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

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10 **Abstract.** The distribution and sources of yttrium and rare-earth elements (YREE) in
11 surface sediments were studied on 78 samples collected in the Tagus estuary (SW
12 Portugal, SW Europe). Yttrium and total REE contents ranged from 2.4 to 32 mg.kg⁻¹
13 and 18 to 210 mg.kg⁻¹, respectively, and exhibited significant correlations with
14 sediment grain-size, Al, Fe, Mg and Mn, suggesting a preferential association to fine-
15 grained material (e.g. aluminosilicates but also Al hydroxides and Fe oxyhydroxides).
16 The PAAS (Post-Archean Australian Shale) normalized patterns obtained allowed to
17 identify three distinct YREE fractionation pattern groups along the Tagus estuary: a first
18 group, characterized by medium to coarse-grained material, a depleted and almost flat
19 PAAS-normalized pattern, with a positive anomaly of Eu, representing one of the
20 lithogenic components imprint; a second group, characterized mainly by fine-grained
21 sediment, with higher shale-normalized ratios and an enrichment of LREE relative to
22 HREE, associated with waste water treatment plant (WWTP) outfalls, located in the
23 northern margin; and, a third group, of fine-grained material, marked by a significant
24 enrichment of Y, a depletion of Ce and an enrichment of HREE over LREE, located
25 near an inactive chemical-industrial complex (e.g. pyrite roast plant, chemical and
26 phosphorous fertilizer industries), in the southern margin. The obtained results allowed

to quantify 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.

Keywords: Rare earth elements, yttrium, contamination, surface sediments, Tagus estuary, Portugal

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 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 has played an essential role in the development of innovative environmental technologies and, with increasing application 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 is expected, e-waste and recycling emissions, surface run-off and atmospheric deposition. 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 km² 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 presents, in general, a low altitude variation (up to 60 m) and shows an irregular, notched shape due to incision of several small tributaries, developing in widespread boulders 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; Canário et al., 2005; Carvalho, 1995; Cobelo-García et al., 2011; Duarte et al., 2010; Monteiro et al., 2016; Vale, 1990), and have been adversely affected by the inflow of untreated effluents from about 2.5 million inhabitants, together with industry (chemicals, petrochemicals, metallurgic, shipyard and repair and cement manufacture) and agriculture (fertilizers and pesticides). Despite these historical facts, in the last years, there have been major

increases in the treatment of both industrial and urban effluents (Duarte and Caçador, 2012).

This estuarine system has been contaminated mainly by two industrial areas located in the north and south margins (Canário et al., 2005; Cotte-Krief et al., 2000; De Bettencourt, 1988), particularly in the southern margin where an inactive chemical-industrial complex is located. This inactive complex had a peak of industrial production in the 60s-70s for fertilizers, food products, nitric, hydrochloric and sulphuric acid, ore processing for metallurgy, among others. No dedicated wastewater treatment plants existed during this period apart from a primary treatment. One of the legacies of this plant is a large aboveground and open-air phosphogypsum stack (approx. 450 000 m³) resulting from the production of phosphate fertilizer industry using the wet process of phosphate rock (phosphorite). This material contains high contents of Y (92 mg.kg⁻¹, unpublished data) and has been exposed to atmospheric dispersion associated with rain and wind for decades (Carvalho, 1997). Since the stack was build up in the margin of the estuary, the input of particulate material to the estuary through air and rain is highly expected.

2.2. Sediment sampling

Surface sediments (0-5 cm layer) were sampled in 78 sampling sites from the Tagus estuary (Fig. 2 and Table S1 in supplementary material) in May 2016. Sampling was carried out using a Van Veen grab sampler from a small boat, sediments were removed with a plastic spatula, stored in pre-cleaned LDPE bottles and kept at 4°C until analysis. All the material used to handle the sediment was previously washed with nitric acid (10 %) for at least 24 hours and rinsed with ultra-pure Milli-Q water (18.2 MΩ.cm²). Sub-samples were dried at 40° C and the coarse fraction was separated by

dry sieving through a 2-mm sieve (Retsch AS200). The <2 mm fraction was homogenized, grounded with an agate mortar and stored for further analysis.

2.3. Grain-size analysis

Grain-size analysis was performed by dry sieving following the procedure described in Gaudêncio et al., (1991). Sediment fractions, expressed as a percentage of total dry weight of each sample, were used to determine the contents of gravel ($\geq 2000 \mu\text{m}$), sand (2000-63 μm) and silt and clay ($< 63 \mu\text{m}$), according to the Folk classification (Folk, 1954).

2.4. Elemental analysis

Sediment samples ($\approx 100 \text{ mg}$) were digested in two steps. The first step consisted of a complete dissolution with 1 mL of Aqua Regia (HCl -36%: HNO_3 -60%; 3:1) and 6 mL of HF (40%) at 100°C for 1 h in closed Teflon bombs (Loring and Rantala, 1992). The resultant solution was evaporated to near dryness in Teflon vessels (DigiPrep HotBlock-SCP Science), re-dissolved with 1 mL of distilled HNO_3 and 5 mL of Milli-Q water, heated for 20 min at 75°C and diluted with Milli-Q water to a final volume of 50 mL (Caetano et al., 2009). Major and rare earth elements were determined in the same samples using a quadrupole ICP-MS (Thermo Elemental, X-Series) equipped with a Peltier impact bead spray chamber and a concentric Meinhard nebulizer. The isotopes used for quantification, free or subject to minimum isobaric and polyatomic interferences, were: ^{24}Mg , ^{27}Al , ^{44}Ca , ^{55}Mn , ^{56}Fe , ^{89}Y , ^{137}Ba , ^{138}Ba , ^{139}La , ^{140}Ce , ^{141}Pr , ^{146}Nd , ^{147}Sm , ^{151}Eu , ^{153}Eu , ^{157}Gd , ^{159}Tb , ^{163}Dy , ^{165}Ho , ^{166}Er , ^{169}Tm , ^{172}Yb , and ^{175}Lu . The internal standard chosen was ^{115}In . Polyatomic and isobaric interferences were minimized by setting the ratios $^{137}\text{Ba}^{++}/^{137}\text{Ba}$ and $^{140}\text{Ce}^{16}\text{O}/^{140}\text{Ce}$ ratios to 0.010 under

routine operation conditions. Since the abundances of Ba, Ce and Pr were less than 700, 100 and 10 mg.kg⁻¹ in the samples and the contribution of oxides relative to the analysed ion plus the related measurement error was lower than 5%, the correction for estimates of ¹⁵³Eu and ¹⁵⁷Gd contents was avoided (Smirnova et al., 2003).

A 7-point calibration was used to quantify each element concentration, using a commercial solution of Indium as internal standard (Alfa Aesar, Plasma Standard Solution, Specpure®, In 1000 µg.mL⁻¹). A multi-element Quality Control (QC) solution was run every 10 samples. Coefficients of variation for metal counts (n=3) varied between 0.5 and 2%. Certified reference material (MAG-1, G-2 and BHVO-1 from the United States Geological Survey -USGS) was used to control the precision of the results. Levels of REE in these material (Table S2a and S2b in supplementary material) were not statistically different from certified concentrations (*t*-student; $\alpha=0.05$). Reagent blanks always accounted for less than 1% of total concentrations in samples.

2.5. Data processing

To better understand the YREE spatial distribution, Ocean Data View (ODV) 4.7.8 mapping software (Schlitzer, 2016) was used, and the Data Interpolating Variational Analysis (DIVA) method (Troupin et al., 2012) was applied to extrapolate the measurements to the overall study. DIVA (Data Interpolating Variational Analysis), generates analysed fields similar to those obtained with OI (Optimal Interpolation), but without formally expressing the covariance functions. It is based on the Variational Inverse Method (Brasseur et al., 1996; Brasseur and Haus, 1991), which consists in the minimisation of a cost function measuring the data-analysis misfit and the regularity (or roughness) of the reconstructed field.

3. Results

3.1. Sediment characterization and major elements composition

According to the grain-size analysis, sediments in this study varied from coarse sand to muddy clays (Table S3 in supplementary material). A positive and significant correlation ($r^2=0.72$; $p<0.01$) between Al content and fine-grained fraction ($< 63 \mu\text{m}$) percentage was observed (Fig. 3a).

Aluminium (Al) content ranged one order of magnitude from 1.3 to 11%. The lower Al contents were found in samples with higher percentage in coarse-grained sediments distributed along the estuary (from the inlet channel to the upper estuary), while higher Al contents were found mainly in samples with higher percentage in fine-grained material deposited in the northern margin and in the wide mudflats and salt marshes in the inner bay. Iron, Mg and Mn contents showed a wide variation along the Tagus estuary (Table S2). The content of Fe varied from 0.30 to 8.1%, with lower values observed in coarse sediments from the southern margin (stations #3) and upper estuary (stations #70, #72; #73, #74 and #75). The highest contents of this metal were detected in stations #8 (8.1%) and #43 (7.1%). The contents of Mg and Mn varied from 0.090-2.5% and 74-1093 mg.kg^{-1} , respectively, with no clear distribution pattern found. Calcium content ranged from 0.028 and 4.9%, with sediments from the Tagus river, mudflats and salt marsh areas showing lower contents while higher values were observed mainly near the inlet channel.

3.2. Yttrium and REE contents in surface sediments

Yttrium levels varied within an order of magnitude between 2.4 and 32 mg.kg^{-1} (Table S4 in supplementary material). The higher values were found in the south margin closer to the inactive industrial complex area (stations #18, #21 and #22). The total REE

(Σ REE) contents were higher (up to 210 mg.kg⁻¹) in fine-grained sediments closer to the margins and in the wide mudflats and salt marshes, while lower values (min. 18 mg.kg⁻¹) were found in coarser sandy sediments along the inner bay. The light-REE (LREE, La-Eu) contents displayed similar variance (16-192 mg.kg⁻¹) evidencing their higher abundance in all the sampled sediments, while values of heavy-REE (HREE, Gd-Lu) ranged between 1.6 and 18 mg.kg⁻¹. This variation of LREE and HREE is reflected in the low variability of LREE/HREE ratio (average=8.92±0.98) observed along the estuary, with values close to the ratio calculated in the Post-Archean Australian Shale (PAAS; Taylor and McLennan, 1985).

The contents of YREE and Al were positively ($0.75 < r^2 < 0.80$) and significantly ($p < 0.01$) correlated (Fig. 3b, c and d). In general, coarser sediments (with low Al content) were poor in YREE contents, while fine-grained sediments (with high Al content) had higher YREE contents. Fine-grained sediments from the Tagus northern margin were, in general, enriched in LREE relative to the correlation curve (Fig 3). This pattern was also found for Y and HREE, but in samples from the southern margin and closer to the inactive industrial complex. Considering the strong and significant correlation found between Al content and the fine-grained fraction ($< 63 \mu\text{m}$), Al was used as a proxy for grain-size. The contents of Y and REE were therefore normalized to Al to minimize both the grain-size and mineralogical variabilities observed along the estuary. Aluminium was chosen since it is the second most abundant metal in the earth's crust, not commonly associated with anthropogenic contributions (Windom et al., 1989) and is significantly correlated with fine-grained sediments.

The spatial distribution obtained for the Y/Al ratio showed a general homogeneity with low variation in the estuary except for samples near the inactive industrial complex area (Fig. 4). Ratios varied from 0.81-5.8, with highest values (3.4-5.8) found near the

inactive industrial complex area (stations #6, #8 and #11). The lowest ratios (0.81-1.0) were observed in the coarse-grained sediments from the upper estuary (stations #71, #73, #75, #76 and #78). The REE spatial distribution patterns presented in figure 4 (Ce/Al - LREE and Yb/Al - HREE) showed a similar variation pattern for all the La-Lu series. The normalization of each REE content to Al showed a different spatial distribution pattern relative to Y, with a larger heterogeneity and a higher variation along the Tagus estuary. Higher ratios were detected in sediments collected in the northern margin (stations #16, #18, #26, #27, #53, #55, #57 and #69) but also near the inactive industrial chemical (#6 and #8). The lowest values were found in the coarser sediments from the upper estuary (stations #47, #49, #71, #73, and #75).

4. Discussion

4.1. Spatial distribution of YREE in surface sediments

The Σ REE content obtained in this study (18-210 mg.kg⁻¹) were comparable with published data for the Tinto river-estuary (56-187 mg.kg⁻¹; Borrego et al., 2005), the Galician Rias, in Spain (3-233 mg.kg⁻¹; Prego et al., 2012, 2009), the North Australian river-estuary systems (77-263 mg.kg⁻¹; Munksgaard et al., 2003) and the Marabasco river-estuary system, in Mexico (27-157 mg.kg⁻¹; Marmolejo-Rodríguez et al., 2007). Positive and significant correlations among those elements and Al, Fe and Mn suggest that aluminosilicates and Fe-Mn oxyhydroxides are the main scavenging phases of rare earths, pointing to the importance of the role of grain size on YREE transport and settling in the particulate form along the Tagus estuary. Interestingly, Al showed higher correlation with LREE ($0.77 < r^2 < 0.80$; $p < 0.01$) relative to HREE ($0.67 < r^2 < 0.77$; $p < 0.01$), while, Fe revealed an opposite behaviour marked by higher levels of correlation with HREE ($0.68 < r^2 < 0.74$; $p < 0.01$) over LREE ($0.59 < r^2 < 0.68$; $p < 0.01$).

This contradicts Caccia and Millero (2007) in Florida Bay sediments and Marmolejo-Rodríguez et al. (2007) in Marabasco River, reflecting a distinct sediment composition. Florida Bay sediments composition was dominated by carbonates and Marabasco River sediments were derived from intrusive rocks of Peña Colorada iron ore deposits. Sediments from Tagus were enriched in LREE relative to HREE, as observed in other studies (Elderfield et al., 1990a; Haskin et al., 1966; Merschel et al., 2015).

Obtained results showed a clear wide variation of YREE contents in the surface sediments along the estuary (Fig. 4). The upper estuarine sediments (river end-member) were distinguished from the other estuarine sediments, due to the relatively coarse-grained particles and consequently low Σ REE content that were explained by the high hydrodynamic conditions responsible by winnowing the fine-grained material.

Several accumulation areas were found in the north margin that hosts the city of Lisbon and the heritage of the inactive industrial complex is clear in the southern margin (Fig. 4, e.g. Y/Al and Yb/Al). Although the absolute contents of YREE may vary, the relative contents in most sediments are quite similar (Taylor and McLennan, 1985). So, the normalization of YREE to a shale composite such as the Post-Archean Australian Shale (PAAS), allows to identify within the typical sedimentary YREE patterns, an enrichment or depletion of a single element or group of elements (Henderson, 1984). The degree of LREE enrichment is also discussed on the basis of the normalised $(La/Yb)_{PAAS}$ ratio (Sholkovitz, 1988; Taylor and McLennan, 1985). The PAAS-normalized ratios obtained in this study allowed to identify distinct groups of sedimentary YREE fractionation patterns in the Tagus estuary (Fig. 5a, b and c).

4.1.1. Lithogenic sources

The first distinctive group of PAAS-normalized patterns was observed mainly upstream in the main freshwater end-member, the Tagus River (Fig. 5a), but also dispersed in some stations in the inner bay (e.g. stations #11, #21, #33 and #56). These sediments, characterized mainly by medium to coarse sands, represent the local source of sediment, namely the Plio-Pleistocene adjacent outcrops (Freire et al., 2007), but also material from anthropogenic related activities mainly connected with the estuarine margins and dredging, while marine source seems to have low or no contribution in the inner bay. This group revealed a fractionation pattern depleted in YREE relative to the shale, and a significant enrichment of LREE over HREE, with average $(La/Yb)_{PAAS}=1.46\pm0.19$. The fractionation pattern observed, with a large enrichment of LREE over HREE, might be derived from intermediate and felsic rocks (McLennan, 1989). Ramesh et al. (1999) also reported a large LREE enrichment in four estuaries of India resultant from an intense silicate weathering of crustal materials and a subsequent increase in LREE in the detrital material. A significant peak of Eu was also found in these sediments. The best way to evaluate Eu distinctive deviations (positive or negative) from their neighbouring pairs of elements is calculating the Eu-anomaly (Eu/Eu^*) (Elderfield and Greaves, 1982; Leybourne and Johannesson, 2008; Taylor and McLennan, 1985). The approach proposed by these Authors use the following equation:

$$Eu/Eu^*=(Eu/Eu_{PAAS})/[(Sm/Sm_{PAAS})\times(Gd/Gd_{PAAS})]^{1/2}$$

A value of 1 means that the element is not fractionated relative to the crustal composition, while a depletion relative to its REE neighbours yields values less than 1 (negative anomalies). Positive anomalies (values greater than 1) found in upstream sediments revealed an average value of $Eu/Eu^*=1.41\pm0.26$. The positive Eu-anomaly found in these coarser sediments, although not common in most estuarine sediments, has been also reported for other estuaries associated with feldspar-rich sources (Ramesh

et al., 2000). The existence of feldspar sources in the Tagus basin was reported by Simões (2003) that described deposits of orange/red silty clays and thin sandstone beds, from the Upper Miocene, with coarse fraction comprising quartz, feldspars and micas, located in the northern margin of the Tagus river. A significant feldspar content (including plagioclase) was found in selected samples, analysed by XRD, pointing to the contribution of these minerals to the Eu enrichment in coarser sediments (unpublished data).

4.1.2. Anthropogenic sources

The second group showed high PAAS-normalized ratios, enriched in LREE relative to HREE, with average $(La/Yb)_{PAAS}=1.24\pm0.14$ (Fig. 5b). These sediments were characterized mainly by fine-grained sediments from the northern estuary margin, although some muddy sands were also present in this part of the estuary. These samples were located close to the outfalls of WWTP but also near a smaller urban area up the Tagus river (stations #76 and #78), suggesting that LREE input from urban effluents and runoff material are associated mainly with the particulate load (Merschel et al., 2015). According to Sholkovitz (1995), dissolved REE from WWTP are transferred to particles via surface complexation, most importantly Fe–Mn oxyhydroxides and organic colloids and particles. This transfer is more effective for LREE than for the HREE (Elderfield et al., 1990b). The "lanthanide contraction" often causes a tendency of stability constants of complexes with particulate ligands to decrease with decreasing atomic numbers (Cantrell and Byrne, 1987; Jong Hyeon Lee and Byrne, 1993). The distribution patterns influenced by external contributors, including industrial activities, harbour pollution and agricultural pollution, was also found for trace elements in the Tagus estuary (Duarte et al., 2010; Vale, 1990; Vale et al., 2008). An enrichment of

middle-REE (MREE; Sm to Gd) relative to LREE was also observed although no acid mine drainage conditions seems to occur in this area, as reported for other estuaries (Borrego et al., 2005, 2004; Carro et al., 2011). Slight negative Eu-anomalies ($0.84 < \text{Eu}/\text{Eu}^* < 0.93$) were also found, particularly in the fine-grained sediments. These negative anomalies might be explained by the reductive remobilization of Eu (II) from the sediments to the surface waters leading to negative Eu-anomalies in the sediment (Elderfield and Sholkovitz, 1987). Prego et al. (2009) also reported slightly Eu-negative anomalies, suggesting that these were attributed to sediment parent material. The enrichment in Eu relative to the PAAS, observed in the medium-grained samples, are probably the result of Eu-enriched sandy sediment increase in the fine material. This enrichment in coarser sediment also contributed to a dilution effect on the YREE contents and subsequent lower PAAS-normalized ratio, as observed in stations #19, #24, #28, #53 and, to a great extent, in station #18.

In the third group (Fig. 5c), the PAAS-normalized ratios had a broader range from 0.37 to 1.18. The profile was characterized by a large enrichment of Y, a depletion of Ce and an enrichment of HREE relative to LREE. The average $(\text{La}/\text{Yb})_{\text{PAAS}}$ were in line with the increase of Gd-Lu series elements, with values below one (0.84 ± 0.09). Sediments from stations #6, #8 and #11 are constituted mainly by fine-grain material, and were collected near the inactive industrial complex and close to the open-air phosphogypsum stack. In fact, sediments from the neighbouring area presented a YREE profile with a sharp Y peak suggesting an input of phosphogypsum to the estuary in the last 5 decades. The relationship between high levels of Y in sediments and the proximity of phosphogypsum stacks from phosphorus fertilizers industries has been reported previously (Borrego et al., 2004; Tranchida et al., 2011). Previous studies have

shown that phosphogypsum contains increased contents of this element (Arocena et al., 1995). As showed for Eu, the anomaly of Ce can be calculated from:

$$Ce/Ce^*=3(Ce/Ce_{PAAS})/[2(La/La_{PAAS})+(Nd/Nd_{PAAS})]$$

The negative anomaly of Ce ($0.68 < Ce/Ce^* < 0.83$) found in sediments closer to the inactive chemical plant corroborate the hypothesis phosphogypsum derived contamination. In fact, the average Ce/Ce^* in particles from phosphogypsum were 0.18 ± 0.03 , which were similar to values were reported by Arocena et al. (1995). Furthermore, the enrichment of HREE in these sediments also point to other contamination sources. The input from ore processing material over decades resulted in drainage of non-treated acidic effluents to the estuary. The ore was from the Pyrite Iberian Belt that is characterized by ratios contents of REE-normalized shale higher than 1 (Delgado et al., 2012; Pérez-López et al., 2010). Presumably, HREE was transferred from the ore through a dissolution process to sediment particles due to their affinity for the solid phase (Borrego et al., 2012; Carro et al., 2011; Verplanck et al., 2004). The depletion of LREE may reflect their preferable retention in the dissolved phase at lower pH, whereas the HREE are removed preferentially from the solution to the suspended matter and thereafter to the sediments due to higher affinity for the solid phase (Borrego et al., 2012; Carro et al., 2011; Verplanck et al., 2004). A similar fractionation pattern was also found in sediments collected in the harbour of an inactive steel industry (station #1 and #2), located 5 km southwest of the industrial chemical plant, although no relationship was found between the two areas except that pyrite-ash by-product that resulted from the sulphuric acid production in the inactive chemical plant was later transformed in iron oxide pellets to feed the steel industry blast furnace.

4.1.3. Mixed YREE sources

Apart from the fractionation pattern found in sediments closer to specific sources, YREE distribution pattern was, in general, very heterogeneous, particularly in the middle estuary. This variability is related not only with the sediment nature but also with the high estuary hydrodynamics. The estuary is a macrotidal system ebb-dominated in the 40 km reach upstream from the mouth (Fortunato et al., 1999), but switches to flood-dominated further upstream and will tend to silt-up more rapidly. Thus, suspended matter in the middle estuary zone originates from both river-borne particles and oceanic particles that enter the estuary (Vale, 1990). Additionally, suspended particulate matter (SPM) are originated inside the estuary through shoreline erosion and re-suspension of bottom sediments. Intense sediment deposition and erosion in this area is permanently changing the estuary bathymetry (Castanheiro, 1982) and strongly damping and retarding the tides (Fortunato et al., 1996). Thus, sediment particles from anthropogenic and lithologic sources are intensely mixed in the middle estuary. Different proportions of particulate material from each source coupled with local hydrodynamics, rules the YREE profile not allowing to point out a clear distribution pattern.

5. Conclusions

The distribution of yttrium and rare earth elements in sediments from Tagus estuary identifies potential sources of these elements in a high hydrodynamic system. The major impact areas of effluents from WWTP were identified in the north margin and the heritage of an inactive industrial complex in the south margin of the estuary was found in surface sediments. The environmental conditions of exposure imply a continue contamination of the estuary. Therefore, the implementation of mitigation strategies should be considered to minimize the legacy of anthropogenic activities. The obtained

results heighten the use of rare earth elements as tracers of anthropogenic activities in highly hydrodynamic estuaries.

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Figure captions

Figure 1– Tagus estuary a) bathymetry (source: Portuguese Hydrographic Institute, <http://www.hidrografico.pt>); and, b) sediment grain-size distribution (adapted from Vis and Kasse, 2009).

Figure 2 – Surface sediment sampling sites in the Tagus estuary (black dots), the location of Lisbon's waste water treatment plants (WWTP) outfalls, in the northern margin (black arrows) and the inactive industrial chemical complex (factory icon), in the southern margin.

Figure 3. Plots of the contents of a) fine-grained fraction (%); b) Y; c) La; and d) Gd (mg.kg^{-1}) vs. Al content (%) in surface sediments from Tagus estuary. Samples in white dots (Y vs. Al) correspond to sediments collect near the phosphogypsum stack and were excluded from the linear regression estimation.

Fig. 4. YREE (e.g. Y, Ce and Yb) content (mg.kg^{-1}) and Al-elemental normalized ratios distribution patterns in the surface sediments collected along the Tagus estuary.

Figure 5. The Post-Archean Australian Shale (PAAS) normalized YREE fractionation pattern groups identified in the Tagus estuary: A – medium to coarser sediment fractionation patterns (e.g. stations located in the river Tagus); B – fine -grained sediment fractionation patterns (e.g. stations near the Lisbon's waste water treatment plants); and, C – phosphogypsum contaminated sediments collected near the inactive industrial chemical plant (station #2 was collected in the harbour of an inactive steel industry, located 5 km southwest of the industrial chemical plant).

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