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Sedimentary record of anthropogenic metal inputs in the Tagus prodelta (Portugal)

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ABSTRACT

Favourable oceanographic and environmental conditions allow the formation of a fine-grained deposit (Tagus prodelta) located at the mouth of the Tagus River. This fine-grained deposit results from the sink and accumulation of terrestrial and marine-derived materials. Three short sediment cores collected in the Tagus prodelta were investigated through the variability in grain-size, major and trace elements, C_{org}, N_{tot}, $\delta^{13}C$ and ^{210}Pb dating to characterise the historical development of trace metal contamination. Historical trends indicated significant anthropogenic enrichments for Hg, Pb, Zn, Cu, Sb and Sn since the 1930s. Hg presents the highest level of anthropogenic enrichment (ca. $EF_{Hg} = 20$) in cores 3576 (PO287-26-1B) and 3579 (PO287-27-1B) collected closer to the shore. Despite these elements were derived from distinct industrial sources, all of them presented similar temporal trends, which points to the importance of estuarine mixing processes originated by the tidal regime and wind before transfer to the adjoining coastal areas. The cores were characterised by smoothness of down-core variations and river flood events occurred in the last decades were not registered. Furthermore, the improvement of effluents treatment together with the closing of some industrial point sources in the last two decades is not evidenced in recent sediment composition of the Tagus prodelta. Besides sediment reworking in the upper sediment layers, sediment mixing inside the estuary may explain minor abrupt alterations with the depth.

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1. Introduction

Rivers represent 95% of the sediment input to the ocean system (Syvitski et al., 2003). Composition of suspended sediments reflects both natural and anthropogenic-derived components, resulting from weathering of soils and rocks and human activities occurred in the catchment's area (Soto-Jimenez and Paez-Osuna, 2001). During transport to the sea suspended sediments participate in repeated deposition-erosion cycles associated with the tidal currents, wind and river flood (Vale and Sundby, 1987; Williams, 1994). Depending upon the trapping efficiency of estuaries, part of the fine particulate material escapes continuously to shelf areas (Ridgway and Shimmield, 2002), although the most substantial exported quantities occur in periods of river flood conditions (Avoine, 1987).

The coastal oceanographic conditions adjacent to great rivers may favour the occurrence of mud deposits, consisting in general of a mixture of fluvial/estuarine-derived material and local biological productivity (McCave, 1972; Nittrouer and Stenberg, 1981; Nittrouer et al., 1986; Nittrouer and Wright, 1994; Díaz et al., 1996; Roussiez et al., 2005). The prodeltaic deposits are generally good geological records of past climatic, sea level and geological changes that happened in the adjacent catchment's area (Fernandez-Salas et al., 2003; Grossman et al., 2006). By the end of the XIX century, shelf areas adjacent to estuaries in Europe surrounded by cities and industrial complexes started to receive a cocktail of contaminants associated with the fine particles that escape from the estuary. The increase of metal concentrations in sediments from the Tagus estuary occurred later (Vale, 1990) due to the delay in the Portuguese industrial development coincident with World War II. Changes of chemical composition in vertical section of sediments of shelf depositional areas have been related to the historical use of contaminants (Valette-Silver, 1993), although the record may be masked by diagenetic processes, bioturbation and episodes of re-suspension (Finney and Huh, 1989).

The intense urban and industrial growth of the Lisbon's neighbourhoods (approximately 2.5 million inhabitants) have

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been responsible for the loads of anthropogenic metals and persistent organic pollutants to the Tagus estuary which are well documented (Figuères et al., 1985; Vale, 1990; Caçador et al., 1996; Araújo et al., 1998; Vale et al., 1998, 2008; Canário et al., 2003, 2005; Nogueira et al., 2003). Few works approached the temporal characterisation of metal inputs in the study area (Vale, 1990; Jouanneau et al., 1998). Moreover the presence of contaminated particles is known to extend to the surface sediments of the shelf area adjacent to the estuary (Paiva et al., 1997; Jouanneau et al., 1998; Queralt et al., 1999; Silva et al., 2004). Nevertheless, time variation of sediment composition of the Tagus prodelta has not been investigated. This work aims to reconstruct the temporal distribution of metals and to investigate the anthropogenic enrichment for Hg, Pb, Zn, Cu, Sb and Sn during the Twentieth Century.

2. Regional setting section

The study area is the shelf area adjacent to the Tagus River. The Tagus River is the largest Iberian River with a total length of 1076 km (Bettencourt and Ramos, 2003). Its hydrographical basin is approximately 80,629 km^2, shared between Spain (69%) and Portugal (31%) (Loureiro et al., 1986). It is characterised by a large water flow ($15.5 \times 10^9\, m^3\, yr^{-1}$; Fiúza, 1984). The river presented periodic floods and abrupt discharges of suspended load (Vale and Sundby, 1987). The weekly survey of the 1978 flood showed that the estuary received during 1 week is equivalent to 10 years of sediment load (Vale, 1981). The Tagus estuary is one of the largest European estuaries with an area of roughly 320 km^2 formed by several channels and islands (Vale et al., 1998) being connected to the sea by a relatively narrow channel (c.a. 2 km). The Tagus classified as a mesotidal system with a mean tidal range of 2.4 m, varying from about 1 m at neap tides to about 4 m at spring tides (e.g. Ribeiro et al., 2003). The circulation in the Tagus estuary is mainly tidally driven, with small high-frequency wind waves responsible by enhanced turbidity in shallow areas of upstream part of the estuary. The shelf ranges from 20 to 34 km in width, while the shelf break varies between 130 m water depth at the Cape Raso and 150 m water depth at 38°30′N (Fig. 1). At this latitude, Cascais and Lisbon submarine canyons incises the shelf, probably creating conditions to a rapid sediment transport from the shelf to deep waters. Vanney and Mougenot (1981) in the shelf area adjacent to the estuary identified the occurrence of a deltaic system. The inner shelf is characterised by sands representing the delta front, with bottom currents strong enough to avoid the deposition of fine-grained particles (Paiva et al., 1997). The decrease of velocity, together with depths unaffected by waves and storms, allow the deposition of fine particles forming a large muddy shelf sediment body between 50 to 130 m water depth. The Tagus prodelta accumulates riverine and marine-borne fine-grained materials (Lima, 1971; Monteiro and Moita, 1971; Gaspar and Monteiro, 1977; Jouanneau et al., 1998). The wave regime of the Portuguese shelf has a strong, seasonal variability (Costa, 1992/3/4). During the summer, it is characterised by a low energy regime (NW swells with wave heights lower than 2 m and mean periods of 8 s for all the Portuguese west coast). The winter and early spring is characterised by high energy from NW swells mean periods of 8–9 s and wave heights of 2 m. Storm events occur mainly during the winter months, usually decreasing their intensity from north to south. The most part of the storms are characterised by NW and WNW swells with wave heights lower than 6 m (Costa, 1992/3/4). Summer conditions are characterised by persistent winds from N, developing conditions for the occurrence of seasonal upwelling, being the shelf area off the Tagus estuary mainly influenced by the Cape Roca upwelling filament (Fiúza, 1984; Abrantes and Moita, 1999; Abrantes et al., 2005).

3. Materials and methods

3.1. Sampling

Three sediment box-cores (3576–PO287-26-1B, 96 m water depth; 3579–PO287-27-1B, 85 m water depth; 3580–PO287-28-1B,

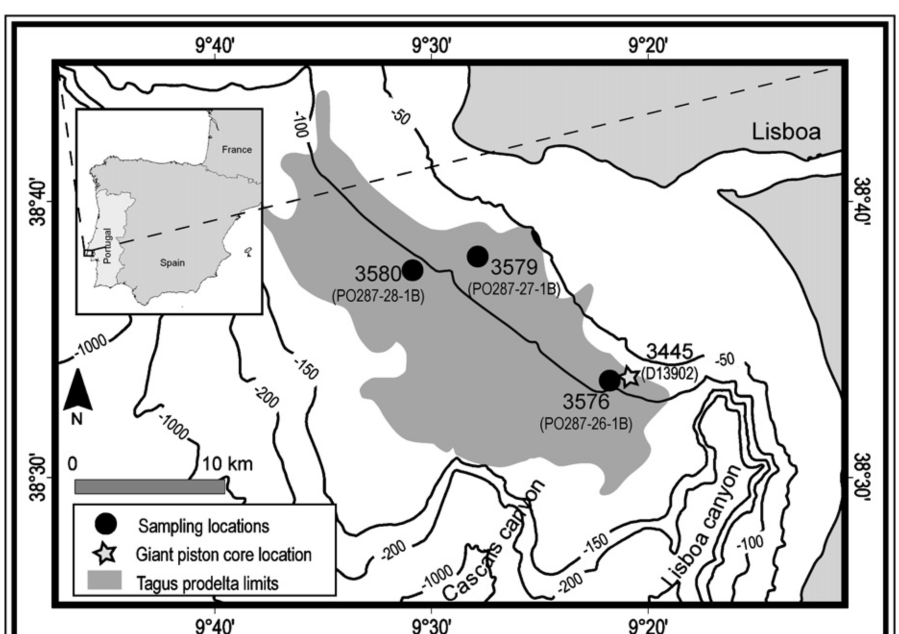

Fig. 1. Location of sampling sites in the Tagus prodelta. The Tagus prodelta limits are extracted from the Surface Sedimentary Chart of the Portuguese shelf (sheet number 5; between Roca and Sines capes) published by the Portuguese Hydrographical Institute in 2005 and corresponds to the class of lithoclastic mud characterised by more than 90% of mud and less than 30% of $CaCO_3$.

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