Lanthanides and yttrium in the sediments of the low Minho River course (NW Iberian Peninsula).

Imprint of tributaries

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Abstract

Purpose Rare Earth Elements have been used as sediment tracers in river, estuarine and coastal environments, but they were barely applied as fluvial tributary tracers. Lanthanides (Ln) and yttrium were quantified in fluvial sediments of the lower course of the Minho River (NW Iberian Peninsula), which catchment has a heterogeneous lithology, to define the characteristic imprint of tributaries and their relevance in the riverine system.

Materials and methods Surface sediments were sampled in 36 points located in the lower Minho riverbed and its nine main tributaries. The <2 mm fraction was sieved, ground and ≈ 100 mg were completely acid-digested with HF and Aqua Regia in closed Teflon bombs at 100°C for 1h. The residue was evaporated and re-dissolved with HNO₃ and Milli-Q water, heated 20 min at 75°C and diluted to 50 cm³ with Milli-Q water. Lanthanides and yttrium were determined using a quadrupole ICP-MS equipped with a Peltier Impact bead spray chamber and a concentric Meinhard nebulizer. Blanks accounted for less than 1% of element concentrations in the samples. The precision and accuracy of the analytical procedures were controlled through reference materials AGV-1 and MAG-1.

Results and discussion Contents ranged 22-153 mgLn·kg⁻¹ and 1.5-22.9 mgY kg⁻¹ and light-heavy Ln fractionation, ES-normalized (L_N/H_N), between 0.6 and 2.6. These wide ranges, together with Eu and Ce anomalies and element-by-element Ln varied according to changes in parental rocks of the lower Minho basin and the relative predominance of granites. Minho sediments show a negative Ce anomaly (0.79 ± 0.28) and a positive Eu anomaly (1.26 ± 0.19). Sediments stand out the trace of granitic pegmatites and gneissic peralkaline rocks from two tributaries: the Gadanha (22.9 mgY kg⁻¹; 83 mgLn kg⁻¹; L_N/H_N :0.63; Eu/Eu*:0.52; Ce/Ce*:0.85) and the Louro (15.9 mgY kg⁻¹; 100 mgLn kg⁻¹; L_N/H_N :0.96; Eu/Eu*:0.70; Ce/Ce*:1.49). Being the lowest source the Tamuxe tributary (1.6 mgY kg⁻¹; 28 mgLn kg⁻¹; L_N/H_N :2.59; Eu/Eu*:1.03; Ce/Ce*:0.52), flowing through a slate and quartzite fault.

Conclusions Lanthanides and Y signature in sediments may be used to trace the land-tributary-river influences. The imprints are observed downstream of fluvial confluences, but not in all cases, responding the basin lithological changes, particularly for pegmatites and peralkaline rocks. General REE trend be described only using Y contents. Tributaries, being responsible of one fifth of the Minho waterload, provides one half of its sediments. Sedimentary non-homogeneity pattern may be magnified in dammed rivers as the Minho.

Keywords Minho River • Rare earth elements • Sediment • Tracer • Tributary

1 Introduction

Rare earth elements (REE) form a chemically coherent group of 17 elements, which include Sc, Y and lanthanides, or lanthanoids (Ln) according to the name suggested by IUPAC. The ionic radii in lanthanides decrease from the lightest element, La, to the heaviest element, Lu. Olmez et al. (1991) refers to this lanthanide contraction as the reason for the characteristic signatures found in its relative abundances in different types of rocks, sediment, and water. Ronov et al. (1967) and Piper (1974) highlighted the usefulness of REE to investigate the origin and destination of sediments. Later, the role of sediments as carriers and potential sources of REE were established from land-sea systems (e.g. Sholkovitz and Szymczak 2000; Prego et al. 2009; Pourret and Tuduri 2017).

For fluvial sediments, REE were applied as tracers of sources and distribution from terrigenous origin (e.g. Ramesh et al. 2000; Marmolejo-Rodríguez et al. 2007; Bayon et al. 2015). Moreover REE were used as anthropogenic indicator when anomalous REE contents in river and marine sediments could come from industrial plants or acid mine drainage (Olmez et al. 1991; Pérez-López et al. 2015). The aforementioned studies only tackle one river system each. There are few studies on the REE as sedimentary tracers of several rivers together. Ramesh et al. (2000) investigated the distribution of REE in the surficial sediments of the Himalayan river system reporting minor influence of anthropogenic activities in the elemental distribution and suggesting that erosion seem to be a major controlling factor for the distribution in the sediments. Recently, REE were applied to the provenance discrimination of sediments from major rivers to the Yellow Sea (Xu et al. 2009), from a land geological complexes to the Northern Galician Rias (Prego et al. 2012), and from watershed and marine sources to Yalu estuarine sediments (Liu et al. 2015). However, the REE purpose as tributary tracer has been only explored by Albarede and Sehmi (1995) in the Meurthe River (France), regarding the suspended and bedload transport.

Nine tributaries flow into the lower course of the Minho River (NW of Iberian Peninsula), which catchment basin has a varied lithology comprising plagioclases, biotite, riebeckite gneiss, two-mica granites,

quartzite-schist, granodiorites and migmatic granitoids. So, lanthanides and/or yttrium can be suitable tracers of tributary sediments. The aims of this study are (a) to quantify Ln and Y sediment contents in the lower Minho riverbed, to (b) to define the Ln and Y sediment characteristic imprint of each tributary, in order to (c) set the relevance of the tributary sediments in the lower Minho River.

2 Survey area

The Minho River, with 310 km length and 17,080 km² of drainage area, runs into the Atlantic West coast of the Iberian Peninsula. The salt-wedge reaches 4 km upstream Minho mouth (Moreno et al. 2005). In the fluvial Minho network there are 122 operating hydroelectric plants with a total water capacity of 3040 hm³ (CADC, 2017). The closest dam to the sea is the Frieira reservoir, built in the 1960's, from where the 77 km length of the lower course of the Minho River begins. This international sub-basin of Minho (Fig. 1) drains 1,934 km² with an annual average flow of 316 m³ s⁻¹ from the Frieira dam (Río-Barja and Rodríguez-Lestegás 1992). Minho River receives the contributions of Deva, Tea, Louro and Tamuxe tributaries (altogether 39.6 m³ s⁻¹; Table 1) along the northern bank (Spain) and Trancoso, Mouro, Gadanha, Manco and Coura tributaries (32.2 m³ s⁻¹; Table 1) in the southern bank (Portugal). Tributary flow rates vary seasonally according to the climate pattern that is rainy-temperate with warm-dry summers. The lower Minho basin is located in the geological Domain of Galicia-Trás-Os-Montes of the Iberian Massif. The basin is N-S crossed at its middle by a paragneiss band with plagioclases and biotite. The band is the southern boundary of the ophiolitic Malpica-Tui Unit (Llana-Fuñez 2001). Western (seaward) that Unit, two-mica granites and a granodiorite crossed by a quartzite-schist band composed the lithology of the Minho lower basin. Eastern (landward) of the aforementioned Unit there are granodiorites, migmatic granitoids and granite with small areas of mica-schist and biotitic para-gneisses. For details, see Fig. 1.

3 Materials and methods

3.1 Sampling

Surface sediments (0-1 cm layer) were sampled in the lower Minho River and its main nine tributary riverbeds (Fig. 1; Appendix Table A) during summer 2011. Downstream Sta. 10 sampling was carried out onboard a small boat using a Van Veen grab sampler. Upstream that station and in the tributaries, sediments were hand-sampled near shore using a small grab. The top sediment layer removed with a plastic spatula and sediments were stored in plastic containers and kept at 4 °C until analysis. The material used to handle the

sediment was previously washed with hydrochloric acid (10%) for 24 hours and rinsed with ultra-pure Milli-Q water. Afterwards, sub-samples were dried at 45 ± 5 °C and the coarse fraction was separated by dry sieving through a 2 mm sieve (Retsch AS200). The <2 mm fraction with an average sediment content of $84 \pm 17\%$ DW in the fluvial samples, was homogenized, grounded with an agate mortar (Fritsch Pulverisette 06.102) and stored for further analysis.

3.2 Analytical methodologies

For the analysis of Ln (except promethium which content in the whole Earth crust is estimated in ≈ 570 g; Belli et al. 2007) and Y in each of the twenty seven (river) and nine (tributaries) sediment samples, approximately 100 mg of sediment were completely digested with 6 cm³ of HF (40%) and 1 cm³ of Aqua Regia (HCl-36%:HNO₃-60%;3:1) in closed Teflon bombs at 100 °C for 1h (Rantala and Loring 1975). The residue was evaporated to near dryness to remove fluorides in Teflon vials (DigiPrep HotBlock-SCP Science), dissolved with 1 cm³ of double-distilled HNO₃ and 5 cm³ of Milli-Q water, heated for 20 min at 75 °C and diluted to 50 cm³ with Milli-Q water (Hu and Gao, 2008; Caetano et al. 2009).

Metals were determined using a quadrupole ICP-MS (Thermo Elemental, X-Series) equipped with a Peltier Impact bead spray chamber and a concentric Meinhard nebulizer. The experimental parameters were, forward power 1400 W, peak jumping mode, 150 sweeps per replicate, 10 ms of dwell time and 30 ns of dead time. Procedural blanks were prepared using the analytical procedures and reagents, and included in each batch of 20 samples. The isotopes used for quantification were, ⁸⁹Y, ¹³⁹La, ¹⁴⁰Ce, ¹⁴¹Pr, ¹⁴⁶Nd, ¹⁴⁷Sm, ¹⁵³Eu, ¹⁵⁷Gd, ¹⁵⁹Tb, ¹⁶³Dy, ¹⁶⁵Ho, ¹⁶⁶Er, ¹⁶⁹Tm, ¹⁷²Yb and ¹⁷⁵Lu, free or subject to minimum isobaric and polyatomic interferences. Polyatomic and isobaric interferences were minimized by setting the ratios ¹³⁷Ba⁺⁺/¹³⁷Ba and ¹⁴⁰Ce¹⁶O/¹⁴⁰Ce ratios to 0.010 under routine operation conditions. Coefficients of variation for metal counts (n=5) were lower than 2%. A 7-point calibration within a range of 1 to 100 µg·L⁻¹ was used for quantification. Detection limits for Ln and Y ranged between 8 and 12 ng·L⁻¹. Blanks always accounted for less than 1% of element concentrations in the samples. The precision and accuracy of the analytical procedures was controlled through repeated analysis of the studied elements in certified reference material AGV-1 and MAG-1 (USGS). Quality Control solutions were analyzed every 20 samples. Obtained contents (Appendix Table B) were statistically consistent with the certified values (Student's t-test, p<0.05) indicating that a complete digestion of accessory minerals, such as zircon, was obtained (Hu and Gao 2008).

3.3 REE anomaly calculations

The European Shale (ES) normalized anomalies of Ce (Ce/Ce*) and Eu (Eu/Eu*) may be expressed in several different ways. For the “Ce anomaly” different formulae have been used; however, the most common one (Sholkovitz et al. 1994; Holser 1997; Kuss et al. 2001; Chaillou et al. 2006) is:

$$\text{Ce/Ce}^* = 3 \cdot (\text{Ce/Ce}_{\text{ES}}) / [2 \cdot (\text{La/La}_{\text{ES}}) + (\text{Nd/Nd}_{\text{ES}})]$$

Conversely, there is more agreement on the formula for the “Eu anomaly” (Taylor and McLennan 1985; Chaillou et al. 2006; Leybourne and Johannesson 2008):

$$\text{Eu/Eu}^* = (\text{Eu/Eu}_{\text{ES}}) / [(\text{Sm/Sm}_{\text{ES}}) \cdot (\text{Gd/Gd}_{\text{ES}})]^{1/2}$$

where Ce, La, Nd, Eu, Sm and Gd are the contents of these elements in the sediment sample and Ce_{ES}, La_{ES} and Nd_{ES}, Eu_{ES}, Sm_{ES} and Gd_{ES} are their contents in the European Shale (Bau et al. 2018).

4 Results

4.1 Yttrium and lanthanides in lower course sediments of the Minho River

The abundance of Ln and Y in Minho riverbed sediments are presented in Fig. 2 from the data compiled in Appendix Table C. The average contents of Ce exceed 10 mg kg⁻¹ while those of La and Nd were between 5 and 10 mg kg⁻¹. Yttrium, Pr, Sm and Gd ranged from 1 to 5 mg kg⁻¹, and the remaining Ln below 1 mg kg⁻¹, among which Tm and Lu did not exceed 0.1 mg kg⁻¹. The total Ln contents in surface sediments varied within an order of magnitude, between 22 mg kg⁻¹ (Sta. 4) and 153 mg kg⁻¹ (Sta. 14). The sediment contents of Ln in Minho riverbed (Fig. 3) decreased after Frieira dam (65 mg kg⁻¹) to 22-30 mg kg⁻¹ at Sta. 2-9, except for Sta. 8 (69 mg kg⁻¹), close to the Tea tributary mouth. The highest Ln values were found at Sta. 13 (122 mg kg⁻¹) and Sta. 14 (153 mg kg⁻¹), downstream Louro river. From here to the estuary mouth sediments revealed contents comparable to the upstream sections except for Sta. 22 and Sta. 25-27 (58-65 mg kg⁻¹), close to the Coura tributary outlet. Yttrium contents (Fig. 3) ranged from 1.5 to 15.1 mg kg⁻¹. This metal followed a similar distribution pattern to the total Ln, decreasing from Frieira dam (9.0 mgY kg⁻¹) to 1.5-3.3 mg kg⁻¹ at Sta. 2-7, and 2.5-5.0 mg kg⁻¹ at Sta. 9-27, except for enrichments in Sta. 8 (7.4 mg kg⁻¹) and Sta. 11-14 (6.6-15.1 mg kg⁻¹) with a peak at Sta. 14.

The longitudinal variability of Ln in Minho River sediments can be complementary evaluated normalizing its contents, on an element-by-element basis, to the European Shale standard (data in the Appendix Table C) in accordance with Bau et al. (2018). The relationship between light and heavy REE, together and separately between elements, were calculated from the data compiled in Appendix Table C.

Ratios between the sum of normalized Light-REE, (LREE, from La to Gd) and the sum of normalized Heavy-REE (HREE from Tb to Lu), typified as L_N/H_N , ranged from 1.2 to 2.5 (Fig. 3). In general, the fluvial sediments of Minho River normalized LREE values were about twice as high as normalized HREE values such as the average value of L_N/H_N (1.8 ± 0.3 ; Table 2). Upstream Sta. 14 (≈ 25 km to the sea) L_N/H_N were lower than 1.7 while downstream that station higher ratios were found. The lowest L_N/H_N ratios were observed just after the Frieira dam in Sta. 1 and in Sta. 11 (1.3), right before the Louro tributary mouth. Conversely, the L_N/H_N maximums occurred in stations 6 (2.5) and 25 (Fig. 3).

Another useful approach used to understand the Ln fractionation are the ratios of $(La/Yb)_N$, $(La/Sm)_N$ and $(Sm/Yb)_N$ showed in Table 2. The $(La/Yb)_N$ average value of 1.75 ± 0.51 , like the L_N/H_N ratio, pointing to a major abundance of LREE over the HREE in almost all stations. An enrichment of Sm versus La and Yb was also found in all Minho River stations. The average $(La/Sm)_N$ ratio of 0.78 ± 0.14 shows the enrichment of Nd, Eu and Gd relative to the remaining LREE, while the average value of 2.25 ± 0.47 for $(Sm/Yb)_N$ does with respect to all the HREE.

Results of Ce and Eu anomalies are presented in the Table 2. The general trend in the Minho River sediments is a positive anomaly of Eu ($Eu/Eu^* = 1.26 \pm 0.19$) and a negative anomaly of Ce ($Ce/Ce^* = 0.79 \pm 0.28$), with the main exception of Sta. 15 ($Ce/Ce^* = 1.30$), 24 (1.26) and 25 (1.48).

4.2 Yttrium and REE in the Minho tributaries

The sediment contents of Ln and Y in the Minho tributaries samples are shown in Appendix Table C. Average contents (Fig. 2) varied from $24 \text{ mg} \cdot \text{kg}^{-1}$ of Ce to $0.14 \text{ mg} \cdot \text{kg}^{-1}$ of Lu. The other Ln averages were in the range of $10\text{--}15 \text{ mg} \cdot \text{kg}^{-1}$ for La and Nd, $5\text{--}10 \text{ mg} \cdot \text{kg}^{-1}$ for Y, $1\text{--}5 \text{ mg} \cdot \text{kg}^{-1}$ for Pr, Sm, Gd, Dy, Er and Yb and below $1 \text{ mg} \cdot \text{kg}^{-1}$ for the remainder (Eu, Tb, Ho, Tm and Lu). For all tributaries, the contents of Ln and Y were higher than in the Minho River sediments (Fig. 2). In particular, the tributary content of Y in their sediments showed a broad variation from 1.6 to $22.9 \text{ mg} \cdot \text{kg}^{-1}$ (Table 2). Sediments from Tamuxe River had the lower values while the highest contents were observed at Gadanha tributary. Moreover, for the tributaries, their interquartile ranges showed higher scattering than those of the Minho River, particularly for Y and HREE (Fig. 2 and 3). On the other hand, the total sedimentary content of REE varied within an order of magnitude ranging from 28 to 100 mg kg^{-1} (Table 2) where the lowest content was detected in the Tamuxe tributary and the highest at Louro tributary.

The ES shale-normalized patterns in sediments from the tributaries, calculated from Appendix Table C data, showed different Ln fractionation among them. The observed ratios between L_N/H_N indicate a general decrease of HREE in the sediments from Deva, Mouro, Tamuxe and Coura with relationships between 1.6 and 2.6 (Fig. 3). This enrichment in LREE is also evidenced by the $(La/Yb)_N$ values ranging from 1.7 to 3.5 to those river sediments (Table 2). Otherwise, Trancoso ($L_N/H_N=0.91$), Tea (0.82) and, especially Gadanha (0.63) showed an opposite behaviour, indicating an enrichment of HREE when compared to the LREE. The $(Sm/Yb)_N$ ratios (Table 2) varied between 2.4 and 4.3, indicating a higher enrichment of the Sm-Dy contents than the Ho-Lu contents in the Deva, Mouro, Tamuxe and Coura tributaries. The other Minho tributaries revealed small or no fractionation between Sm and Yb, $(Sm/Yb)_N$ varied from 1.0 to 1.5 (Table 2).

A depletion of Ce/Ce^* (0.52, Table 2) was found in the Trancoso, Deva and Tamuxe sediments. The contrary occurred in the Louro and Coura tributaries, where Ce/Ce^* increased to 1.04 and 1.11, respectively. The ratios observed in the other tributaries were close to 1.0 indicating no Ce anomalies (Table 2). Values of Eu/Eu^* higher than unity (i.e. Eu enrichment) were found in the sediments from Deva and Coura tributaries, 1.59 and 1.25, respectively (Table 2). Otherwise, the Eu/Eu^* in sediments of Mouro, Tea, Gadanha and Louro tributaries were lower than 1 (0.89, 0.77, 0.52 and 0.70, respectively), indicating a depletion of this element. The other tributaries showed no Eu anomalies.

4.3 Tributary sediments in the Minho riverbed

There are two main sources of sediments to the lower Minho River, the Frieira Dam and the tributaries. The percentage of tributary sediments in the Minho riverbed can be roughly estimated from the sediment contents of Ln in the Minho River, its tributaries and the Frieira Dam. In this way, the average Ln content of tributary sediments (Ln_T) can be calculated from each tributary (Ln_i , data in Table 2) weighted with its annual average flows (Q_i , data in Table 1):

$$Ln_T = (\sum Ln_i \cdot Q_i) / (\sum Q_i) = 70.7 \text{ mg} \cdot \text{kg}^{-1}.$$

On the other hand, the contents of Ln in the sediments coming from the Frieira Dam (Ln_F) can be estimated from the contents of stations 2-4 which are close to the dam but out of the tributary influence. The Ln_F average content is $25.1 \text{ mg} \cdot \text{kg}^{-1}$ (see data collected in the Appendix Table C).

Finally, in the lower Minho River the sediment content of Ln (Ln_M) can be calculated from the average of Sta. 1-27, weighted according to the distance between stations, i.e. for each station the half distance with its preceding and next stations. Ln_M is $45.7 \text{ mg} \cdot \text{kg}^{-1}$ (from the data in Appendix Tables A and C).

Therefore, Ln content in the sediments of the lower Minho (45.7 mg kg^{-1}) should be the result of the mixing of sediments from the Frieira dam (25.1 mg kg^{-1}) and the Minho tributaries (70.7 mg kg^{-1}). Consequently, 45% of the lower Minho sediment comes from the tributaries. Comparatively, the annual average contribution of tributaries to the Minho River is $71.8 \text{ m}^3 \text{ s}^{-1}$ (Table 1) while the Frieira Dam outflow is $316 \text{ m}^3 \text{ s}^{-1}$ (Río-Barja and Rodríguez-Lestegás 1992).

5 Discussion

The sedimentary imprint of Ln and Y clearly varied along the lower Minho scenario as shows the distribution patterns of Ln and Y contents, ES-normalized LREE/HREE fractionation, La/Yb, La/Sm and Sm/Yb ES-normalized ratios and anomalies of Ce and Eu compiled in Table 2 and Figures 3 and 4. Thereby, Ln and Y trace highlight how the changing parental rocks in the lower Minho basin influence the river and tributary sediments. A representation in four sections A-D (Appendix Table A), according to the local lithology and the tributaries' mouth ranges, was performed to evaluate that imprint.

Section A includes the station 1 (near to Frieira dam), Trancoso, Deva and Mouro tributaries and sediments downstream in stations 2-8. The lithology of the Trancoso basin is varied including granite and granitoid, schist, slate and quartzite (Fig. 1). Stations showed similar Ln and Y contents in the sediments (Fig. 3) and Ln flat curves with negative Ce anomaly (Fig. 4) but, comparatively, the Frieira and Trancoso and Mouro points presented highest contents of Ln, Y and HREE in this section A (Fig. 3 and Table 2). The Y levels triplicate and the double of Ln contents were found, while L_N/H_N is the half (≈ 1), indicating that sediments exported from the tributary, even through it is a stream with a very low flow ($1.8 \text{ m}^3 \text{ s}^{-1}$; Table 1), settle closer to its mouth. In the rest of section A, the influence of granites and granitoids of the Minho banks prevails, as reflected the enrichment of LREE relative to HREE (Cullers and Graf 1984). Downstream the river basin geology of Deva and Mouro tributaries remain granitoids with a graphite-schist area in the case of the Mouro basin. The curve of Ln normalized shale in sediments from the Deva tributary is characterized by a positive anomaly for Eu and negative for Ce, which is also in the nearby fluvial stations 5-7, but in a lesser extent. The Minho River sediments of stations 2-8 are similar to those of the Deva Tributary (Fig. 4) while in station 1 sediments are mainly influenced by the Trancoso Tributary. In the Mouro tributary, there is a difference, like in the station 8. Contents of Ln and Y increased and the anomalies of Eu (closer to the unit) and Ce are reversed. The influx of this tributary on Minho sediments is scarce (Fig. 4).

In the next section (B), covering stations 9-11 and the Tea, Gadanha and Manco tributaries, the biotitic granitoids prevails in the Tea and several areas of the Gadanha and Manco basins. In the basin of the Gadanha tributary has been observed the presence of pegmatites (SGP 1989). The presence of REE-enriched granitic pegmatites is evidenced by the enrichment in HREE, Y and a pronounced negative Eu anomaly (Hanson et al. 1992; Ercit 2005), which is mimic in the Gadanha Ln curve (Fig. 4) and Y contents (Fig. 3). This was also observed in a lesser extent in the Tea (Fig. 4), although no prior knowledge of that lithological fact was found. In spite the different signatures of these three tributaries, no similar record was found in sediments from the main river course. Therefore, minor particle export should exist from Tea, Manco and Gadanha. The last two tributaries have very low river flows (1.3 and $4.8 \text{ m}^3 \text{ s}^{-1}$, respectively), which can explain the minor transport. Otherwise, Tea has the highest river flow ($25.3 \text{ m}^3 \text{ s}^{-1}$) from all tributaries suggesting a minor eroding process.

In the section C, which includes stations 12-23 and the Louro tributary, another lithological change occurred in the tributary basins. The Louro sediments present higher Ln and Y contents than the correspondent in Minho main course sediments (Fig. 3). The potential REE source of this tributary is in the west part of the Louro basin where is located the Galiñeiro orthogneissic Complex (Fig. 1). This geological complex is composed of pre-Hercinyan gneissic peralkaline granitic rock (Floor 1966) rich in REE that are present in a great variety of accessory minerals such as bastnasite, allanite, monazite and xenotime (Montero et al. 1998). The tributary has not a high flow ($8.4 \text{ m}^3 \text{ s}^{-1}$) but the export of sediments from it was found until 4 km Minho downstream (stations 13 and 14; Fig. 3). Those two stations triple the Ln and Y contents of neighboring Minho stations and in Sta. 14 its content are 70% higher than in Louro station (may be influenced by REE contributions from quaternary terraces in the riverbeds of the Minho-Louro confluence) but their normalized shale profiles are similar to the Louro (Fig. 4), including the negative Eu anomaly. In the same way, though up- and downstream of that Minho-Louro zone the Ln content of sediments were enriched in LREE (Sta. 10 and 15; Fig. 3). Moreover, Y also traces the influence of the Galiñeiro complex since in the aforementioned Louro-Minho sediment zone this element triples its content (Fig. 3). Yttrium, present in the xenotime (Murad 1978), is usually transported in the streams associated with terrestrial particles (Lawrence et al. 2006). So, the REE imprint of Galiñeiro geological complex is extended to all its surroundings, the Minho River and the Ria of Vigo. In this Ria, Ln (Caetano et al. 2009; Prego et al. 2009) and Y (Marmolejo-Rodríguez et al. 2008) were already used as sediment tracers.

The last section (D) of the Minho includes the salt mixing estuarine zone (stations 24-27) and two tributaries, Coura and Tamuxe. The Coura tributary runs by granites and schist and in its Ln fractionation prevailing LREE and Eu positive anomaly (Fig. 4). A different lithologic environment is the Tamuxe river basin, consisting of slates and quartzite. For this reason, the Tamuxe tributary shows the lowest contents in Ln and Y and the highest L/H ratio (2.5; Table 2) in the Minho lower course. According to the Ce anomaly, the influence of Tamuxe tributary on Minho sediments would only affect the station 27 (Fig. 4). No differences in the Ln profile were found between the main river (stations 24-27; Fig. 4) and the Coura tributary suggesting a relevant exportation of sediment from the Coura, which flow is $15.9 \text{ m}^3 \text{ s}^{-1}$ (Table 1), and sediment homogenization due hydrodynamics induced by tides.

Lanthanide and Y sedimentary contents and the element-by-element ES normalization along the lower course Minho River is showing a non-homogeneity distribution of fluvial bed sediments, although to a lesser extent than its tributaries (Fig. 1 and 4). These changes are remarkable in comparison with the studied REE trace of large rivers that are more spatially homogeneous (Bayon et al. 2015 and referenced cited therein). Yttrium and Ln showed similar patterns (Table 2 and Fig. 3); since Y determination is simpler, less expensive and faster than the set of fourteen Ln, Y can be used to describe the river-tributaries sediment trend in the lower Minho basin.

If the Ln distribution in Minho sediments is entirely attributable to geology, as Fedele et al. (2008) concluded from the large-scale distribution patterns of REE over Europe. Then, the contribution of tributaries to the Minho lower course sediments can be roughly estimated from the Ln contents in the Minho River basin (Section 4.3). In the Minho lower course 45% of sediments come from the tributaries while they only contribute with 19% of water. A decline of sediment supply to the lower course of the Minho River is occurring due to the commissioning of dams, like was observed in other dammed fluvial systems (Dang et al. 2010; Yang et al. 2015). The observed heterogeneity may be magnified due to the Minho is a flow regulated river. Numerous hydroelectric dams along its course regulate the water flow of Minho River being the Frieira hydropower dam the nearest to the sea.

6 Conclusions

Lanthanides and Y imprint in the lower course of the Minho River shows them as sediment tracers where the signature of some tributaries may be observed directly downstream of their confluence. Contents of Ln and Y, together with European Shale normalized relationships of LREE/HREE, La/Yb, La/Sm and

Sm/Yb, as well as the anomalies of Ce and Eu in the sediments of the lower Minho basin are associated with the characteristics of its changing lithology. They are mainly due to a paragneiss band with plagioclases and biotite that crosses a zone mainly composed by granite and granodiorite rocks. The granitic pegmatites and accessory REE-minerals of the Galiñeiro orthogneissic Complex highlight particularly the sedimentary influence through the Gadanha and Louro tributaries, respectively.

Rare earth elements has been routinely applied to the investigation of the source and transport of fluvial sediments, as advanced Piper (1974). Hitherto, the REE purpose as tributary tracer was explored by Albarede and Sehmi (1995) and now the Ln and Y results from the Lower Minho basin provide a new argument in that sense. The river Minho has several large hydroelectric dams through its watercourse that retains part of fluvial sediments, as occurs in lots of World Rivers. In the Minho lower course tributaries contribute approximately with half of the sediments although their combined flow is only a fifth of which receives the Minho River. Therefore, in this final course section of the Minho River the sedimentary influence of tributary sources increases significantly, which may be usual in the world-dammed rivers.

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Figure 1. Geographical location and main lithological and hydrological features of the lower course of the Minho River (77 km of length). Empty points represent the sampling sites (coordinates in the Electronic Supplementary Table A) from Fieira dam (station 1) to the Minho mouth (station 27) and near the nine tributary mouths. Dashed lines are showing the limits of each catchment tributary. In the Minho riverbed the section A covers from station 1 to Tea tributary mouth, the section B from there to Louro, the section C to Tamuxe and the section D to station 27.

Figure 2. Box-and-whisker plots with the contents of yttrium and lanthanides in the lower course sediments of the Minho River and its tributaries (data are in the Electronic Supplementary Table C). The straight horizontal line inside the box indicates the median and the dotted line the average. The length of the box represents the interquartile range containing 50 % of the values. The whiskers lines extent from the box to the highest and lowest values excluding the outliers (empty circles) and the extremes (stars). Outliers are defined as cases in which the values are between 1.5 and 3 times larger than the length of the box from its upper or lower border; those greater than three times are extremes.

Figure 3. Frieira Dam to sea profile of sediment content of yttrium, lanthanides (Ln) and European Shale normalized relationship (L_N/H_N) through the lower course sediments of the Minho River (grey circles) and its tributaries (black triangles). Fluvial sections (Electronic Supplementary Table A) are also showed, i.e. sections A (Sta. 1-8), B (9-11), C (12-23) and D (24-27).

Figure 4. Sediment curves of lanthanides normalized to European Shale in the lower Minho sections (A-D). Minho River stations (empty points) with similar values are averaged ($\pm$ standard deviations as perpendicular bars). Tributary curves are shown as grey points. Station 1 is right after the Frieira Dam at 77 km seaward and station 27 is in the estuary mouth.

Table 1. Characteristics of main tributaries from the right (Spanish) and left (Portuguese) banks in the lower watercourse of the Minho River.

Tributary	Length (km)	Basin area (km ²)	Annual average flow (m ³ ·s ⁻¹)
Right bank:			
Deva	21	92	3.7
Tea	50	411	25.3
Louro	28	153	8.4
Tamuxe	15	76	2.2
Left bank*:			
Trancoso	14	30	1.8
Mouro	36	142	8.4
Gadanha	19	82	4.8
Manco	8	22	1.3
Coura	46	270	15.9

* Flows (Q ; m³·s⁻¹) estimated from basin area (S ; km²) according to the Spanish tributaries relationship: $Q/S = 0.059$ ($r = 0.985$)

Table 2. Yttrium and lanthanide (Ln) contents ($\text{mg}\cdot\text{kg}^{-1}$) in sediments and European Shale relationships for the Minho River and its tributaries.

River	Yttrium	Ln	L_N/H_N	$(La/Yb)_N$	$(La/Sm)_N$	$(Sm/Yb)_N$	Ce/Ce*	Eu/Eu*	Reference
Trancoso tributary	8.1	40	0.85	0.72	0.72	0.99	0.55	1.13	This study
Deva tributary	2.8	32	1.96	2.48	1.01	2.46	0.54	1.69	
Mouro tributary	6.9	73	1.56	1.72	0.83	2.08	1.00	0.87	
Tea tributary	12.8	68	0.78	0.64	0.72	0.89	0.90	0.76	
Gadanha tributary	22.9	83	0.60	0.41	0.47	0.88	0.89	0.51	
Manco tributary	6.0	73	1.07	1.02	0.77	1.32	0.95	1.01	
Louro tributary	15.9	110	0.97	0.85	0.72	1.20	1.08	0.69	
Tamuxe tributary	1.6	28	2.48	3.50	0.93	3.78	0.55	1.01	
Coura tributary	5.4	73	1.96	1.84	0.75	2.44	1.16	1.32	
Minho lower course	4.9 ± 3.0	54 ± 33	1.69 ± 0.31	1.82 ± 0.59	0.92 ± 0.23	1.98 ± 0.41	0.81 ± 0.29	1.23 ± 0.18	Gouveia et al.,1993
Minho estuary	---	---	---	1.54 ± 0.35	1.06 ± 0.07	1.42 ± 0.26	---	---	