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Natural and Anthropocene fluxes of trace elements in estuarine sediments of Galician Rias

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ABSTRACT

The Anthropocene has been proposed as a new geo-stratigraphic epoch where humans have become a global factor affecting the ecosystems. Estuarine sediments constitute a biogeochemical reservoir where trace elements (TEs) from natural sources mix with a fraction generated by human activities. This study assessed the natural lithogenic imprint of TEs from uncontaminated sedimentary records to study anthropogenic changes. Sediment cores were sampled in the estuarine part of the low populated and low industrialized rias of Ares (A), Betanzos (B) and Cedeira (C), which are located in the NW of the Iberian Peninsula. Cores were dated by the ^{210}Pb method, covering up to the last century period. Sedimentation rates (in mm yr^{-1}) were 3.4 ± 0.6 (older than 1961) and 8.2 ± 3.2 (younger than 1961) for core A, 0.9 ± 0.2 (<1940) and 4.2 ± 2.3 for core B, and 13.4 ± 1.4 for core C. The background fluxes of TEs were in the ranges of (in g m^{-2} yr^{-1}) 50–560 for Al and Fe, 20–320 for POC and 8–100 for PS, and (in mg m^{-2} yr^{-1}) 20–120 for As, 0.2–2.0 for Cd, 7–110 for Co, 40–870 for Cr, 20–230 for Cu, 0.1–0.6 for Hg, 290–2800 for Mn, 4–24 for Mo, 20–410 for Ni, 20–150 for Pb, 60–800 for V and 70–700 for Zn. The three cores showed an anthropogenic influence since the mid-20th century. The detected human impact during the Anthropocene was due to the Eume River damming and As-Pontes lignite mining (the largest mine open-pit in the Iberian Peninsula) in core A, by bridge/road constructions, vehicles emissions and river mouth urbanization in core B, and changes in land use in core C. Sediment accumulation rates increased 2.4 (core A) and 4.7 times (core B) while TEs fluxes increased 2.4 times in core A and between 3.6 and 5.1 times in core B. Pre-industrial sedimentary records showed the lithogenic differences of the drainage basins, mainly granitic watersheds for cores A and B and the prevalence of basic rocks of the Ortegal Geological Complex for core C. This explains the high concentrations and fluxes of Cr, Ni and V of core C. The different lithogenic imprints highlight the value of using local background references in contamination studies, such as those on the Anthropocene influence in estuaries, which occurred after the Spanish Civil War in the studied rias.

1. Introduction

Rivers are the main route of entry of materials to coastal areas and the global ocean. These materials come mainly from the weathering of rocks in the continental realm, and travel through the fluvial courses as bedload, in suspension or in solution (Nichols, 2009). In estuaries, sediments which have not been anthropogenically altered constitute, therefore, a historical record of the natural quality of the estuarine environment. Sediments, depending on their source, incorporate a 'natural lithogenic component' (Schropp and Windom, 1988) and a 'natural biogenic component' (Álvarez-Iglesias and Rubio, 2012). When sediments become contaminated

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they include the supply derived from human activities, usually referred to as the 'anthropogenic component' which includes both inorganic and organic inputs. This has been especially significant since the beginning of 20th century when many estuaries were severely affected by human actions (Meybeck and Vörösmarty, 2005) as a result of a 'drastic release' of different contaminants to the environment (Gaillardet et al., 2003). This period, not yet formally defined, has been proposed to be called the Anthropocene (Steffen et al., 2011; Waters et al., 2016), when the human imprint is felt globally, with estuaries among the most impacted environments (Birch et al., 2015).

Rae (1997) says that the anthropogenic contribution of some trace elements (TEs) currently equals or exceeds the amount released by weathering, especially in intertidal coastal areas which, in many cases, is where industrial effluents and other wastes are discharged. This author highlights the estuaries often as sites of intense human pressure. In order to evaluate this human imprint it is necessary to establish background levels (Ruiz, 2001; Álvarez-Iglesias et al., 2006; Prego et al., 2008). In this sense, the study of undisturbed sediments, or pre-industrial layers from sediment cores, is valuable in determining the degree of contamination in estuarine and coastal areas (Santschi et al., 2001). When coupled with geochronological techniques by determining radionuclides (e.g. ^{210}Pb, ^{137}Cs, ^{241}Am) it allows the concentration of TEs to be related to a deposition date, and thus, reconstructing the temporal evolution of those sediments (Sanchez-Cabeza and Ruiz-Fernández, 2012). In this sense, there are many works devoted to the study of TEs in the river-ocean boundary in different sedimentary environments: sediments accumulated in inland reservoirs (Audry et al., 2004), in estuarine areas (Santschi et al., 2001; Riba et al., 2002; Spencer et al., 2003; Qi et al., 2010), in embayments (Santschi et al., 2001; Álvarez Iglesias et al., 2007), or on the continental shelf (Costa et al., 2011). In addition, there are studies covering larger spatial areas having a more regional character (Birch et al., 2015). However, the sediments of the inner or estuarine zones of the Galician Rias have been scarcely investigated related to their background levels and, even less, to their natural fluxes of TEs.

The rias have been defined from geomorphological and hydrological points of view as incised valleys where the estuarine zone can move according to climatic changes (Evans and Prego, 2003). In the Galician Rias only the innermost part can be considered similar to an estuary from both its hydrographic and sedimentological characteristics, with the main estuarine processes being confined to the inner relatively small brackish water zone (Evans and Prego, 2003; Vilas et al., 2010). The main effort from core dating in inner rias has been developed in the San-Simón Inlet, the inner part of the Ria of Vigo, regarding metal contamination in recent decades from intertidal and subtidal sediments (Álvarez Iglesias et al., 2006, 2007; Álvarez-Iglesias and Rubio, 2009). Apart from this, there are very few studies on Galician ria sediments where ^{210}Pb or ^{137}Cs dating were used to study the timing of TEs inputs related to anthropogenic inputs or establishing sedimentation rates, such as that by Rubio et al. (2001) on the Ria of Pontevedra or that by Lorenzo et al. (2007) on three rias of the northern Galician coast. A recent review on TEs in the shallow marine sediments of the Ria of Vigo, which includes its inner part, recommended the use of local or regional background levels to take into account the geological variability of the study area (Álvarez-Iglesias and Rubio, 2012).

Against an increase of anthropogenic pressure, two key features have yet to be addressed in the estuarine areas of the inner part of the rias: (i) the natural fluxes and background levels of TEs and (ii) changes in TEs concentrations and fluxes during the Anthropocene. To address these features, three sediment cores were sampled, analyzed and dated from estuarine areas with low human pressure, to serve as a useful reference of sedimentation rates and TEs fluxes for comparisons at estuarine and inner ria zones. This information can be useful for management of vulnerable estuaries (Elliott et al., 2014) and decision making of anthropogenic chronic chemical hazards (Elliott et al., 2010), specially for ria-type coastal systems.

2. Survey area

The Northern Atlantic shoreline of the Iberian Peninsula is characterized by a ria-coast system, a succession of ancient river valleys flooded by the sea as a result of tectonic and eustatic changes. These rias are divided into two main zones from a hydrological point of view, an external or oceanic part under the sea domain with little influence of river water (Varela et al., 2001), and another internal or estuarine that moves depending on climate changes (Evans and Prego, 2003). From the Cape Ortegal to the Artabro Gulf there is a set of five rias (Fig. 1). The main rivers usually discharge at the head of the rias, partially closed by sandy bars, while rocky bottoms appear in the ria mouths (CMATI, 2011). This study is focused on three of these rias due to their low population and absence of important industries in the drainage area of the main fluvial inputs. The selected rias (5–20 km^2) are the Ria of Ares (A), the Ria of Betanzos (B), and the Ria of Cedeira (C), being the main rivers the Eume River, the Mandeo River and the Das-Mestas River, respectively, which are relatively small (Fig. 1). A comparison of their surface areas and flow rates is presented in Table 1. The Eume River has two impoundments in its course. After the first - the Ribeira dam- is located the former As-Pontes open-pit lignite mine devoted to the energy production industry. The mine exploitation began in 1955, but the main activity was carried out between 1972 and 2007, year of its closed. During that period it became the largest open-pit mine of the Iberian Peninsula (Aréchaga et al., 2011). Downstream of the mine is located the Eume Dam, built between 1955 and 1960. In the lower course of this river is placed the Fragas-do-Eume Natural Park, an example of a temperate rainforest defined as a Site of Community Importance by the European Habitats Directive (92/43/CEE). The Mandeo River (15.4 m^3 s^{-1}) has the largest fluvial discharge of the three rivers under consideration. The Das-Mestas Stream shows human activities in its basin that are limited to rural traditional agriculture and livestock, except former small Cu-mining activities located in the river head (IGME, 2015).

The lithology of the study area (presented as background in Fig. 1 and summarized in Table 1) is composed mainly by alternating bands of granites and metamorphic rocks (schist and gneiss), disposed parallel to the coast. Rounding the Ria of Cedeira is the Ortegal Geological Complex containing basic rocks and the massifs of Limo, Herbeira and Uzal with ultrabasic rocks and ophiolitic units in their boundaries. Some Quaternary sedimentary deposits are also present. Numerous mineral deposits containing trace elements are reported or suspected in the area (e.g. As, Au, Co, Cu, Sn, Ti, W, Zn; IGME, 2015). The land is covered by forests, mainly *Eucalyptus* spp. plantations (up to 37% of the territory), and crops, which represent one third of the total area (CMATI, 2011). A more complete description of land-use per ria basin is presented in Table 1. The population is mainly along the margins of the rias, and is widely dispersed inland (33–62 inhab·km^{-2}; Table 1), appearing as small villages along the river drainage basins.

3. Material and methods

Sediment cores were sampled in July 2012 during low tide in the estuarine intertidal muddy zones of the ria of Ares (core A: 43°24.833′N & 08°09.837′W), Betanzos (core B: 43°19.079′N & 08°12.236′W) and Cedeira (core C: 43°38.095′N & 08°02.857′W).

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