Major factors influencing the elemental composition of surface estuarine sediments: The case of 15 estuaries in Portugal

M. Mil-Homens [a,b,*], C. Vale [a,b,*], J. Raimundo [a,b], P. Pereira [a], P. Brito [a], M. Caetano [a,b]

[a] IPMA, Portuguese Institute of Sea and Atmosphere, Division of Environmental Oceanography and Bioprospection, Av. Brasília, 1449-006 Lisboa, Portugal
[b] CIIMAR, Marine and Environmental Research Center, Rua dos Bragas, 289, 4050-123 Porto, Portugal

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ABSTRACT

Upper sediments (0–5 cm) were sampled in 94 sites of water bodies of the fifteen Portuguese estuaries characterized by distinct settings of climate, topography and lithology, and marked by diverse anthropogenic pressures. Confined areas recognized as highly anthropogenic impacted, as well as areas dominated by erosion or frequently dredged were not sampled. Grain size, organic carbon (C_{org}), Al and trace elements (As, Cd, Co, Cr, Cu, Hg, Ni, Pb and Zn) were determined. Normalisation of trace element concentrations to Al and C_{org}, correlations between elements and Principal Component Analysis (PCA) allowed identifying elemental associations and the relevance of grain-size, lithology and anthropogenic inputs on sediment chemical composition. Whereas grain-size is the dominant effect for the majority of the studied estuaries, the southern estuaries Mira, Arade and Guadiana are dominated by specific lithologies of their river basins, and anthropogenic effects are identified in Ave, Leça, Tagus and Sado. This study emphasizes how baseline values of trace elements in sediments may vary within and among estuarine systems.

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1. Introduction

Estuaries are transition environments where fresh and marine waters meet, being characterized by gradients of physical and chemical properties and high biological value. Morphology of these environments greatly influences the mixing of solutes and suspended particles, and the fate of particulate matter derived from weathering and anthropogenic sources (Postma, 1967; Allen et al., 1980). Funnel-shape type estuaries tend to retain lower amounts of particulate loads than inner-bay estuaries that may act as temporary or permanent repositories. Urban centres have been settled in the margins of river basins and estuaries. This human occupation led to the development of industrial and maritime activities that benefiting from navigational natural conditions. Most of these activities constitute potential pressures to the ecosystem. Estuarine sediments may record the impact of these pressures through changes on chemical composition of deposited layers, if erosion or post-depositional reactions do not mask the anthropogenic signal (Berner, 1980; Aller, 2004).

Among the contaminants present in sediments, trace elements are of major environmental and health concern (Libes, 1992). Emissions from industry, agriculture, mining and urban activities have introduced large amounts of potentially toxic elements in estuaries that are dispersed physically or through the food web, or retained in confined areas (Benjamin and Honeyman, 1992). The nature of the sediment particles also influences the ability to retain these elements in the bottom of estuaries (Windom et al., 1989; Li et al., 2000). Because trace elements in sediments result also from weathering of rocks and soils, the separation between natural and anthropogenic components of the sediment chemical composition should be determined. Differentiation is harder to achieve in systems highly influenced by specific lithology rich in trace elements that are also derived from human activities (Soto-Jimenez and Paez-Osuna, 2001; Prego et al., 2014).

Monitoring programmes and investigations linked to sediment contamination and inhabitant fauna in estuarine and coastal lagoon systems search for good indicators to separate anthropogenic pressure from natural signal (Tueros et al., 2008; Legorburu et al., 2013). The distinguish between these two components is crucial for the implementation of measures to prevent deterioration of water quality status under the Water Framework Directive (WFD; Directive 2000/60/EC). Sediment composition is a useful tool to evaluate anthropogenic pressures on aquatic environments (Vale et al., 2008). Additionally, the distinction between both

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natural and anthropogenic sources of trace elements in sediment samples can also be assessed by solid speciation analysis using sequential-selective leaching (e.g., Tessier et al., 1979; Grotti et al., 2013).

This work aims to weight the influence of grain-size, lithology and anthropogenic inputs on the trace element distribution in surface sediments, and to examine difficulties in identifying reference conditions for sediment composition in estuaries influenced by various lithologies and anthropogenic pressures. To the best of our knowledge, this is the first time this approach is applied to fifteen Portuguese estuaries presenting distinct environmental settings (lithology, geology, morphology and climate) and historically impacted by human activities.

2. Material and methods

2.1. Study areas

Portugal is characterized by contrasting topography climate and lithology. The northern part of the country is marked by rough relief, with a set of mountains higher than 1000 m height (Fig. 1a), and annual mean precipitation exceeding 1000 mm (Fig. 1b). The estuaries located in the northern coast of Portugal (Minho, Lima, Neiva, Cávado, Ave, Leça, Douro, Mondego and Lis) are characterized as narrow channels. The rivers Minho and Douro presented the highest freshwater discharges. Ria de Aveiro is a large coastal lagoon-type estuary fed by river Vouga and characterized by its wide sand and mudflats. The southern Portugal has a gentler topography and the climate is much drier. Tagus and Sado systems are located in central/southern coast and have the largest semi-enclosed estuarine areas. Southern estuaries (Mira, Arade and Guadiana) are also defined by narrow channels connected to the sea. The main characteristics of these river basins, including morphology, hydrology, lithology and human pressures, are summarised in Table 1.

Concentrations of major and trace elements in sediments from the studied estuaries have been reported in various works, namely: Minho (Mil-Homens et al., 2013), Cávado (Gonçalves et al., 1994), Ave (Gonçalves et al., 1992; Soares et al., 1999), Douro (Mucha et al., 2003), Ria de Aveiro (Monterroso et al., 2003; Pereira et al., 2009), Mondego (Pereira et al., 2005), Tagus (Canário et al., 2005; Vale et al., 2008), Sado (Cortesão and Vale, 1995; Caeiro et al., 2005), Guadiana (Delgado et al., 2010). To the best of our knowledge no information concerning trace elemental composition of bottom sediments was found for Lima, Neiva, Leça, Lis, Mira and Arade.

2.2. Sampling design

The sampling sediment sites (n = 94, Fig. 1) were selected in order to cover all the water bodies of estuarine systems of Portugal defined in the Water Framework Directive (Ferreira et al., 2003). Confined areas recognized as highly anthropogenic impacted, like in the Aveiro lagoon (Hall et al., 1987) and Tagus estuary (Canário et al., 2005; Vale et al., 2008) were not selected for sediment sampling. Sediments from navigational channels, where bottom are eroded frequently by strong tidal currents or dredging operations, were also not sampled. The number of samples and the sampling dates at each estuarine system are given in Table 2. Coordinates of the sampling sites are given as Supplementary data (Table S1).

The upper layer (0–5 cm) was obtained from sediments collected with a Van-Veen grab, sub-sampled on board and stored refrigerated (ca. 4 °C). Sub-samples were used for subsequent determinations of textural and geochemical parameters, including organic carbon (C_{org}), aluminium and trace elements. All sub-samples for geochemical determinations were freeze-dried and the fraction smaller than 2 mm was powdered and homogenized with a Retsch mill.

2.3. Grain-size and organic carbon analyses

Grain size was determined on 5–10 g of surface sediments using the traditional sieving method (Retsch AS200). Organic carbon contents (C_{org}) was obtained using a CHN Fisons NA1500 Analyzer. Briefly, the combustion of organic carbon in the sediment sample for 2 h at 450 °C allows the subsequent measurement of inorganic carbon content. Organic carbon content was obtained from the difference between total carbon and inorganic carbon contents.

2.4. Elemental analysis

Aluminium and trace elements (As, Cd, Co, Cr, Cu, Ni, Pb and Zn) determinations were performed by a quadrupole ICP-MS (Thermo Elemental, X-series) equipped with a Peltier Impact bead spray chamber and a concentric Meinhard nebulizer after a total sample decomposition with an acid mixture (Aqua Regia and HF) following the procedure described by Caetano et al. (2007). Briefly, 0.1 g of sediment were totally dissolved with a mixture of 1 mL of Aqua Regia (1 HNO_3: 3 HCl) and 6 mL of HF, in closed Teflon vessels at 100 °C for 1 h. Sample solutions were evaporated until near dryness in Teflon vials (DigiPrep HotBlock—SCP Science), redissolved with 1 mL of double-distilled HNO_3 and 5 mL of Milli-Q water (18.2 MΩ cm), heated for 20 min at 75 °C and diluted to 50 mL with Milli-Q water. After that 20 mL of Milli-Q water (18.2 MΩ cm) was added and the solution was heated again for 20 min at 90 °C. After cooling down the solution was diluted to 50 mL with Milli-Q water (18.2 MΩ cm). Procedural blanks and certified reference materials (CRM) MESS-3 and PACS-2 (National Research Council of Canada) were prepared using the same analytical procedure and reagents and analysed for quality assurance / quality control (QA/QC). Mercury was determined by atomic absorption spectrometry using a silicon UV diode detector (LecoAMA-254) after pyrolysis of each sample (approximately 0.1 g) in a combustion tube at 750 °C under an oxygen-rich atmosphere and collection on a gold amalgamator (Canário et al., 2005). Analytical precision was expressed as relative standard deviation (RSD in%) of 7 replicate samples of the CRM varied between 2% and 1% for MESS-3 and PACS-2, respectively. The accuracy was checked by analysing 7 replicate samples of each CRM. In general, the results indicate good agreement between certified and analytical values. The recovery (%) of measured elements, based on the mean values calculated for the CRM, was 84–114% (Table 3).

2.5. Principal Component Analysis

Multivariate analysis was carried out using the Statistica software for Windows (Statsoft, Inc., USA; version 6.0). Principal Component Analysis (PCA) was used to determine relationships among variables and simplify the analytical dataset through the reduction of variables into major controlling components that simplifies the interpretation of the variables' distribution (common sources, sedimentological and geochemical processes) in studied sediments. The sample matrix is composed by 94 surface sediment samples and 10 descriptors (sand, As, Cd, Co, Cr, Cu, Hg, Ni, Pb and Zn). All variables were standardized to the same scale using the Z-score transformation to eliminate the influence of different measurement units and minimize the variance. In this study factors with eigenvalues greater than 1 were retained (Kaiser, 1960).