Science of the Total Environment 621 (2018) 317–325

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Sources and distribution of yttrium and rare earth elements in surface sediments from Tagus estuary, Portugal

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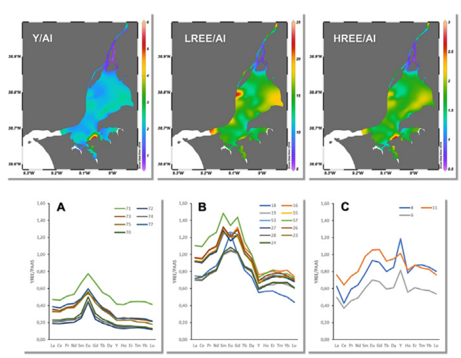
HIGHLIGHTS

- Yttrium and rare earth elements (YREE) are emerging contaminants in the environment.
- Sediment grain size and mineralogical composition rule the YREE distribution.
- Lithogenic and anthropogenic sources of YREE are identified in the Tagus estuary.
- Yttrium high content is a sign of the phosphorus fertilizer industry heritage.
- Distinct REE fractionation patterns observed in the vicinities of WWTP outfalls

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 28 April 2017
Received in revised form 17 October 2017
Accepted 21 November 2017
Available online xxxx

Keywords:
Rare earth elements
Yttrium
Contamination
Surface sediments
Tagus estuary
Portugal

ABSTRACT

The distribution and sources of yttrium and rare-earth elements (YREE) in surface sediments were studied on 78 samples collected in the Tagus estuary (SW Portugal, SW Europe). Yttrium and total REE contents ranged from 2.4 to 32 mg·kg^{-1} and 18 to 210 mg·kg^{-1}, respectively, and exhibited significant correlations with sediment grain-size, Al, Fe, Mg and Mn, suggesting a preferential association to fine-grained material (e.g. aluminosilicates but also Al hydroxides and Fe oxyhydroxides). The PAAS (Post-Archean Australian Shale) normalized patterns display three distinct YREE fractionation pattern groups along the Tagus estuary: a first group, characterized by medium to coarse-grained material, a depleted and almost flat PAAS-normalized pattern, with a positive anomaly of Eu, representing one of the lithogenic components; a second group, characterized mainly by fine-grained sediment, with higher shale-normalized ratios and an enrichment of LREE relative to HREE, associated with waste water treatment plant (WWTP) outfalls, located in the northern margin; and, a third group, of fine-grained material, marked by a significant enrichment of Y, a depletion of Ce and an enrichment of HREE over LREE, located near an inactive chemical-industrial complex (e.g. pyrite roast plant, chemical and phosphorous fertilizer industries), in the southern margin. The data allow the quantification of the YREE contents and its spatial distribution in the surface sediments of the Tagus estuary, identifying the main potential sources and confirming the use of rare earth elements as tracers of anthropogenic activities in highly hydrodynamic estuaries.

1. Introduction

The rare earth elements (REE) are a group of 15 elements from the lightest lanthanum (La) to the heaviest lutetium (Lu). Yttrium (Y) has

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https://doi.org/10.1016/j.scitotenv.2017.11.245
0048-9697/

an identical charge and very similar ionic radius to holmium (Ho) and its geochemical cycling has been studied with the rest of lanthanides (Bau et al., 1996; Caccia and Millero, 2007; Dai et al., 2016; Möller et al., 2014; Tepe and Bau, 2016). Yttrium and REE are trivalent, with the exception of Ce and Eu, which have multiple valences (Ce^{3+}, Ce^{4+}, Eu^{2+} and Eu^{3+}) in natural environments (Aide and Aide, 2012). The YREE distribution in sediments may be controlled by scavenging processes, in particular by Fe–Mn–oxides (Bau, 1999; Bau and Koschinsky, 2009; Caetano et al., 2009; Haley et al., 2004; Marmolejo-Rodríguez et al., 2007); by redox conditions of the overlying water column (Bau et al., 1997); by composition of the terrigenous source (Prego et al., 2009; Taylor and McLennan, 1985) and by anthropogenic inputs (Borrego et al., 2012; Möller et al., 2014; Olmez et al., 1991; Pérez-López et al., 2016; Tranchida et al., 2011). Several authors have studied the geochemical cycling of YREE in rivers, estuarine and coastal systems. These data can be used as geochemical indicators associated with sediment provenance (Taylor and McLennan, 1985) and anthropogenic activities (Olmez et al., 1991). Few investigations have been performed inside well-mixed estuarine systems due to complex hydrodynamics and multiple sediment transport situations (Censi et al., 2007; Chaillou et al., 2006; Hannigan et al., 2010; Lawrence et al., 2006; Nozaki et al., 2000; Sholkovitz, 1990).

YREE have played an essential role in the development of innovative environmental technologies and, with increasing applications in most modern electronic technology and in industrial and medical products, an increase in the form of domestic and industrial waste water emissions to aquatic ecosystems, e-waste and recycling emissions, surface run-off and atmospheric deposition is expected. However, little is known on the environmental behaviour of these elements and their impact on biota in natural transitional systems.

We hypothesise that, although Tagus has complex topography and hydrodynamics, the dominant sources of YREE to the estuary can be established. To the authors' knowledge, there have been no previous studies on distribution and sources of YREE in the Tagus estuary. Therefore, the objectives of this study were: (1) to evaluate the YREE contents and spatial distribution in the surface sediments of the Tagus estuary, and (2) to identify the main sources, anthropogenic and lithogenic, and sinks of these elements in the estuary.

2. Material and methods

2.1. Study area

The Tagus estuary (Portugal), one of the largest in Europe (approx. 320 km^2 total area), has an input of freshwater from the main stream (Tagus River) and from several small tributaries (Fig. 1). It is a semi-diurnal mesotidal system, with tidal amplitudes from 1.0 m (neap tide) to 3.5 m (spring tide) at the mouth. The estuary shows an asymmetric behaviour of tidal currents, with floods typically longer than ebbs (Fortunato et al., 1999), leading to higher velocities during ebbs and to a net export of fine-grained sediments (Valente and da Silva, 2009). The lower Tagus valley crosses the Lower Tagus Cenozoic Basin (Carvalho et al., 2016; De Vicente et al., 2011; Ribeiro et al., 1990) and is suppressed with alluvial sediment, presenting a clear morphologic dissymmetry between both margins mostly related with the geologic setting. The alluvial plain displays a greater development in the southern margin. The northern margin is defined predominantly by silts, clays, limestones, marls and to a lesser extent sandstones, dated from Mesozoic to Mio-Pliocene, added by weathered Neo-cretaceous basalts and pyroclasts from the Lisbon Volcanic Complex (Taborda et al., 2009). The Tagus southern margin has a low altitude variation (up to 60 m) and shows an irregular, notched shape due to incision of several small tributaries, developing in extensive outcrops of sand, gravel, sandstones, conglomerates, silt and clay that constitute Pleistocene fluvial terraces and Miocene and Pliocene formations. The estuary has a deep, straight and narrow inlet channel, and a broad, shallow inner bay. The bay has a complex bottom topography with channels, tidal flats and islands (Fig. 1a). The inner part of the estuary is characterized by extensive mudflats and salt marshes (Fig. 1b) as a result of constant fluvial input of fine sediments (Freire and Andrade, 1999).

The estuary has been receiving agricultural and urban effluents from the large metropolitan area of Lisbon for decades (Caçador et al., 2009;

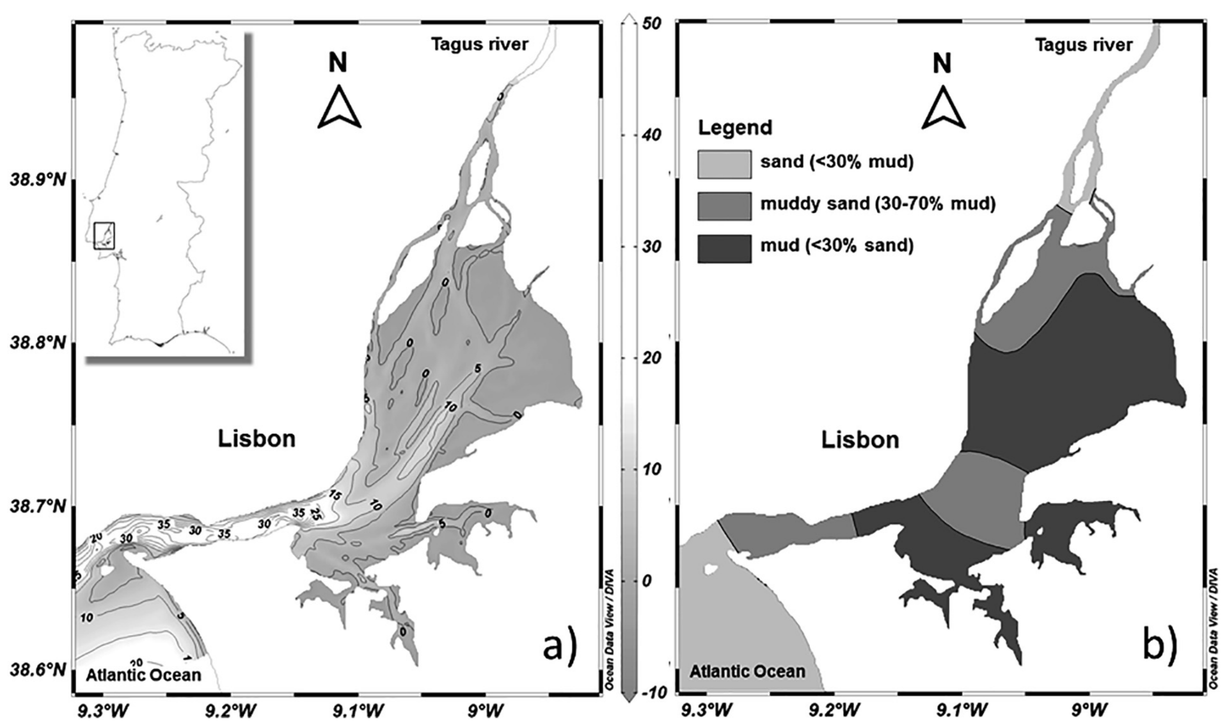

Fig. 1. Tagus estuary a) bathymetry (in meters) (source: Portuguese Hydrographic Institute, http://www.hidrografico.pt); and, b) sediment grain-size distribution. (Adapted from Vis and Kasse, 2009)