data for year 2012, INEbase, 2019). It is important to note that, while the anthropogenic enrichment of TEs in estuarine sediments seems to be historically related to population growth in the Rias of Ares, Betanzos and Coruña (Álvarez-Vázquez et al., 2019), in the estuary of the Xubia River (Cobelo-García and Prego, 2004b) the data point to pure industrial wastes as the major contamination source of TEs.

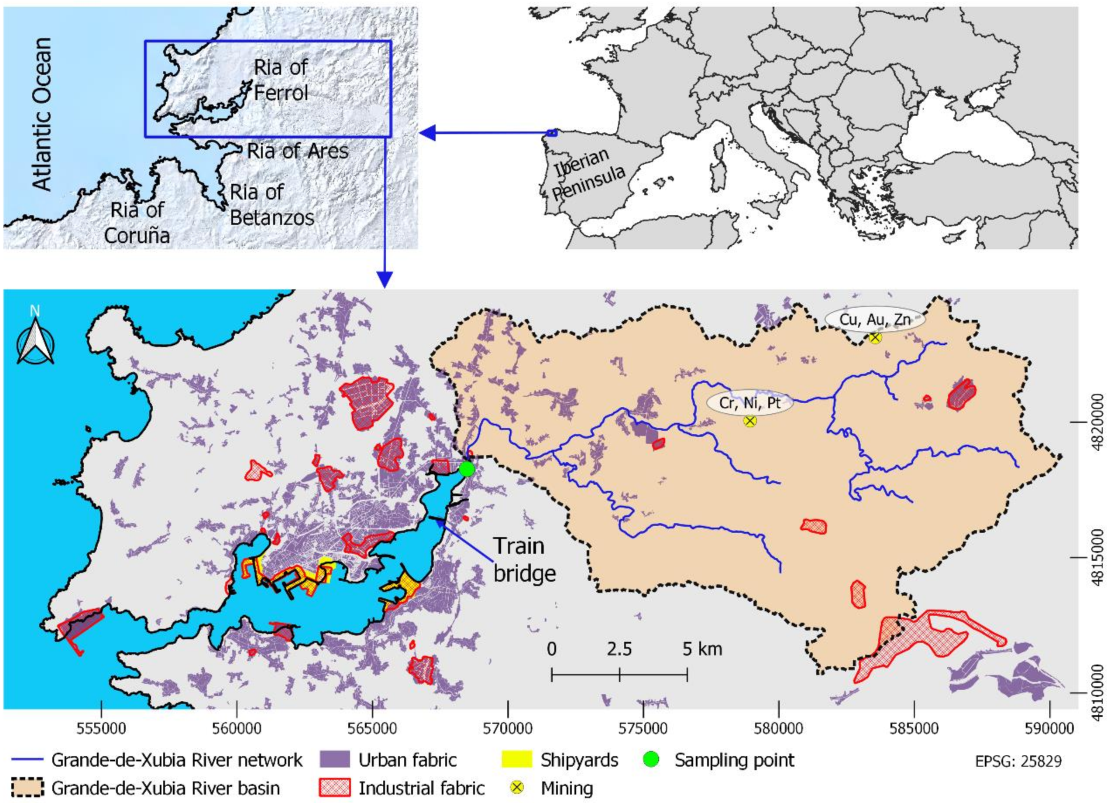

Figure 1. Location map showing the sampling point together with selected human factors around the Ria of Ferrol and the watershed of the Grande-de-Xubia River. Data from the Spanish National Geographic Institute (© IGN) and Instituto de Estudos do Territorio da Consellería de Medio Ambiente, Territorio e Infraestruturas (© Xunta de Galicia).

3. Material and Methods

A sediment short-core was hand collected in July 2012 in the estuary of the Xubia River (the innermost part of the Ria of Ferrol), in the intertidal muddy flats (43.5140N; 8.1528W), during low tide. A stainless steel hand-driven Gouge Augers Sampler, 61 mm inner-diameter and 70 cm long, was used. A 50 cm sediment column was recovered. The core was on-site sliced into 2 cm layers and stored in plastic zip-bags at 4° C. Once in the laboratory, core subsamples were dried at 45±5° C until constant weight. Dry sediment samples were grinded in an agate ball-mill to fine powders. Samples were split into three parts in order to perform different analyses, i.e. the organic matter content, the elemental contents, and dating by means of ^{210}Pb.

3.1. Chemical analysis

The contents of particulate organic carbon (POC) and sulphur (S) were determined by the Analytical Services of the University of A Coruña (SAI-UDC, Spain) using routine procedures. Sediments for POC determination were acid digested with HCl at 80° C to remove carbonates; then, POC was measured in an EA1108 Elemental Analyser (Carlo Erba Instruments). The S determination was performed on bulk samples in a FlashEA1112 Elemental Analyser (ThermoFinnigan). Replicates of a High Organic Sediment Standard (Elemental Microanalysis) was used to determine the precision of the methods, with the standard deviation lower than ± 0.05% (n=6).

The contents of major elements (i.e. Al, Fe and Mn) were determined by Atomic Absorption Spectrometry in the Marine Biogeochemistry laboratory of the Marine Research Institute (IIM-CSIC, Spain). Previously, samples were digested (microwave-assisted) using a 3:1 mix of HNO_3 and HF in Teflon bombs following the US-EPA guideline 3052 (US-EPA, 1996). The final determination was conducted in a Flame Atomic Absorption Spectrometer (SpectrAA 220 FS, Varian inc.) with a nitrous oxide-acetylene flame (Al), or an air-acetylene flame (Fe and Mn). The analysis of the content of trace elements (TEs; i.e. As, Cd, Co, Cr, Cu, Mo, Ni, Pb, V and Zn) was carried out in the Environmental Oceanography laboratory of the Portuguese Institute of Sea and Atmosphere (IPMA, Portugal). Samples were acid digested with HF and *Aqua Regia* according to Rantala and Loring (1975). After that, TEs contents were determined in a quadrupole ICP-MS (Thermo-Elemental X-series, Peltier impact bead spray chamber and concentric Meinhard nebulizer) following the method described by Caetano et al. (2009). Total mercury was also analysed in the IPMA by direct injection of the sample in an Atomic Absorption Spectrometer (silicon UV diode detector Leco AMA-254); samples, in an oxygen-rich atmosphere, were brought under pyrolysis (750° C) and Hg was collected on an Au-amalgamator (Costley et al., 2000). The validity of the methods was checked by the analysis of the certified sediment reference material PACS-2 (National Research Council of Canada). Results, which are presented in Table 1, were in good agreement with the certified contents. Procedural blanks were below the 1% of the element content of the samples.

Table 1. Control of the analytical procedure for the content determination of major and trace elements. Comparison between the analysed and the certified contents (n=5) for the certified reference material PACS-2 (NRC-Canada). Units are expressed in mg kg^{-1} except for Al and Fe which are in g kg^{-1}.

	Al	As	Cd	Co	Cr	Cu	Fe
Analysed	65.1±4.4	25.9±2.6	2.16±0.24	10.9±1.4	87.0±4.8	313±3	41.4±1.5
Certified	66.2±3.2	26.2±1.5	2.11±0.15	11.5±0.3	90.7±4.6	310±12	40.9±0.6
	Hg	**Mn**	**Mo**	**Ni**	**Pb**	**V**	**Zn**
Analysed	3.06±0.05	426±9	5.30±0.19	40.0±1.7	180±10	136±1	375±13
Certified	3.04±0.20	440±19	5.43±0.28	39.5±2.3	183±8	133±5	364±23

3.2. Core dating

Radionuclide analyses were performed in the Ionizing Radiation Laboratory (University of Salamanca, Spain), with a core resolution of 4 cm, in a Canberra n-type coaxial low-level background hyper-pure Germanium (HPGe) detector. The specific activities of ^{210}Pb, ^{226}Ra, ^{214}Pb and ^{137}Cs were simultaneously determined. For details on source preparation, spiking, for equipment background and spectra analyses see Álvarez-Iglesias et al. (2007). All sediment radionuclide concentrations are given in $Bq \cdot kg^{-1}$ dry weight. The $^{210}Pb_{xs}$ specific activity was calculated by subtracting that for the ^{214}Pb at 351.93 keV to that of the ^{210}Pb (46.54 keV) for each sample, assuming secular equilibrium between ^{226}Ra and the $^{210}Pb_{sup}$ fraction (Pfitzner et al., 2004; San Miguel et al., 2004; Álvarez-Iglesias et al., 2007). The core temporal framework was determined by applying the CRS model (Constant Rate of Supply), but first the core missing inventory was obtained (Goldberg, 1963; Appleby and Oldfield, 1978, 1992; Appleby, 1998; Cochran et al., 1998; Sanchez-Cabeza and Ruiz-Fernández, 2012).

Once the chronology is established, the ^{210}Pb-derived sedimentation rate can be estimated by dividing the length of each *i-th* interval by the time spam resulting from the ^{210}Pb chronology.

3.3. Reference values and anthropogenic inputs

TEs background levels (BL) can be estimated by the use of pristine references in similar physiographical areas (Birch, 2017). In this case the normalized (TE-Al ratios) background levels previously established for the nearby estuary of the Eume River (Ria of Ares, NBL_A; Álvarez-Vázquez et al., 2017) were considered due to the similarity of the catchment lithology and similar geographic complexities (Fig 1). Thus, the TE/Al background ratios (NBLs) considered were: As/Al $= 0.21 \cdot 10^{-3}$, Cd/Al $= 2.09 \cdot 10^{-6}$, Co/Al $= 0.15 \cdot 10^{-3}$, Cr/Al $= 1.05 \cdot 10^{-3}$, Cu/Al $= 0.32 \cdot 10^{-3}$, Hg/Al =

$1.09 \cdot 10^{-6}$, Ni/Al = $0.30 \cdot 10^{-3}$, Pb/Al = $0.36 \cdot 10^{-3}$, V/Al = $0.64 \cdot 10^{-3}$, and Zn/Al = $1.40 \cdot 10^{-3}$. In the case of Mo, although a BL was not established for the Ria of Ares, the average Mo/Al ratio calculated by Álvarez-Vázquez et al. (2017) for sediments of $24 \cdot 10^{-6}$ was considered in order to obtain a rough estimation. Although it can be made a direct comparison between the TEs contents ($[TE_{tot}]$) and their corresponding BL (by calculating the Contamination Factor-CF, Eq. 1; Hakanson, 1980), it is better to consider the relationship between the content of a target element normalized with respect to the content of a conservative element in the sample in front of the corresponding NBL (that is, calculating the Enrichment Factor-EF, Eq. 2, Zoller et al., 1974). In this case Al was chosen as the normalizer element, as a good proxy to minimize the grain-size effect, as recommended for the Galician Rias (Rubio et al., 2000; Álvarez-Iglesias and Rubio, 2012). This approach has been successfully applied in estuarine cores of nearby areas and elsewhere (e.g. Birch, 2017; Álvarez-Vázquez et al., 2017). The mathematical expressions of the indicated indexes are presented in the following equations:

$$\text{Eq. 1: } CF = [TE_{tot}]_i / BL$$

$$\text{Eq. 2: } EF = ([TE_{tot}]_i / [Al]_i) / NBL_A$$

The degree of contamination can be discussed according to the obtained CF and EF values. Then, the contamination criteria adopted were: EF $\leq$ 1 negligible, 1 < EF $\leq$ 3 possible/moderate, 3 < EF $\leq$ 6 considerable/severe, 6 < EF $\leq$ 9 very severe and, EF > 9 heavy (adapted from Hakanson, 1980; Prego et al., 2008).

Accordingly, The anthropogenic metal content ($[TE_{anthr}]_i$), for each core subsample (*i-th* depth interval) and TE, can be estimated by subtracting the expected background TE content from the measured total TE content ($[TE_{tot}]_i$). This expected background content was calculated considering Al concentrations as a grain-size proxy (that is, based on TE/Al ratios; Álvarez-Iglesias et al., 2012): ($[Al]_i \cdot NBL_A$). This calculation was performed according to Eq. 3:

$$\text{Eq. 3: } [TE_{anthr}]_i = [TE_{tot}]_i - ([Al]_i \cdot NBL_A)$$

Taking into account the established sedimentation rates, the TE fluxes to the sediment can also be calculated according to Eq. 4 (Cochran et al., 1998):

$$\text{Eq. 4: } F_i = s_i \cdot \rho_i \cdot [TE]_i$$

where F_i is the anthropogenic TE flux for the *i-th* depth interval (mg cm^{-2} yr^{-1}); s_i is the ^{210}Pb-derived sedimentation rate for the *i-th* interval (cm yr^{-1}); ρ_i is the dry bulk density (g cm^{-3}) of the *i-th* interval; and *[TE]* is the TE content for the *i-th* interval (mg g^{-1}). Depending on the TE content considered (total: $[TE_{tot}]$ or anthropogenic: $[TE_{anthr}]$), the total and the anthropogenic fluxes can be respectively calculated.

4. Results and discussion

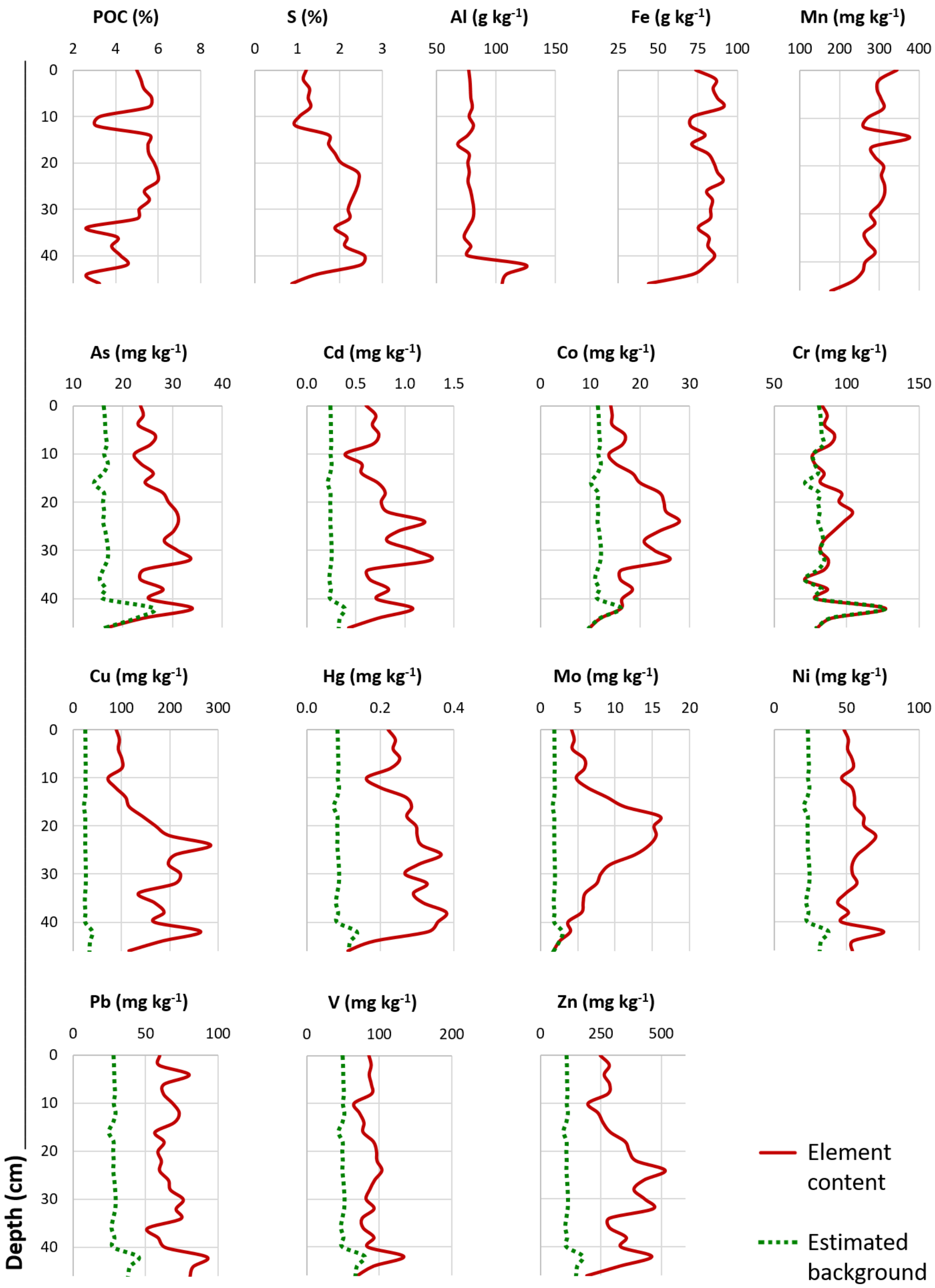

Figure 2. Depth profiles of key variables and trace elements in the core from the Ria of Ferrol. The background estimation according to the Al content of each trace element is also presented as a dotted line.

4.1. Evaluation of general core contents of trace elements

The summary statistics determined for the core contents of key variables (i.e. POC, S, Al, Fe and Mn) and trace elements (i.e. As, Cd, Co, Cr, Cu, Hg, Mo, Ni, Pb, V and Zn) are presented in Table 2. On a consideration of the TE content profiles (Fig. 2), preindustrial deposits were not present in the core as expected considering that the area has been under shipbuilding pressure since 1750. In order to perform a quick review-assessment, first, TEs contents in the studied sediments were compared to previously well-established local BLs: (i) one BL set determined in preindustrial layers from two long cores (1.6-1.8 m long) retrieved in the middle reach of the Ria of Ferrol in 1998 (Cobelo-García and Prego, 2003); (ii) another BL set determined in layers not affected by human activities (in this case those deposited before 1961) from a short core (0.5 m long) retrieved in the intertidal muddy flats of the Eume River Estuary, in the innermost part of the Ria of Ares (Álvarez-Vázquez et al., 2017), see Fig. 1. Both sets of BLs were compared and discussed by the aforementioned authors considering regional (e.g. Galician estuaries, Carballeira et al., 2000) and global scales (e.g. uncontaminated marine sediments, Doherty et al., 2000; composition of the upper continental crust, Rudnick and Gao, 2003).

In the data presented in Table 2, the TEs contents show, in general, well over the BL. Average CF values (Eq. 1) were 7-14 for Cu, 3-6 for Zn, 4 for Cd and Mo, 3 for Hg and Pb, 2-3 for Co and Ni and 2 for As and V. The lowest CF values were obtained for Cr (1.1). According to the considered contamination criteria there is a general heavy contamination by Cu; high for Zn, Cd and Hg; from moderate to high for Co and Ni; moderate for As and V; and from negligible to moderate for Cr. The Mo contents in the studied sediments are higher than those previously established for the Ria of Ares, and are also probably affected by diagenetic processes. If these Mo values are considered as BL, the Mo contents in the Ria of Ferrol would be indicative of a high contamination. Taking into account grain size variability for evaluating contamination, the EFs

(Eq. 2) for each element, arranged in decreasing order, were: 5.9±2.2 for Cu, 3.1±0.9 for Cd, 3.1±0.9 for Hg, 2.9±0.8 for Zn, 2.3±0.3 for Ni, 2.3±0.2 for Pb, 1.7±0.2 for V, 1.6±0.3 for As, 1.6±0.5 for Co and 1.0±0.1 for Cr. The average EF value for Mo was 4.1±2.4. In light of these results, there is detected, on average, a considerable/severe contamination for Cu, Cd, Hg and probably Mo, and a possible/moderate contamination for Zn, Ni, Pb, V, As and Co, while a possible Cr contamination is negligible.

Table 2. Summary statistics of the elemental contents of the studied core. Average ($\bar{x}$) and dispersion as standard deviation (SD) values, and the robust statistics of the 5-number summary (minimum, Min; quartile 1, Q1; median; quartile 2, Q2; and maximum, Max) are also presented. References for comparison are provided: baseline contents for the Ria of Ares (ARE, Álvarez-Vázquez et al., 2017) and background values for the Ria of Ferrol (FER, Cobelo-García and Prego, 2003).

	$\bar{x}$ ± SD	Min	Q1	median	Q3	Max	ARE	FER	
POC	48±11	26	41	52	56	60	21		%
S	18±5	9	13	19	22	26	4		
Al	83±14	68	77	79	81	125	75		g kg^{-1}
Fe	77±17	11	74	82	85	91	62	24±5	"
Mn	284±40	177	265	289	305	377	326		mg kg^{-1}
As	27±4	17	24	26	30	34	15		"
Cd	0.81±0.30	0.39	0.64	0.73	0.83	1.82	0.23		"
Co	19±5	10	15	17	24	28	11	6.1±1.5	"
Cr	88±11	71	82	87	92	127	78	63±14	"
Cu	165±77	72	101	167	199	410	24	12±3	"
Hg	0.27±0.07	0.11	0.23	0.27	0.31	0.38	0.09		"
Mo	7.6±4.2	1.8	4.5	6.0	9.4	16.0	1.9*		"

Ni	56±9	44	51	54	58	79	22	26±10	“
Pb	71±22	51	60	66	74	167	27	27±7	“
V	89±14	65	79	89	93	134	47		“
Zn	338±96	191	278	327	395	551	103	55±11	“

* Rough estimation due to post-depositional mobilisation of Mo.

All these elements are common contaminants linked to the shipbuilding industry, according to OECD (2010), with source in (i) base materials (i.e. Cd, Cr, Cu, Pb, Ni and Zn), (ii) surface coatings (i.e. Cu, Cd, Cr, Pb and Zn), and (iii) abrasive blasting materials (i.e. As, Cd, Cr, Co, Pb, Ni and V); but also linked to urban effluents (i.e. Cd, Cr, Cu, Hg, Ni, Pb and Zn; ICON, 2001). These results agree with previous studies on subsurface middle ria sediments and on surficial sediments from the Ria of Ferrol where contamination by Cd, Cu, Pb and Zn has been described (Cobelo-García et al., 2005; Cobelo-García and Prego, 2003). In these studies maximum enrichments were detected near contamination point-sources, and attributed to the discharge of untreated urban and industrial wastewater, and magnified by accumulation of contaminants in this ria due to its morphology (Cobelo-García and Prego, 2004a).

The natural and anthropogenic inputs to the study area were estimated for each sediment layer (Eq. 3). The average natural inputs for each element are as follows: 17±2 mgAs kg^{-1}, 0.25±0.04 mgCd kg^{-1}, 12±1 mgCo kg^{-1}, 83±10 mgCr kg^{-1}, 26±4 mgCu kg^{-1}, 0.089±0.014 mgHg kg^{-1}, 25±4 mgNi kg^{-1}, 30±5 mgPb kg^{-1}, 53±8 mgV kg^{-1}, and 115±18 mgZn kg^{-1}. A rough estimation for Mo is below 1.9±0.3 mg kg^{-1}. The average anthropogenic contribution of TEs to the sediments, in decreasing order, can be estimated as: 81±7 % for Cu, 65±13 % for Cd, 63±17 % for Hg, 63±12 % for Zn, 57±6 % for Pb, 55±6 % for Ni, 39±10 % for V, 34±12 % for As, 32±18 % for Co, and 5±7 % for Cr.

4.2. Core chronology

Specific activity profiles of ^{214}Pb, total ^{210}Pb, and ^{137}Cs are shown in Fig. 3. The ^{214}Pb specific activity was around 32 Bq kg^{-1}. Total ^{210}Pb specific activity was highest at the surface, reaching values of 87.8 Bq kg^{-1}, and then, decreasing down the core until values about 44.9 Bq kg^{-1} at 36 cm. The specific activity of $^{210}Pb_{xs}$ decreased almost monotonically with depth, with maximum surface values of about 55.3 Bq kg^{-1}. $^{210}Pb_{xs}$ was almost undetectable (6.2 ± 4.9 Bq kg^{-1}) at 36 cm. The total $^{210}Pb_{xs}$ inventory (considering an estimation of the missing inventory below 38 cm) was 4.65(53) kBq m^{-2} and the corresponding $^{210}Pb_{xs}$ flux was 209(24) kBq m^{-2}·yr^{-1}. The ^{137}Cs isotope was detected along the entire core. The specific activity of ^{137}Cs was over 4 Bq kg^{-1}, and showed a maximum at 20-24 cm (16.7 ± 0.7 Bq kg^{-1}). According to the ^{210}Pb geochronology, this maximum corresponds to the year 1974±7. Furthermore, in the ^{137}Cs profile, peaks corresponding to the maximum inputs into the environment (1963, 1987; Nielsen, 1995; Andersen et al., 2000) were not observed for this radionuclide due to diagenetic mobilization (Davies et al., 1984; Zwolsman et al., 1993; Kim et al., 1997; Foster et al., 2006; Álvarez-Iglesias et al., 2007). Taking into account that ^{210}Pb mobility is negligible under anoxic and moderately sulfidic conditions (Crusius and Anderson, 1991), the obtained ^{210}Pb chronology is reliable, but needs to be validated by other techniques independent of age control. In this case, anthropogenically induced changes in the environment have been considered, as discussed below. The chronological framework based in ^{210}Pb CRS dating covers the last 67±33 years (36 cm depth). The estimated average sediment accumulation rate for this dated period was around 6.2 mm yr^{-1}. The gradual reduction in the obtained $^{210}Pb_{xs}$ activity depth-profile points to a progressive accumulation, without remobilisation of sediments, at least since the year 1945±33.

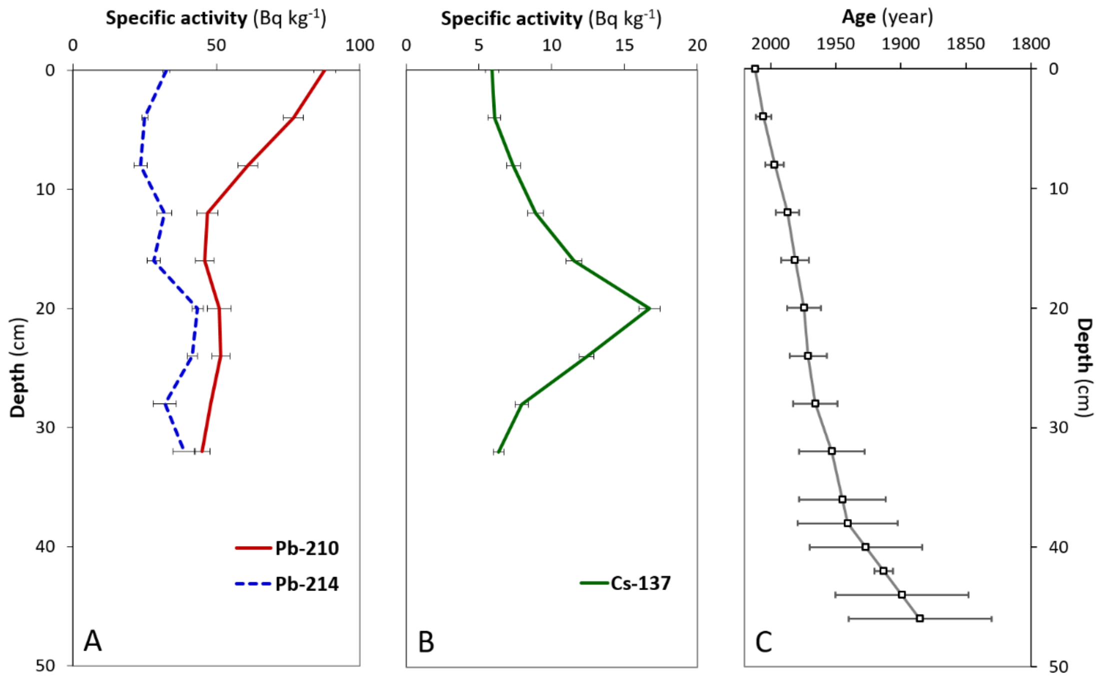

Figure 3. Depth profiles of ^{210}Pb-^{214}Pb (A), ^{137}Cs (B) and the results of the depth/age model (C) in the core from the estuary of the Grande-de-Xubia River, Ria of Ferrol.

In the depth-profiles of As, Cd, Co, Zn and Cu (Fig. 2), a change from lower to higher anthropogenic TE contents can be observed (i.e. considering the difference between the estimated background and the measured total content), that, according to the ^{210}Pb chronology, would have occurred between 1953±25 (32 cm) and 1971±14 (24 cm). This change is also observed in the POC profile. The maximum anthropogenic input is clear in the profiles of Cu and Zn at 24 cm depth, and could be related to the rupture of a mining settlement pond situated inside the Xubia River basin, which happened in the early 1960s, and thus, corroborates the ^{210}Pb chronology. The mine exploited massive Cu-sulphide deposits which presented mineral associations of Fe, Au and Zn (IGME, 2019). The incident, as described in the testimonies, involved a significant release of contaminated sludge into the river, and therefore, into the estuary. In addition, diagenetic processes can modify TEs profiles leading to certain element peaks (Álvarez-Iglesias and Rubio, 2008; Huerta-Díaz and Morse, 1990), such as those observed at 24 cm in the studied core.

Aluminium content is relatively constant from the surface to 40 cm depth (77.7±2.9 g kg^{-1}), increasing by less than 145 % on average (113±11 g kg^{-1}; Fig. 2). This element is commonly used as a lithogenic proxy due to its presence as a major constituent of rocks and its relationship with clay minerals (Birch, 2017). This change is also clearly marked in the depth-profiles of other elements, such as Ni and Cr, elements that are mainly bound to silicates in intertidal and subtidal ria sediments (Álvarez-Iglesias and Rubio, 2008, 2009). Thus, the marked change in Al contents at 40-42 cm could be pointing to a change in the hydrodynamics of the system. This could result from the construction of a railway bridge in 1913 (Yáñez, 2008) with a breakwater that covers around three quarters of the bridge length, and which affected the water circulation patterns in the area, and allowed the settling of fine-grained sediments. According to the ^{210}Pb model, sediments below 40 cm deposited before 1945±33, and thus, around the year of the bridge construction, were assigned to the sample located at 42 cm. Taking into account this temporal marker, sedimentation rates around 1.4 mm yr^{-1} were obtained for the bottom samples of the core. When extrapolating this rate downwards, the studied core will correspond to an estimated period of about 130 years (until 46 cm). Sedimentation rates were low until 1966 (< 5 mm yr^{-1}), and then rose markedly until 1974 (exceeding 12 mm yr^{-1}), then decreased until 1997 (around 4 mm·yr^{-1}), and finally slightly increased up to 2012 (> 6 mm yr^{-1}). According to the established temporal framework, the estimated $^{210}Pb_{xs}$ fluxes are about 200 Bq·m^{-2}·yr^{-1}, coherent with the expected atmospheric fluxes (around 120-140 Bq m^{-2} yr^{-1}; Appleby, 1998) for the study area, considering mean annual rainfall (around 1000-1200 mm; Castillo Rodríguez et al., 2006).

4.3. Integrated view

From a consideration of the time-variation of the anthropogenic fluxes of TEs to the sediments (calculated according Eq. 3) and the Enrichment Factors (EFs, Eq.2), four phases are distinguishable (Table 3 and Fig. 4):

Table 3. Anthropogenic fluxes of trace elements to the sedimentary record of the Grande-de-Xubia Estuary (Ria of Ferrol). Results are divided into four stages of industrial development in the area and presented as mg m^{-2} yr^{-1}- minimum (median) maximum.

	Early Ind. Before 1945	**Acceleration** 1945-1975	**Collapse** 1975-2000	**Maturity** After 2000
As	nd (8.3) 10.9	18 (49) 80	14 (28) 42	12 (18) 21
Cd	0.15 (0.49) 0.79	0.9 (3.0) 3.2	0.4 (1.3) 1.5	0.7 (0.9) 1.3
Co	nd (2.3) 6.3	14 (47) 78	5 (20) 33	4.9 (6.2) 11.0
Cr	nd - 3.6	nd (25) 125	nd (12) 40	3.8 (8.2) 18.5
Cu	119 (149) 253	269 (687) 968	118 (257) 355	127 (145) 195
Hg	nd (0.23) 0.28	0.3 (0.7) 1.2	0.20 (0.47) 0.78	0.27 (0.32) 0.43
Ni	22 (28) 43	47 (117) 261	48 (104) 138	50 (58) 77
Pb	25 (44) 62	60 (146) 184	53 (100) 178	63 (80) 96
V	3 (32) 61	56 (149) 275	41 (91) 127	67 (78) 108
Zn	64 (222) 323	430 (1180) 1594	227 (522) 652	275 (329) 482

Ind.: Industrialization; nd: non detected

(i) **Early industrialization:** before 1945. The year 1750 is considered to be the beginning of this period because, at this time, the ria had become a strategic centre of military shipbuilding and Navy settlement, and it was also coupled with both a strong auxiliary industry (González-Llanos Galvache, 1996; Franco Castañón, 2008) and the exploitation of mineral deposits within the river basin (Castroviejo Bolibar et al., 2004). This period was identified in two long cores retrieved in the centre of the middle ria by Cobelo-García and Prego (2003) by a marked upwards enrichment in the TEs contents depth-profiles. In the studied estuarine sediments, this stage is depicted by the enrichments of Cu and Cd, and, to a lesser extent, Hg, Zn and Pb. Average EFs in this lowest part of the core were indicative of a very severe contamination by Cu (EF = 6.1), considerable/severe by Cd (EF = 3.8), and possible/moderate for Hg (EF = 2.9), Zn (EF = 2.5) and Pb (EF = 2.1). The average anthropogenic sediment fluxes can be arranged by relative importance, as the anthropogenic average and percentage of the total TE flux, as follows: Cu (168 mg m^{-2} yr^{-1}, 82%) > Cd (0.48 mg m^{-2} yr^{-1}, 57%) = Zn (205 mg m^{-2} yr^{-1}, 57%) > Pb (44 mg m^{-2} yr^{-1}, 52%) > Hg (0.18 mg m^{-2} yr^{-1}, 54%) > Ni (29 mg m^{-2} yr^{-1}, 48%) > V (33 mg m^{-2} yr^{-1}, 33%) > As (6.3 mg m^{-2} yr^{-1}, 23%) > Co (2.7 mg m^{-2} yr^{-1}, 16%) > Cr (0.60 mg m^{-2} yr^{-1}, 1%). As can be seen in Fig. 4, the trend between 1885 and 1945 is relatively constant or with a slight tendency to increase.

(ii) **Industrial acceleration or first industrial transition:** 1945 - 1973. The true industrialization observed after 1945 is in agreement with the work of Álvarez-Vázquez et al. (2017). These authors frame the generalization of industrialization in the area after the Spanish Civil War (1936-1939). With the support of the dictatorship, Ferrol developed an important modern industry for military shipbuilding but also, aimed to produce civil vessels. Between the 1930s and the 1950s the industry underwent modernization and restructuring to be competitive in an international context. Production experienced a great expansion, particularly after 1962, employing more than 20,000 people (Cardesín, 2004). In this period, and related to the exploitation of mineral deposits within the river basin (sulphides with mineral associations of Cu, Au and Zn; Fig. 1), the previously mentioned breakage of a Cu-mine pond in the early 1960s could introduce into the estuary important amounts of TEs (the authors did not find any citable reference for this event, nor the precise date; it is only supported by oral unauthenticated oral statements). There is also an important source of contamination in this period (Prego et al., 2003), a siderurgy arose in 1939 to recycle iron and steel by-products from the shipyards, and it located on the shore of the estuary. In between 1945 and 1975, almost all the studied TEs increase their contamination indexes, particularly Cu (average EF in this period = 8.1, with a peak of 11.6 in 1971) and Cd (EF = 5.7, with a peak of 7.5 in 1971); also Zn (EF = 3.7), Hg (EF = 3.6), Ni (EF = 2.5), Pb (EF = 2.4) and Co (EF = 2.0). In decreasing order, the average importance in TEs fluxes was observed to be as follows: Cu (632 mg m^{-2} yr^{-1}, 87%), Cd (2.4 mg m^{-2} yr^{-1}, 73 %), Zn (1066 mg m^{-2} yr^{-1}, 72 %), Hg (0.82 mg m^{-2} yr^{-1}, 72 %), Ni (134 mg m^{-2} yr^{-1}, 60 %), Pb (134 mg m^{-2} yr^{-1}, 57 %), Co (44 mg m^{-2} yr^{-1}, 49 %), V (155 mg m^{-2} yr^{-1}, 44 %), As (48 mg m^{-2} yr^{-1}, 44 %), and Cr (40 mg m^{-2} yr^{-1}, 9 %). All the TEs present similar profiles (see selected elements in Fig. 4). An accelerated increase was detected, with maxima in the late 1960s-early 1970s, as observed e.g. in the Bay of Cadiz in the second half of the 20th century (Ligero et al., 2002) as consequence of industrial and urban impacts. For example, the increase in the Cu fluxes to the sediment can be adjusted to a straight line with a slope of 19.5 mg m^{-2} yr^{-1} ($r = 0.70$, $n = 8$). This phase is simultaneous with the so-called “Great Acceleration” that happened in the mid-20th century (Steffen et al., 2007; 2011), delineated, together with other indicators, by an important release of TEs (Pb and other metals) into the environment as result of industrialization (Lewis and Maslim, 2015).

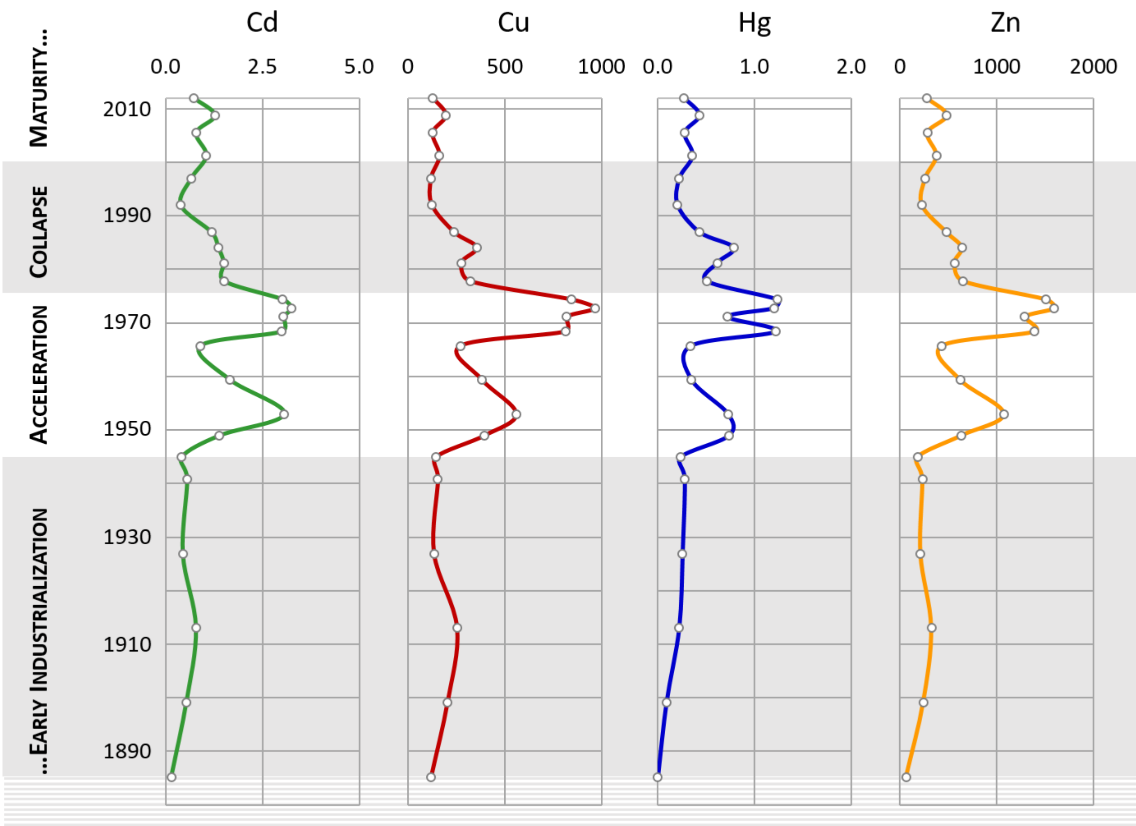

Figure 4. Temporal evolution of the anthropogenic TEs fluxes to the sediment in the estuary of the Grande-de-Xubia River (Ria of Ferrol) and identification of four different phases. Results are presented in mg m^{-2} yr^{-1}.

(iii) **Industrial collapse:** 1973 – 2000. At this stage, the effects of the 1970s international recession are similar to the collapse of economic growth following the Second World War (Tausig and Fenwick, 1999). In the particular case of Ferrol, together with the international crisis according to Cardesín (2004) there are several possibly responsible factors such as the socio-economic instability in the 1970s, just before the change of the political regime; and also the internationalization of Spain in the 1980s, with its entry in the European Economic Community. These resulted in policies of naval reconfiguration that highly impacted the shipyards of the ria. Additionally, some information places the closure of Cu-mine in the late 1960s, but closure of mining activities is not usually followed by a drastic decrease in sediment contamination, e.g. as observed in the sedimentary registry of the Nalón Estuary and the Asturias' coast, N. Spain

(García-Ordiales et al. 2020 ; García-Ordiales et al. 2017). During this period of recession, the EFs drastically decay. Only Cu and Cd present average EFs around 4 (4.3 and 3.9, respectively), the Cu levels drops to a possible/moderate contamination. The average fluxes to the sediment at this stage are: Cu (239 mg m^{-2} yr^{-1}, 75 %), Hg (0.46 mg m^{-2} yr^{-1}, 62 %), Cd (1.1 mg m^{-2} yr^{-1}, 59 %), Zn (470 mg m^{-2} yr^{-1}, 58 %), Pb (116 mg m^{-2} yr^{-1}, 58 %), Ni (95 mg m^{-2} yr^{-1}, 58 %), V (88 mg m^{-2} yr^{-1}, 37 %), As (26 mg m^{-2} yr^{-1}, 35 %), Co (19 mg m^{-2} yr^{-1}, 33 %), and Cr (16 mg m^{-2} yr^{-1}, 6 %). The trend in the last quarter of the 20^{th} century reflects an important reduction in the anthropogenic inputs. Again the example of Cu is illustrative, adjusting to a straight line the slope is -12.3 mg m^{-2} yr^{-1} (r = 0.88, n = 6).

(iv) **Industrial maturity or second industrial transition**, after 2000. With the new millennium the naval industry in Ferrol was reactivated thanks to new policy strategies (Cardesín, 2004). This increase in the industrial activity is not accompanied by an increase in the anthropogenic contributions of TEs to the estuary. The adoption of environmental protection regulations coming from the European Union lead to better production systems and a reduction in human pressure on the ecosystems. This effect was also observed in the industrialized Ria of Bilbao (Fdez-Ortiz de Vallejuelo, 2010), or even in low industrialized areas related to the implementation of the urban wastewater treatment after the European Water Framework Directive (Álvarez-Vázquez et al., 2018). For the first time, Cd is the element that shows the highest average EF (4.1) followed by Cu (3.8), both remaining at levels of possible/moderate contamination. Mercury (2.8), Zn (2.5), Pb (2.3) and Ni (2.2) present average EFs slightly higher than 2. These enrichments are not necessarily linked to new anthropogenic inputs, as observed by Cobelo-García and Prego (2004b), because the resuspension of contaminated sediments in the estuary can be acting as secondary contamination source. During this stage, sediments fluxes are estimated as follows: Cu (153 mg m^{-2} yr^{-1}, 74 %), Cd (1.0 mg m^{-2} yr^{-1}, 64 %), Hg (0.33 mg m^{-2} yr^{-1}, 64 %), Zn (354 mg m^{-2} yr^{-1}, 59 %), Pb (80 mg m^{-2} yr^{-1}, 56 %), Ni (61 mg m^{-2} yr^{-1}, 54 %), As (17 mg m^{-2} yr^{-1}, 32 %), Co (7.1 mg m^{-2} yr^{-1}, 21 %) and Cr (9.6 mg m^{-2} yr^{-1}, 5 %). The TEs content profiles during this stage remain relatively constant (Fig. 4).

These phases are coherent with the environmental zones previously described in the sedimentary record of the Bilbao estuary by Cearreta et al. (2002) attributed to the impact of untreated domestic and industrial effluents. These zones are: pre-industrial (not achieved in Ferrol), older industrial (early industrialization) and younger industrial (acceleration). The work herein describes two additional phases in the sequence: collapse and maturity. The first and second industrial transitions were denominated due to the similarity and chronological parallelism with the population dynamics described for the theories of the First and Second Demographic Transitions (e.g. van de Kaa, 2002).

5. Concluding remarks

The estuary of the Grande-de-Xubia River has been surrounded by important industrial activities since the middle of the 18th century. Its sediments are a suitable record to study the impact and evolution of anthropogenic inputs during the industrial era. The studied core covers 130 years, since 1885, reflecting an acceleration in the human inputs after 1945, when it can be stated that the true industrial era had started. Copper, Cd, Zn and Hg are the most illustrative contaminants, reaching maximum signals around the early 1970s, presenting enrichment factors up to 11.6, 7.5, 4.8 and 4.2, respectively. The average amounts of anthropogenic trace elements entering in the sedimentary record were 82 % for Cu, 64 % for Cd and Hg, 63 % for Zn. Four phases were distinguished by: (i) an early industrialization denoted by a relatively low impact; followed by (ii) an acceleration between 1945 and 1973, that could be related to the mid-20th century "Great Acceleration", presenting the highest values for contamination indexes; (iii) a collapse in the industrial activity, denoting the effects of the 1970s global crisis, which means a drastic fall of anthropogenic contributions to the sedimentary record; and (iv) an industrial reactivation after 2000, when more environmental friendly processes responding to protection policies result in a low contamination.

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