Distribution and fractionation of yttrium and rare earth elements in halophyte plants

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Salt marshes are characterized as being natural deposits of metals in the estuarine system. Several works showed the important role of salt marsh vegetation as preferential retention areas for some metals. However, until now no study has evaluated the role of halophytes on the retention of rare earth elements and yttrium (YREE).

The Rosario salt marsh, one of the marshes in the Tagus estuary (Portugal), which has an historical contamination from different sources, was chosen as a study area.

In order to evaluate the role of two halophytes (Spartina maritima and Sarcocornia fruticosa) on the retention of YREE in their roots, shoots, stems and sediments, in the fractionation and partition between the organs. Sediment cores were sampled, as well the aerial parts of plants. From the sectioning of these cores, 163 sediment samples and 101 plant samples were obtained. The concentrations of the YREE in the samples were determined by the technique of ICP-MS.

The results indicate that the main capture of the YREE in the marsh occurred in the sediments and that roots were the target organ of the plant. The comparison of YREE concentrations in the plants organs pointed to a weak translocation of these elements to the aerial part. They also suggest a weak influence of the interspecific differences in the retention of the YREE and the plant activity in increasing the bioavailability of the YREE. These results suggest that these plants don’t have the ability to phytoremediation the YREE in the sediments and roots.

Keywords: YREE - rare earth elements and yttrium; marsh; Sarcocornia fruticosa; Spartina maritima; metals; bioavailability

1 Introduction

Rare earth elements (REE) are a group of metals that include fifteen lanthanide elements: Lanthanum (La); Cerium (Ce); Praseodymium (Pr); Neodymium (Nd); Promethium (Pm); Samarium (Sm); Européio (Eu); Gadolinium (Gd); Terbium (Tb); Dysprosium (Dy); Holmium (Ho); Erbium (Er); Túlio (Tm); Ytterbium (Yb) and Lutetium (Lu). Often Yttrium (Y) is also included as well (YREE) (Tyler, 2004).

No other group of elements in the periodic system displays such a great similarity as the REE (Wytmtenbach et al., 1998; Tyler, 2004). In the geological environment, the REE typically occur in the oxidation state 3+ (Chakhmouradian e Wall, 2012), however, this is not a rule, some of them may present the 2+ and 4+ status (Gonzalez et al., 2014). The effective ionic radius of the trivalent ions decreases gradually from La3+ (103.1) to Lu3+ (86.1). The radius of Y, however, is similar to that of Ho (90) (Tyler, 2004). Trivalent REE behave coherently due to their similar ionic radii which decrease slightly but systematically from the lightest (La) to the heaviest (Lu) (Wytmtenbach et al., 1998). This notorious feature of this series of elements was called “lanthanide contraction” (Gonzalez et al., 2014).

The term rare earth elements doesn’t mean that these elements are rare in the earth’s crust. Their average abundance in the earth’s crust varies from 66 μg g⁻¹ in Ce, 40 μg g⁻¹ in Nd, and 35 μg g⁻¹ in La to 0.5 μg g⁻¹ in Tm, disregarding the extremely rare Pm (Tyler, 2004). The YREE group were divided according to the natural abundance of these elements (EPA, 2012).The low-atomic number lanthanides (La-Eu) are conventionally termed light REE (LREE), whereas their heavier counterparts (Gd-Lu) are referred to as heavy REE (HREE). Yttrium is grouped with the HREE because its ionic radius is nearly identical to that of Ho. These terms are somewhat arbitrary, some authors applied the term intermediate members of the series and named middle REE (e.g. Hatch, 2012). According to Hatch (2012) there are three subgroups: La, Ce, Pr and Nd are the LREE; Sm, Eu, and Gd are the MREE, and Tb, Dy, Ho, Er, Tm, Yb, Lu, and Y are the HREE.

Due to the increase in the use of YREE in the industry and medicine, these elements are becoming more and more widespread in the aquatic environment (Bau e Dulski (1996); Herrmann et al., 2016; Elbaz-Poulichet et al., 2002; Möller et al., 2000; Kukalsiz e Bau, 2011).

To the best of author’s knowledge, no data exist regarding the accumulation, partition and fractionation of YREE in salt marsh halophyte plants.

The aim of this work was to study the YREE in an estuarine salt marsh system sediment-halophyte plants (S. fruticosa and S. maritima) and evaluate the plants ability to accumulate and translocate these metals in their organs. These studies were carried out at the Rosário salt marsh, in the Tagus Estuary (SW Europe), where some YREE anthropogenic sources have been identified recently (Brito et al., 2018).

2 Sampling and methods

2.1 Study area

This study was done at the Rosário salt marsh, in the Tagus Estuary (SW Europe), one major estuary in Iberian Peninsula. This salt marsh is subjected to high human
pressure with ca. 3 million people living around it and several industries and agriculture fields settled in the margins for decades (Caçador e Vale, 2003; Vale, 1990). It is characterised by a typical zonation with homogeneous stands of S. maritima as a pioneer species, colonizing bare mud in the lower marsh areas, while S. fruticosa colonises the upper salt marsh (Caçador et al., 1996; Caetano et al., 2008). The marsh is inundated twice a day by salt water due to tidal action (2–4 m of tidal amplitude) through a highly branched system of channels (Caçador et al., 2009). The periodic inundation of the marsh and the proximity of pollution sources, made this ecosystem a highly sensitive area for the accumulation of pollutants. In the last decades, various research works has been carried out in order to better understand how this ecosystem is influenced by pollutants, mainly heavy metals (such as: Caçador et al., 1993; Caçador et al., 2000a; Caetano et al., 2008; Reboreda et al., 2008).

2.2 Sampling
Sediment cores were sampled with species of S. fruticosa and S. maritima, and in the adjacent non-colonised area at Rosário salt marsh in March 2017 (Erro! A origem da referência não foi encontrada.). All sediment cores (3 replicates per species, plus 3 replicates from the non-colonised area; n=9) were treated equally. Briefly, all sediment cores were sliced in 2–5 cm thickness layers and transported to the laboratory in plastic bags under refrigeration. Aboveground plant organs were removed from each core and stored in plastic bags. The belowground plant material in each layer was separated carefully from the sediment under a flux of ultra-pure water (Milli-Q water - 18.2 MΩ) using a 100-μm mesh size and sieved to remove any adhering particles. The aboveground plant biomass collected was washed with Milli-Q water to remove dust and sediment and separated into photosynthetic and non-photosynthetic organs. S. fruticosa do not have a true shoot system with leaves and stems. From these plant the swollen photosynthetic stems (referred to as “leaves” hereafter) were separated from the dry perennial shoots (referred to as “stems” hereafter) (Caçador et al., 2009; Duarte et al., 2010). The similar procedure was followed for S. maritima where the tillers were divided in leaves and in non-photosynthetic organs (referred to as “stems” hereafter). Sediment and plant organs (roots, stems and leaves) were oven dried at 40 °C, weighted to determine belowground biomass and homogenised in a mill for further analysis.

2.3 Elemental analysis
Dry sediment samples (≥100 mg) were totally decomposed with a mixture of HNO₃, HCl and HF in closed Teflon vessels following the method described by Loring and Rantala (1992). Dry roots, stems and leaves samples (≥100 mg) were digested with 1 mL of HNO₃ at 200°C using a microwave (CEM, MARS 5), for 15 minutes. After they were diluted to 25 mL with Milli-Q water. The YREE and Aluminium (Al) were determined using a quadrupole ICP-MS (ELAN DRC-e), from Perkin-Elmer.

2.4 Quality control
A 9-point calibration was used to quantify each element concentration, using a commercial solution of rhodium (Rh). Certified reference materials (MAG-1, G-2 and BHVO-1 from the United States Geological Survey – USGS, for sediment; and, OBTL-5, IPVTL-6, from the Institute of Nuclear Chemistry and Technology – INCT, and IAEA-140, from the International Atomic Energy Agency - IAEA, for plants) were used to control the precision of the results.

3 Results
3.1 General characteristics
The non-colonised sediments presented the lowest percentages of organic matter (OM (%)) and water (H (%)), de 2.5±1.2 % and 37±13%, respectively. Followed
by the sediments colonised by S. maritima (6±1 % and 53±5.9%, respectively). And finally, the sediments colonised by S. fruticosa 1±4:5.2% of MO and 69±10% of H. So, the three sediments showed the following pattern in terms of MO (%) and H (%): sediments colonised by S. fruticosa > colonised by S. maritima > non-colonised.

Regarding the percentage values of aluminium (Al (%)), the pattern obtained was: (1) non-colonised sediments had the lowest percentages 5.6±1.8%; (2) 16±0.73% in sediments colonised by S. fruticosa; (3) sediments colonised by S. maritima (11±0.8%).

The values of belowground biomass were relatively similar between species, 189±148 g/m² in S. fruticosa and 180±86 g/m² in S. maritima. The highest belowground biomass values were found in S. fruticosa, with 598 g/m² at 37.5 cm of depth. The maximum for S. maritima was 321 g/m² also found at 37.5 cm of depth.

3.2 YREE depth profiles

The Y and rare earth elements (YREE) have a very similar chemical behaviour among them (Wytenbach et al., 1998). In this way, the results presented will be related to the sum of the total rare earth elements (ΣREE), light rare earth elements (ΣLREE), heavy rare earth elements (ΣHREE) and Y.

3.3 ΣREE and Y contents depth profiles

As described in the sampling section, according to the type of sediments the processing of samples were different, as result, the non-colonised sediments analysed correspond to the granulometric fractions < 200 μm, while the colonised correspond to <100 μm. Thus, the non-colonised sediments may be subject to a greater effect of dilution of the samples caused by the larger sediments particles that by nature have less affinity with trace elements (Padeiro, 2014). In order to minimize the differences associated with changes in sediments granulometry, the concentrations of ΣREE, ΣLREE, ΣHREE and Y were normalized with Al (Loring, 1991).

The values of ΣREE/Al, ΣLREE/Al, ΣHREE/Al and Y/Al were very similar in the three types of sediments, highlighting the difference between LREE and HREE (Table 3-1).

In the case of the plants roots, the pattern was the same, highlighting that the values between species were very similar (Table 3-2).

3.4 YREE fractionation patterns

The YREE fractionation patterns are described by normalizing the individual absolute concentrations of each element with reference values of YREE (normalization base) (Olmez et al., 1991). There are several normalization bases or shales, that are usually used as proxy. In this study, the normalization basis used to describe YREE fractionation in sediments and plants was PAAS (Post Archean Australian Shale) (McLennan, 1989).

After normalization, it’s evaluated which elements present an enrichment or depletion, and which elements (Kulaksiz e Bau, 2011). In order to facilitate the interpretation of the presented graphs, the axis of YREE/PAAS ratio is presented in logarithmic form. From the analysis of the fractionation patterns in sediments (Figure 3), the following patterns were verified: (i) in all sediments the fractionation had a very similar behaviour between the top and base depths of the core; (ii) colonised and non-colonised sediments are enriched in MREE compared to LREE and HREE; (iii) compared to PAAS, colonised sediments are enriched in MREE and depleted in LREE and HREE, (iv) compared to PAAS, non colonised sediments are depleted in LREE, MREE and HREE.

From the analysis of the fractionation patterns in plants roots (Figure 3-), it was highlighted that: (a) all elements had a very similar fractionation patterns between the top and base depths of the core; (b) the roots of the two species are enriched in MREE compared to LREE and HREE; (c) relative to PAAS, the roots are impoverished in LREE, MREE and HREE; (iv) the patterns of the two species were very similar.
Figure 3-1: YREE fractionation patterns in sediments colonised by *S. fruticosa* (A), *S. maritima* (B) and non-colonised (C).

Figure 3-2: YREE fractionation patterns in plants roots: *S. fruticosa* (A) and *S. maritima* (B).
4 Discussion

4.1 General characteristics

The total belowground biomass found in S. fruticosa was 3595 g/m² and 3052 g/m² of S. maritima. Comparing with the values reported in Caetano et al. (2008), it was found that for S. fruticosa the values were similar between the studies (4030 g/m²). However, for S. maritima the value observed in this work were higher than those found by Caetano et al. (2008) (1292 g/m²). These differences may be associated with the sampling season. In fact, one of the factors that can influence the amount of belowground biomass is the seasonal variation. Variations such as temperature, salinity, nutrient availability, and oxygenation in the zone of the root system can occur on a monthly basis. Other parameters, such as elevation, may also influence biomass production (Lana et al., 1991). The total values of belowground biomass obtained demonstrate that S. fruticosa is the most productive plant. This difference found between the two species is in agreement with Caetano et al. (2008) and Duarte et al. (2010) in Rosário salt marsh.

A greater variation of belowground biomass was observed at medium depths and/or at the base of the core. In the case of S. fruticosa, the maximum obtained can be associated to a high biomass production that these species are characterized, generating high amounts of litter. In fact, the sediments colonised by S. fruticosa obtained the greater content of organic matter, probably due to the decomposition of the root system and, consequently the incorporation of the organic matter in the sediments (Cesário, 2007)

The roots of S. fruticosa presented a greater penetration in the sediment. This result is in agreement with Cesário (2007), in Rosário salt marsh. This difference found between the two plants may be associated with adaptive responses to the environment in which plants are found (Groenendijk e Vink-Lievaart, 1987), suggesting a competition to capture nutrients in the surrounding environment.

4.2 ∑REE and Y contents depth profiles

Most studies with contaminants and plants, have addressed belowground biomass as a whole (ex: Weis and Weis, 2004). Consequently, these studies haven’t tested the hypothesis if there are preferential depths of accumulation of metals in roots tissues and distribution of the YREE in depth.

In general, the concentration (µg/g) of ∑REE and Y in roots (Figure 4-1) was similar between the two species. However, this result contradicts the fact that the root system of S. maritima has a lower specific area than S. fruticosa, which leads to minor root-sediment interaction (Lee, 1999) and less bioavailability of the elements for this plant. This absence of differences in the concentration of YREE isn’t in line with observed in Cesário (2007) and Caetano et al. (2008) with other metals (Zn, Cu, Cd and Pb), where the roots of S. fruticosa accumulated higher values than S. maritima. It should be considered that in this work, for a methodological question, it wasn’t possible to distinguish between dead and alive portion of roots, so the levels recorded are for the all belowground, with the possible organic material in decomposition derived from the roots. This point may be of extreme importance, since the behaviour of REE in soils may be affected by the existence of organic compound produced by microorganisms during the decomposition of organic waste (Tyler, 2004). From the decomposition of this organic litter results matter with negatively charged groups, and so, a high affinity for divalent and trivalent cation (Zhenghua et al., 2001). As the YREE are mostly in the oxidation state (+3) (Chakhmouradian e Wall, 2012), the presence of this waste probably influences the bioavailability of these elements in the sediments.

In fact, observing the REE/Al ratios in the non-colonised and colonised sediments (Figure 4-1), it was found that from the 29 cm depth to the bottom, the sediments colonised by S. fruticosa presented the highest values. It’s important to note that the plants roots not only have the ability to concentrate metals but also to release them to the sedimentary environment (Reboreda e Caçador, 2007b; Duarte et al., 2010), functioning as a source of metals to the environment. In this particular case, it was found low concentrations of ∑REE e Y in roots, so, a possible elimination of these elements for the surrounding environment would only be vestigial and wouldn’t influence the concentration of these elements in sediments. Considering that the small differences found between the non-colonised and colonised sediments (Figure 4-1) are mainly induced by the activity of the plants, the result obtained suggests that the plants practically didn’t provoke disturbances in the sediments for the accumulation of YREE. Several studies (ex. Williams et al., 1994; Duarte et al., 2010) report that due to plant activity (respiration) is created a different microenvironment in the surrounding sediment (rhizosphere) that influences the
bioavailability of metals (ex. Fe, Mn, Zn, Cu and Cd) present in that environment. This hypothesis was also verified in a work done by Almeida et al. (2004), in Douro river estuary (Portugal) with the *Juncus maritimus*, and in Cesário (2007) with the same two species studied in this work.

The comparison of the ∑REE contents (µg/g) in the sediments and roots, showed that the colonised sediments had concentrations of one order of magnitude higher than the roots (Figure 4-2). This result doesn’t comply with values recorded for the same species for other elements. In Cesário (2007) it was observed that the concentration of Zn, Cu, Cd and Pb was higher in the roots of plants compared to the sediment near the roots. However, in the study conducted by Reboreda e Caçador (2007b) with two halophytes (*S. maritima* and *H. portulacoides*) in Rosario salt marsh, was observed the opposite, with the main accumulation of Cu, Cd and Pb occurring in the sediments near the roots. In fact, not only the accumulation of metals in the roots, but also in the surrounding sediment, plays an important role in the retention of metals, reducing the availability to the ecosystem (Reboreda e Caçador, 2007b).
4.3 Concentration of YREE in plants

According to the results obtained (Table 4-1), it was observed that the concentrations of YREE in the stems and leaves of *S. fruticosa* and *S. maritima* were quite low compared to the roots. In fact, observing the concentrations obtained for each element in the two parts of the plants *(Erro! A origem da referência não foi encontrada.)* it’s verified that the belowground part had concentrations that were two orders of magnitude higher than the aerial part. These are in agreement with Caçador et al. (2000b), Reboreda e Caçador, (2007b) and Caetano et al. (2008). Other species such as *Spartina alterniflora* and *Phragmites australis*, also demonstrated the same metal partition (Windham et al., 2003). The differences observed in concentrations between the two parts of the plants are also in agreement with recent studies of REE distribution in plants of crops such as corn, wheat, rice and paprika (Cao et al., 2000; Hu et al., 2002; Xu et al., 2002). These works had showed a decreasing REE concentrations in the order: root > leaf > stem > grain or fruit in a variety of crops such as maize, wheat, rice and paprika. The analysis of REE in five species of terrestrial plants (*Vicia villosa*, *Sasa nipponica*, *Thea sinensis*, *Taxodium japonicum* and *Populus sieboldii*) at Japan, it was verified that the underground organs (main and secondary root) had the higher values than in aerial organs (leaves and stems) (Fu et al., 2001).

4.4 YREE fractionation patterns

The YREE fractionation patterns (PAAS ratio) obtained in colonised and non-colonised sediments were very similar to each other, with the exception of a slight increase of Eu observed for sediments colonised by *S. maritima*. All sediments are enriched in MREE compared to LREE and HREE. These results are supported by the following reasons: (i) light rare earth element/medium earth element, (Al/Sm)PAAS; medium rare earth element/heavy rare earth element (Sm/Yb)PAAS; light rare earth element/heavy rare earth element (La/Yb)PAAS (Table 4-1). From this it was confirmed the above suggested: (a) there is the same proportion of light, medium and heavy for the three types of sediments; (b) there is an enrichment of the averages in comparison to the light and heavy ones; (c) and also allows to verify that there is an enrichment of the light ones compared to the heavy ones. In this way for the three sediments the following pattern was observed: MREE > LREE > HREE.

Comparing the fractionations patterns of the colonised sediments with the respective plant, in General, it was observed that the behaviour of these sediments was identical, highlighting only differences in the last two elements of the series (Yb and Lu) (Figure 4-3). This result suggests that the accumulation by plants is not selective, since the fractionation of sediment/plant is very similar, except for Lu. This element presented an increment in relation to Yb in the sediments and not in the roots. The same increase has also been observed for other works (Fu et al., 2001; Xu et al., 2002). It’s also noteworthy that the behaviour of the two species was very similar, pointing out to be independent of the plant species. This result is in agreement with the study by Fu et al. (2001).

Regarding the aerial part of the plants, a great difference was observed in the behaviours between this and the underground part (Table 4-1). This difference may be associated with a mobility and/or affinity different of YREE for the plants parts. These differences have also been documented in the study by Fu et al. (2001).

<table>
<thead>
<tr>
<th>Sediments</th>
<th>(La/Sm)PAAS</th>
<th>(Sm/Yb)PAAS</th>
<th>(La/Yb)PAAS</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>S. fruticosa</em></td>
<td>0.8±0.010</td>
<td>1.6±0.060</td>
<td>1.3±0.050</td>
</tr>
<tr>
<td><em>S. maritima</em></td>
<td>0.8±0.020</td>
<td>1.6±0.060</td>
<td>1.4±0.020</td>
</tr>
<tr>
<td>Non colonised</td>
<td>0.8±0.010</td>
<td>1.7±0.060</td>
<td>1.4±0.060</td>
</tr>
</tbody>
</table>

Table 4-1: Ratios of rare earth elements in the sediments: (i) La/Sm)PAAS; (ii) Sm/Yb)PAAS; (iii) (La/Yb)PAAS.
Table 4-2: Concentration (µg/g) of the YREE in the aerial organs (leaves and stems) and in the roots.

<table>
<thead>
<tr>
<th>Element (µg/g)</th>
<th>S. fruticosa</th>
<th>S. maritima</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Leaves</td>
<td>Stems</td>
</tr>
<tr>
<td>Y</td>
<td>0.18–0.69</td>
<td>0.23–1.4</td>
</tr>
<tr>
<td>La</td>
<td>0.29–1.1</td>
<td>0.26–2.1</td>
</tr>
<tr>
<td>Ce</td>
<td>0.63–2.2</td>
<td>0.53–4.2</td>
</tr>
<tr>
<td>Pr</td>
<td>0.070–0.25</td>
<td>0.060–0.50</td>
</tr>
<tr>
<td>Nd</td>
<td>0.25–0.96</td>
<td>0.23–2.0</td>
</tr>
<tr>
<td>Sm</td>
<td>0.060–0.20</td>
<td>0.050–0.39</td>
</tr>
<tr>
<td>Eu</td>
<td>0.010–0.040</td>
<td>0.010–0.070</td>
</tr>
<tr>
<td>Gd</td>
<td>0.005–0.18</td>
<td>0.040–0.34</td>
</tr>
<tr>
<td>Tb</td>
<td>0.010–0.020</td>
<td>0.007–0.045</td>
</tr>
<tr>
<td>Dy</td>
<td>0.030–0.11</td>
<td>0.030–0.23</td>
</tr>
<tr>
<td>Ho</td>
<td>0.004–0.024</td>
<td>0.005–0.042</td>
</tr>
<tr>
<td>Er</td>
<td>0.010–0.050</td>
<td>0.010–0.10</td>
</tr>
<tr>
<td>Tm</td>
<td>0.001–0.004</td>
<td>0.001–0.011</td>
</tr>
<tr>
<td>Yb</td>
<td>0.010–0.040</td>
<td>0.011–0.080</td>
</tr>
<tr>
<td>Lu</td>
<td>0.002–0.006</td>
<td>0.002–0.011</td>
</tr>
</tbody>
</table>

Figure 4-3: YREE fractionation patterns in roots (—) and sediments (•-•) of S. fruticosa (A) and, in roots (—) and sediments (•-•) of S. maritima (B).
5 Conclusions

This study showed that *S. fruticosa* and *S. maritima* exhibited a low ability to extract YREE from the sediments and to retain them in the roots. These results are a novel aspect of this work because, halophytes plants are known to present an ability to retain heavy metals in their roots, being classified by several authors as hyper-accumulators of metals. In addition to this remarkable capacity, halophytes are also characterized by altering the characteristics of the sediments, especially those among plants roots (rhizosediments) and, consequently, immobilize metals in the surrounding area. These capabilities have shown that this species can be useful for phytoremediation of polluted coastal areas. However, this wasn’t observed in this work. So, *S. fruticosa* and *S. maritima* don’t have the capacity for phytostabilization of YREE in their roots and surrounding sediment.

The main concentration of YREE in the plants was in the roots, being very identical between plants. This lack of differences between the two species was also verified in the fractionation patterns results. Thus, another novel aspect of this work, is that intraspecific differences don’t appear to be significant in the accumulation of YREE.

As with most other metals, this work also showed a weak accumulation of YREE in the aerial part compared to the underground part of the plants. This suggests that there is a weak translocation of YREE from the underground to the aerial part.

Although in other metallic elements a differentiated accumulation in depth was verified, in the present work for YREE this effect wasn’t notorious.

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