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RESEARCH PAPER

RARE EARTH ELEMENTS USED AS FINGERPRINTS OF DIFFERENTIATED SEDIMENT SOURCES IN THE RIA DE AVEIRO (PORTUGAL)

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Abstract

This work focuses on the distribution and the controlling factors of rare earth element (REE) total concentrations and fractionation patterns in fine sediment fractions of 53 samples collected along the main channels of the Ria de Aveiro, a northern Portuguese coastal lagoon. Total and available concentrations and residual phases of REE and total concentrations in three chemically partitioned fractions (S1 - adsorbed by clay and co-precipitated with carbonates; S2 - adsorbed by organic matter; S3 - adsorbed by amorphous Mn hydroxides) are analysed. These data are joinly analysed with physicochemical, textural and mineralogical and other geochemical data.

Sediment samples mainly consisted of phyllosilicates, quartz, plagioclase and K–feldspars. Cerium (Ce) is the most abundant REE in the residual phase and displays the lowest total available percentage, whereas Yttrium (Y) is the most available. The highest total concentration and residual concentration (R) of Ce, Lanthanum (La), Scandium (Sc) and Y are mostly related to fine grained sediments, suggesting that their distributions are conditioned by lagoon hydrodynamics.

The dissimilar distribution of REE-S1, REE-S2 and REE-S3 indicates differentiated sedimentary processes. The enrichment of REE-S2 and REE-S3 is related essentially to biogeochemical processes inside the lagoon. The REE-S1, as well as Ce-S1/Sc-R, trace sediments supplied from the northern areas suplyed mostly by the Douro River outflow and from the Antuã River.

In the past, the sediments suplyed by the Douro River through the litoral drift contributed to the formation of the lagoon islands. Thus the relatatively high Ce-S1/Sc-R values inside the lagoon allowed the identification of: sediments supplied from the litoral drift and deposited near the lagoon mouth, erosional processes of the lagoonal islands and sediments supplied by the Antuã River. This work demonstrates that the available concentrations of rare earth elements can be considered as important tools for investigating sediment sources and dispersion in a coastal system.

Keywords: Rare earth elements. Total concentrations. Sequential chemical extraction. Sedimentary dynamics. Coastal lagoon.

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1. Introduction

During the last few decades, rare earth elements (REE) have become important geochemical tracers in paleoenvironmental and paleoclimatic studies to indicate source-area weathering, provenance, and tectonic settings (Budakoglu et al., 2015, and references herein). REE are considered to have a great potential as sediment tracers due to their strong binding capability with sediments, low natural background levels, chemical stability and low mobility (Zhu et al., 2011). REE show limited variations in their physical and chemical properties that allow their fractionation and enrichment in different surface sediment conditions (Das et al., 2006). The geochemical behaviour of REE in aquatic systems represents a relatively new field of study (Verplanck et al., 2004).

Understanding sediment sources and dispersion throughout a coastal system is essential in order to know the sedimentary processes taking place. However, little is known about REE distribution and fractionation in transitional systems such as lagoons. As far as we know, no study has yet been performed to find a fingerprint of differentiated sources of sediments in the Ria de Aveiro, based on REE.

In order to distinguish sediment source areas and to infer about possible processes involved in the dispersion and deposition of sediments throughout the lagoon, analyses of REE were performed. The study was based on multivariate statistical analysis. Total and available concentrations in three extracted phases of REE, and their residual phase's content were confronted with physicochemical, textural, mineralogical and other geochemical data from surface sediments of the lagoon.

1.1. *Study area*

The Ria de Aveiro is a shallow lagoon located in the coastal zone of central Portugal (40°38'N, 08°45'W) with a geologically complex history related to the sea level rise since the last glaciation (Dias et al., 2000a) (Fig. 1a). During the last, coldest event of the last glaciation, the Younger Dryas, the sea level was approximately 100 m below the current level (Dias et al., 2000a). After this event, sea level rose significantly until approximately 5 ka BP (Dias, 1985). When the sea level reached approximately the current level, between 3-5 ka BP, the Aveiro region coast corresponded to a large and wide bay (Dias et al., 2012). This bay (approximately 70 km long and 20 km wide) was connected with the mouth of the Vouga River (Duck and Silva, 2012) and was open to the Atlantic Ocean (Dias et al., 2012). Since then, the relative sea level rise and the supply and accumulation of sand deposits through littoral drift, mainly from the north, by the estuaries of the Douro River and other northern Portuguese rivers was massive. These sediments contributed for the establishment and growth of the sand bar that isolates nowadays the lagoon area from the open ocean (Dias et al., 2000b).

The natural inlet of Ria de Aveiro that allowed the exchange between the lagoon and the ocean has become progressively narrower and migrated to the south as the spit grew (Dias et al., 2012). The rapid southerly accretion of this spit had almost completely enclosed the lagoon by the end of the 16th century (Duck and Silva, 2012). With this natural evolution, the water body would have become progressively filled with land-derived sediments introduced by the Vouga River and other effluents, to ultimately take the form of a deltaic wetland. By the beginning of the 19th century, there was no navigable connection between the Atlantic Ocean and the Ria de Aveiro (Dias et al., 2012).

The natural evolution of this coastal lagoon was interrupted in 1808 by human intervention, with the construction of an artificial inlet, in response to the persistent accretion of the natural inlet (Dias et al., 2012). Since then, successive interventions and engineering works were carried out, such as those in 1932, between 1949 and 1958, 1987 and 2002 (the largest one), which were necessary to maintain the bar open and workable (Plecha et al., 2010; Dias et al., 2012).

The water exchange with the ocean today occurs through an artificial inlet (the Aveiro inlet), that is approximately 1.3 km long, 350 m wide and 30 m deep. The lagoon system occupies an area of approximately 110 km^2 (Dias et al., 1999) and exhibits a complex morphology, including four main channels: S. Jacinto/Ovar, Mira, Espinheiro and Ílhavo, and large, recent alluvial deposits that sometimes form islands, islets and extensive salt marshes (Fig. 1). The average depth is approximately one meter, reaching up to 4 m in navigation channels and more than 8 m in dredged port areas (Borrego et al., 1994). Semi-diurnal tides are the major driving force of circulation in the lagoon (Dias et al., 1999).

The lagoonal channels have an asymmetrical cross configuration. The navigation canal is generally located next to one of the margins. The slope of these margins is sharp and sinks quickly to relatively deeper depths. The currents of the navigation canals are in general very strong, mostly in the outer sector of the lagoon where current velocities reach about 2 m/s (Dias et al., 2003; Vaz and Dias, 2008). The substrate in these margins and bottom of navigable canals is commonly constituted of sand (Duarte et al., 2003) and mostly of quartz (Rocha et al., 2000, 2005).

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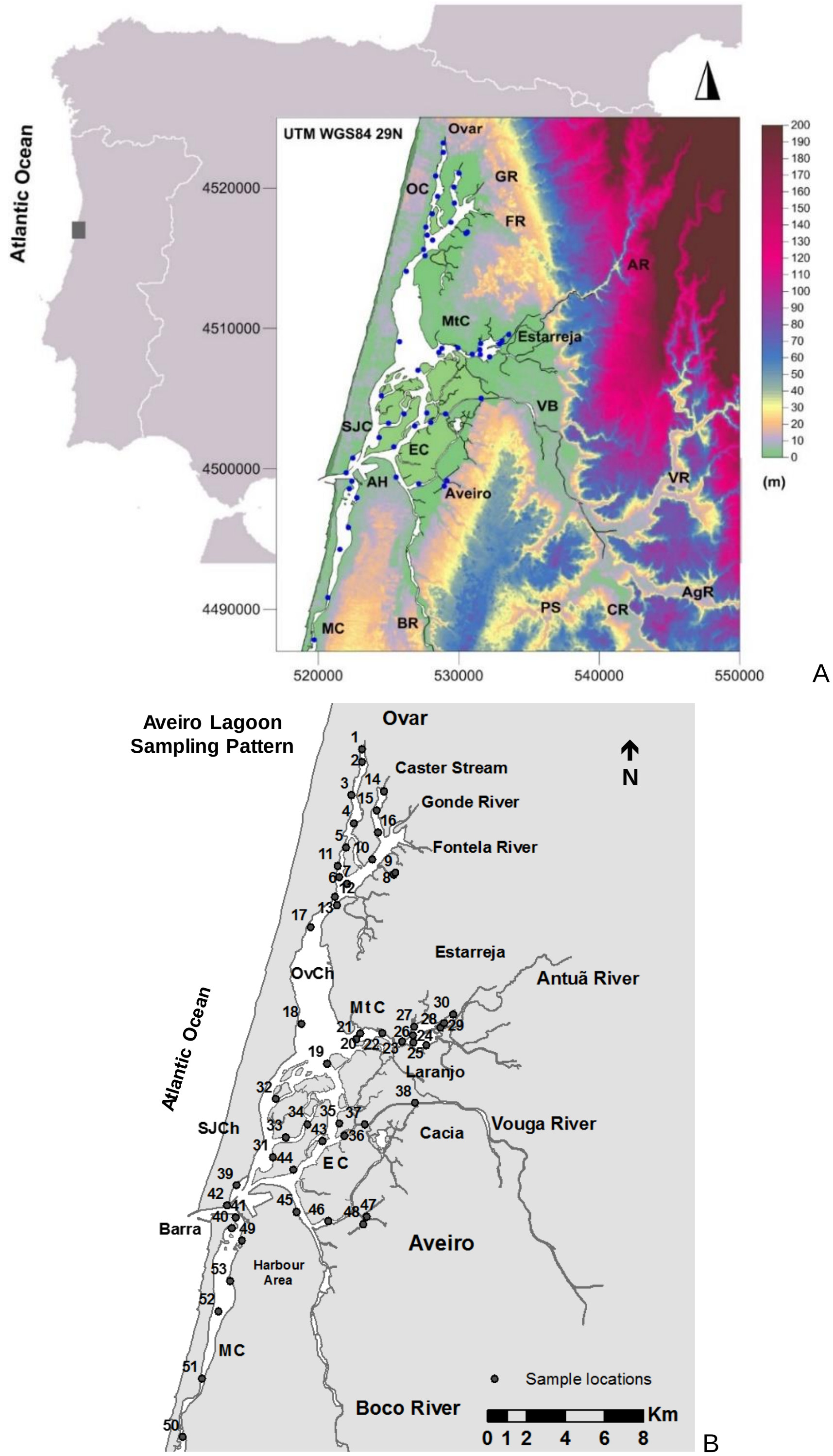

Fig. 1. Study area in Ria de Aveiro (A) showing the sampling location (A) and the related code (B). Legend: OC – Ovar Channel; MtC – Murtosa Channel; EC – Espinheiro Channel; MC – Mira Channel; SJC – S. Jacinto Channel; AH – Aveiro Harbour; BR – Boco River; AR – Antuã River; FR – Fontela River; GR – Gonde River, VB – Vouga Basin including, VR – Vouga River, PS – Pano Stream, AgR – Águeda River and CR – Cétima River. The image (B) is adapted from Martins et al. (2015 b).

On the opposite margins, the substrate is softer and the prevailing weak current conditions allow the deposition of fine-grained sediments that are much more diversified in terms of mineralogical and geochemical composition (Rocha et al., 2000).

The area now occupied by the lagoon is characterized, in the peripheral part of the landward side, by the presence of rocks of Late Proterozoic to Carboniferous age, forming the wide Variscan or Hercynian orogenic outcrop in the western part of the Iberian Peninsula, called Iberian or Hesperian Massif (Ribeiro et al., 1979). Pre-Ordovician schists and greywackes, Hercynian granites belonging to the Paleozoic Hesperic Massif, and the more recent sedimentary rocks that are part of the Meso-Cenozoic edge are separated by a first-order tectonic structure. This structure is the Porto-Tomar - Ferreira do Alentejo fault (Ribeiro et al., 1979). The area over which the lagoon (past and present) developed is characterized by the presence of unconsolidated Pleistocene and Holocene sediments (Dias et al., 2012). River basins provide the main source of continental sediments introduced in the Ria de Aveiro.

The river system of the Ria de Aveiro is dominated by the Vouga River catchment (length: 148 km; watershed: 3635 km^2) with an annual average discharge of about 25 m^3s^{-1} (Borrego et al, 1994). This river, which descends from 930 meters above sea level in the Lapa mountain, and has several tributaries, such as the Águeda and Cértima rivers and Pano Stream (Fig. 1). Vouga River contributes approximately with 69% of the drained area that provides fresh water and sediments to the Ria de Aveiro (Silva, 1994).

The mountainous part of the Vouga River basin is composed of Paleozoic metasedimentary rocks intruded by syn- to post-tectonic Hercynian granites (Van der Weijden and Pacheco, 2006 and references herein). The metasediments consist of phyllites and greywackes that locally alternate with conglomerates, amphibolites and, in the vicinity of granites, with migmatites and mica schists with high-grade metamorphism (Van der Weijden and Pacheco, 2006). The syn-tectonic granitoids consist mostly of medium- to coarse-grained two-mica granites to granodiorites; the post-tectonic granitoids consist mostly of porphyritic coarse-grained biotite, or two-mica granites (Van der Weijden and Pacheco, 2006).

The Vouga River, along with the Antuã River and other small streams, introduce into the lagoon a total freshwater flow estimated at approximately 40 m^3s^{-1} (Vicente, 1985). Vouga River represents the major source of freshwater discharging into the lagoon (Vicente, 1985) and is connected to the sea by the Espinheiro Channel, which is an east-west oriented waterway 10 km long (Fig. 1). The Vouga River discharges into the lagoon through the Rio Novo do Príncipe, a long (approximately 3200 m) and narrow canal (approximately 60 m wide) approximately 5 m deep (Vaz et al., 2005). The end of Rio Novo do Príncipe is restricted by an irregular dam-like structure with a lock. Rivers flow in the extreme interior of the main lagoon channels are an important factor for movement and transport of sediments (Lopes et al., 2006).

Sediment grain size and composition in the Ria de Aveiro are highly variable (Duarte et al., 2003; Martins et al., 2014, 2015 a, b). The bottom sediments of most of the channels with strong current are commonly composed of sand. In places, the gravel fraction increases, due to the biogenic contribution (mollusks shells). The coarse sediments transported by rivers are deposited near the river mouths. The solid load carried by the rivers that reach the Ria de Aveiro is essentially composed of fine cohesive sediments (silt and clay), which correspond to the grain size of the sediments of the intertidal flats, salt marshes, harbours and shipyards (Lopes et al., 2001).

The first attempts to study the cohesive sediments transported in the Ria de Aveiro was carried out by Lopes et al. (2001, 2006). These studies revealed that, for instance, the S. Jacinto and the Espinheiro channels, as well as part of the Murtosa Channel, are the areas of the lagoon most affected by hydrodynamics and sediment transport mechanisms. They are the most affected by the ocean, as well as by the two major freshwater lagoon contributors, the Vouga and the Antuã Rivers. In most areas of the lagoon, namely the shallow ones, deposition is the dominant process, evidencing a long-term trend leading to a mean water depth decrease.

2. Material and methods

The uppermost centimetre of fifty-three surface sediment grab samples were collected with a Petit Ponnar Sampler at water depths between 0.5 m and ~2 m, in sites located in intertidal and subtidal areas, surrounding the main channels of the Ria de Aveiro (Fig. 1). In order to trace the distributional pattern of REE within the lagoon, the sampling sites were intentionally located in the slower current margin of the channels, where potentially fine-grained sediments should have accumulated. The methodology for geochemical analyses of both total sediment digestion and chemical sequential extraction, as well as mineralogical analysis, namely Kubler Index determination, and grain size data evaluation, were described in Martins et al. (2015a).

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This work analyses the distribution of total elemental concentrations (obtained by total digestion of the sediments) of Ca and several REE, such as Ce, La, Sc and Y, as well as available concentrations of Ce, Dy, Eu, Gd, Ho, La, Lu, Nd, Pr, Sc, Sm, Tm, Y and Yb in S1 (adsorbed by clay and elements co-precipitated with carbonates); S2 (adsorbed by organic matter); and S3 (adsorbed by amorphous Mn hydroxides).

The distribution of REE in S1, S2 and S3 phases (REE-S1, REE-S2 and REE-S3) and total available concentration (REE total available concentration = REE-S1 + REE-S2 + REE-S3) were analysed. Total available concentrations of Ce, La, Sc and Y were also accounted for in the determination of the residual phase. The residual phase concentration (R) of Ce, La, Sc and Y, corresponding approximately to the elemental concentrations retained in the mineralogical crystalline structure, were calculated by the difference between total concentration (TC) and total available concentrations (TA) (R = TC – TA). Since the residual phase of Sc shows very small variability in the studied sites and is related to grain size parameters, it was used to normalize the available concentration of Ce, La and Y in S1 (Ce-S1/Sc-R; La-S1/Sc-R and; Y-S1/Sc-R) and R (Ce-R/Sc-R; La-R/Sc-R and; Y-R/Sc-R).

The REE results were related through multivariate statistical analyses to other selected physicochemical (Eh), geochemical (Ca and TOC content), mineralogical and grain size data to evaluate possible factors that controlled their sedimentological distribution.

2.1. Statistical analysis

Data were logarithmically transformed (log(x+1)) before statistical analyses were performed. Principal Components Analysis (PCA) and Cluster Analyses (CA) in R-mode, based on the "weighted pair group average" method for agglomeration and 1-Pearson r correlations, were performed in Statistica 7.0 software.

A Q-mode CA based on Euclidean distance and Ward's method for data agglomeration was also performed using the same software. Maps were prepared with ArcGIS 9.2®, using metric coordinates, according to the datum WGS84 (UTM Zone 29). Altimetry was provided by the SRTM ver4.1 (Hirt et al., 2010).

3. Results

The substrate of most of the sampled sites is composed of mud or sandy mud. Thus, in most of the samples, sediment mean grain size (SMGS: 18-368 μm; average: 85 μm; Fig. 2a) the sediments are composed mostly by fine particles with sorting values >2.6 (1.5-5.7; average 3.8; Fig. 2b), indicative of sediments that are poorly or extremely poorly sorted.

The values of SMGS reveal that despite the fact that the selected sites were in areas of relatively slow current, grain size tends to increase in the outer sector of the lagoon near the entrance (Fig. 2a). Coarse substrates were also found in some areas throughout the channels.

Most of the studied sediments display negative Eh values (Fig. 2c; from -72 to 134 mV; average -17 mV) and have pH values >7.0 (Fig. 2d; from 4.2 to 8.9; average 7.0) and TOC content >1.5% (Fig. 2e; 0.1-7.4%, average 2%). The highest values of TOC are found in the internal areas of Murtosa and Ovar channels and in the canals of Aveiro city (Fig. 2d).

The sediments are mainly composed of phyllosilicates (22-68-%; average 45%; Fig. 2f), quartz (15-44%; average 31%), plagioclase (<34%; average 6%) and K–feldspars (2-7%; average 4%). Calcite has a low abundance (0.1-7%; average 2%). Pyrite is present in all studied sites (1-5%; average 1%; Fig. 2g).

Illite dominates the composition of the clay mineral assemblages (85-51%; average 72%) with Kubler Index values varying between 0.7-0.2 (average 0.4) and followed by kaolinite (49-11%; average 25%). The highest values of illite content (Fig. 2h) and Kubler Index (Fig. 2i) are recorded mostly in the external and central lagoonal areas near the mouth of Ria de Aveiro.

The total concentrations of Ce (30-112 mg kg^{-1}; average 52 mg kg^{-1}), La (12-54 mg kg^{-1}; average 24 mg kg^{-1}), Sc (4-12 mg kg^{-1}; average 5.5 mg kg^{-1}) and Y (6-28 mg kg^{-1}; average 10 mg kg^{-1}) increase mostly in three main zones: at the northern part of Ovar Channel, along the Murtosa Channel and close to the lagoon inlet, and have intermediate concentrations in the study area along the Espinheiro Channel.

The residual concentrations of these REE varies for Ce (18-102 mg kg^{-1}; average 542 mg kg^{-1}), La (9-49 mg kg^{-1}; average 19 mg kg^{-1}), Sc (1-11 mg kg^{-1}; average 4 mg kg^{-1}) and Y (1-23 mg kg^{-1}; average 4 mg kg^{-1}), also following the same pattern of total concentrations.

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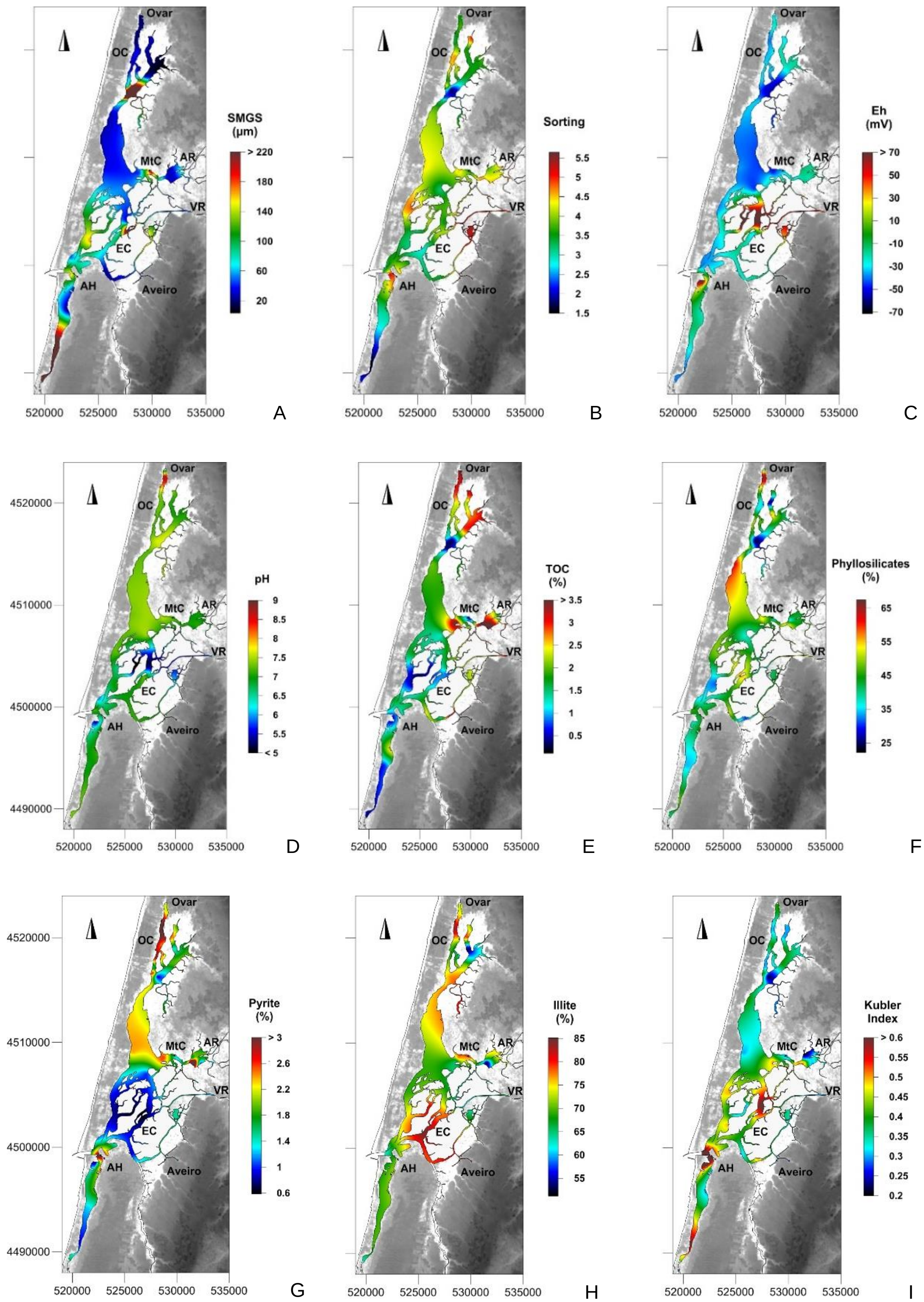

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Fig. 2. Maps of distribution of the following variables: A) SMGS: sediment mean grain size (μm); B) sorting; C) Eh (mV); D) pH; E) TOC: total organic carbon (%); F) phyllosilicates (%); G) pyrite; H) Illite (%); I) Kubler Index. Legend: OC – Ovar Channel; MtC – Murtosa Channel; EC – Espinheiro Channel; AH – Aveiro Harbour; VR – Vouga River; AR – Antuã River.

Cerium is the most abundant REE in the residual phase, followed by La, and displays the lowest total available percentage (Ce-TA%), whereas Y is the most available (Y-TA%) among REE (Fig. 3). The residual concentrations (R) of Sc have the lowest variability in the studied sites, compared with the other REE.

The highest sedimentary Ce-R and La-R contents are encountered in the northern area of Ovar Channel (A8-A13; A15-A19), in the inner part of Murtosa Channel (A23-A24) and in the outer sector of the lagoon (A39-42). The highest Y-TA% is in the northern area of Ovar Channel (A14); along the Murtosa Channel (A22-A23; A25-A30); around the islands of the main lagoonal body (A31-A43); and in the coastal fishing harbour (A49). The Sc-TA% only increases locally, such as in the confluence of S. Jacinto, Ovar and Murtosa channels (A18-A21) and in Laranjo Bay at Murtosa Channel (A27).

In addition, Ce, Y, La and Nd have the highest available concentration in all the analyzed extracted phases (S1, S2, and S3), whereas Eu, Yb, Ho, Tm and Lu have the lowest available concentration (Table 1). Most of the REE display higher available concentrations over most of the sites in S3, except, for instance, in A23, A27 and A30 (located in the inner zone of Murtosa Channel), and by decreasing order of abundance, in S2 and S1 (Suppl. Fig. 1). Scandium is an exception since it reaches higher concentrations in S2 than in other extracted phases (Suppl. Fig. 1).

Tab. 1. Maximum (Max), Minimum (Min) and average (Aver) available concentrations (μg kg^{-1}) in S1, S2 and S2 of the analyzed REE by sequential order of the maximum values determined in each extracted phase (S1 to S3).

REE	Max	Min	Aver	REE	Max	Min	Aver	REE	Max	Min	Aver
S1				S2				S3			
Ce-S_1	4139	416	1478	Ce-S_2	7468	762	3326	Ce-S_3	8982	38	5628
Y-S_1	2264	304	912	Y-S_2	3393	259	1876	La-S_3	5513	34	2715
La-S_1	1527	135	481	La-S_2	3330	435	1290	Y-S_3	4137	36	2443
Nd-S_1	1291	282	668	Nd-S_2	2550	299	1240	Nd-S_3	2924	29	1829
Sm-S_1	556	68	189	Sc-S_2	2079	493	847	Sc-S_3	927	50	311
Gd-S_1	417	77	226	Gd-S_2	706	58	364	Gd-S_3	760	5	487
Pr-S_1	326	58	133	Dy-S_2	583	47	307	Pr-S_3	689	5	441
Dy-S_1	271	61	163	Sm-S_2	578	64	325	Sm-S_3	658	3	407
Sc-S_1	243	33	76	Pr-S_2	575	82	285	Dy-S_3	614	3	375
Eu-S_1	84	13	43	Yb-S_2	331	37	155	Yb-S_3	220	3	130
Yb-S_1	76	16	47	Eu-S_2	136	11	70	Eu-S_3	139	3	82
Ho-S_1	61	15	30	Ho-S_2	102	15	57	Ho-S_3	122	15	68
Tm-S_1	24	2	7	Tm-S_2	49	3	23	Tm-S_3	35	3	21
Lu-S_1	14	3	7	Lu-S_2	41	3	22	Lu-S_3	32	3	17

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3.1. Distribution of REE available concentrations assessed by PCA analysis

The analysis of the distribution of the REE available concentrations in S1, S2 and S3 as well total concentration, R and TA% of Ce, La, Sc and Y was assessed by PCA analysis. The first four factors explain an overall 86% of data variability (Factor 1: 35%; Factor 2: 23%; Factor 3: 17% and; Factor 4: 11%) and discriminate seven main groups of variables (Fig. 4a, b). The plot of Factor 1 against Factor 2 separates the REE-S1, as well as Ca total concentration, and S2 and S3 (Fig. 4a). The plot of Factor 3 against Factor 4 (Fig. 4b) indicates that the distribution of the REE in S1 and S2 (Group V) is more similar than in S3 (Group VI) and that the distribution pattern of the percentage of TA of Ce, La, Sc and Y (Ce-TA%, La-A%, Sc-TA% and Y-TA%; Group VI) is dissimilar from the total concentration and the R of Ce, La, Sc and Y, which are part of Group VII.

According to the PCA results (Fig. 4a), all the REE associated with each analyzed sedimentary phase (S1, S2 and S3) show similar patterns of distribution. In the case of the study area, the light REE (LREE: Ce, Eu, Gd, La, Nd, Pr, Sc and Sm, also known as the cerium group) cannot be distinguished from the heavy REE (HREE: Dy, Ho, Lu, Tm, Y and Yb; known as the yttrium group). The total available concentration of REE associated with S1, S2 and S3 (REE-S1, REE-S2 and REE-S3), as well as their total (REE-TA= S1+S2+S3) were mapped (Fig. 5a-d). These maps show that: REE-S1 reaches the highest values in the external sector of the lagoon (Fig. 5a); REE-S2 values rise mainly in the central and external zones of the lagoon (Fig. 5b); REE-S3 increases more at the northern extremity of Ovar Channel, along the Espinheiro Channel and near the lagoon mouth (Fig. 5c). The highest values REE-TA include all the aforementioned zones, particularly the outer sector of the lagoon, the northern extremity of Ovar Channel and the inner zone of Murtosa Channel (Fig. 5d).

3.2. Relationships of REE with other variables assessed by R-mode cluster analysis

R-mode cluster analysis (CA) compares the similarity of the REE distribution with some selected physicochemical, textural, geochemical and mineralogical variables (Fig. 6). This R-mode CA results in two main clusters related to sedimentary grain size parameters: variables of cluster 1 are related to relatively coarser grained sediments, whereas those of cluster 2 are related to finer ones. In each of these main clusters two sub-clusters can be recognized, composed of the following variables: sub-cluster 1.1 includes REE-S1, Ca total concentration, SMGS, Kubler Index and Eh; sub-cluster 1.2 includes REE-S3, Y-TA%, La-TA%, Ce-TA%, K-feldspars and quartz; sub-cluster 2.1 includes REE-S2, Sc-TA%, phyllosilicates, sorting and TOC; sub-cluster 2.2 includes Ce, La, Sc and Y total concentration, and Ce-R, La-R, Sc-R, Y-R, kaolinite and pyrite. Illite and plagioclase are part of cluster 1, but despite being associated with relatively coarse sediments, their distribution differs slightly from the remaining variables of this group.

3.3. Distribution of REE assessed by Q-mode CA and complementary geochemical results

The results of Q-mode CA based on R, TA% of Ce, La, Sc and Y and the REE in S1, S2 and S3 differentiate two main clusters of stations and two sub-clusters (Fig. 7a). The stations of sub-cluster 1.1 are characterized by the highest concentrations of REE-S2; those of sub-cluster 1.2, by the highest concentrations of REE-S3; and those of cluster 2 by the highest concentrations of REE-S1 and the lowest ones of REE-S2 content (Table 2). Sub-cluster 1.1 includes stations of Ovar Channel (A1, A7), Murtosa Channel (A18-21, A24, A27), Aveiro canals (A46, A48) and Mira Channel (A53). These stations are also characterized by the highest values of TOC, plagioclase, calcite, illite, Ca total concentration, Y-R, SC-TA%, and the lowest of quartz, REE-S1, CE-TA, LA-TA, Y-TA, REE-S3 and REE-TA (Table 2). Most of the stations of sub-cluster 1.2 are located in the northern zone of Ovar Channel and are characterized by higher values of pH, phyllosilicates and pyrite, as well as of total concentration and R concentrations of Ce, La, Sc and Y, and also of REE-TA and REE-S3, and lower values of Eh, SMGS, K-feldspars, plagioclase, calcite, Ca total concentration and REE-TA. The stations of cluster 2 that are located in the main lagoonal body have the highest values of Eh, SMGS, sorting, quartz, Kubler Index, Ce-TA%, La-TA%, Y-TA% and lower values of TOC, phyllosilicates, pyrite and concentrations of Ce-R, La-R, Y-R and also of REE-S2.

The distribution of the Ce-S1/Sc-R ratio shows increases near the lagoon mouth, the Antuã River mouth and around the central islands of the lagoon near Espinheiro Channel (Fig. 8a). The distribution of La-S1/Sc-R and Y-S1/Sc-R values also follow the same pattern of distribution. The distribution of Ce-R/Sc-R reveals that the highest values occur near the Antuã River mouth (Fig. 8b).

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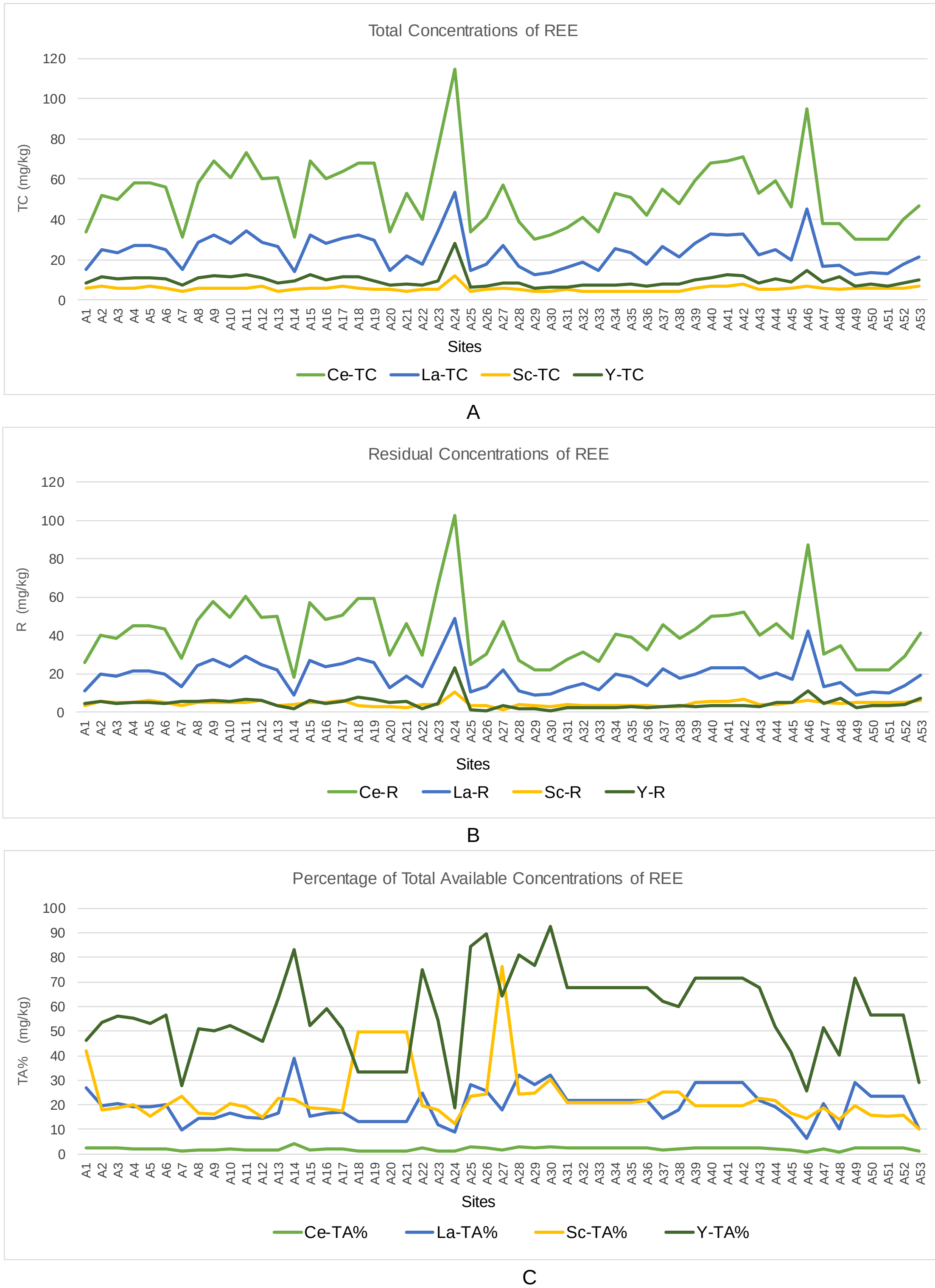

Fig. 3. (A) Total concentrations (mg kg-1); (B) Residual concentrations (mg kg-1) and; (C) percentage of total available concentrations of La, Sc, Y and Ce in the studied sites.

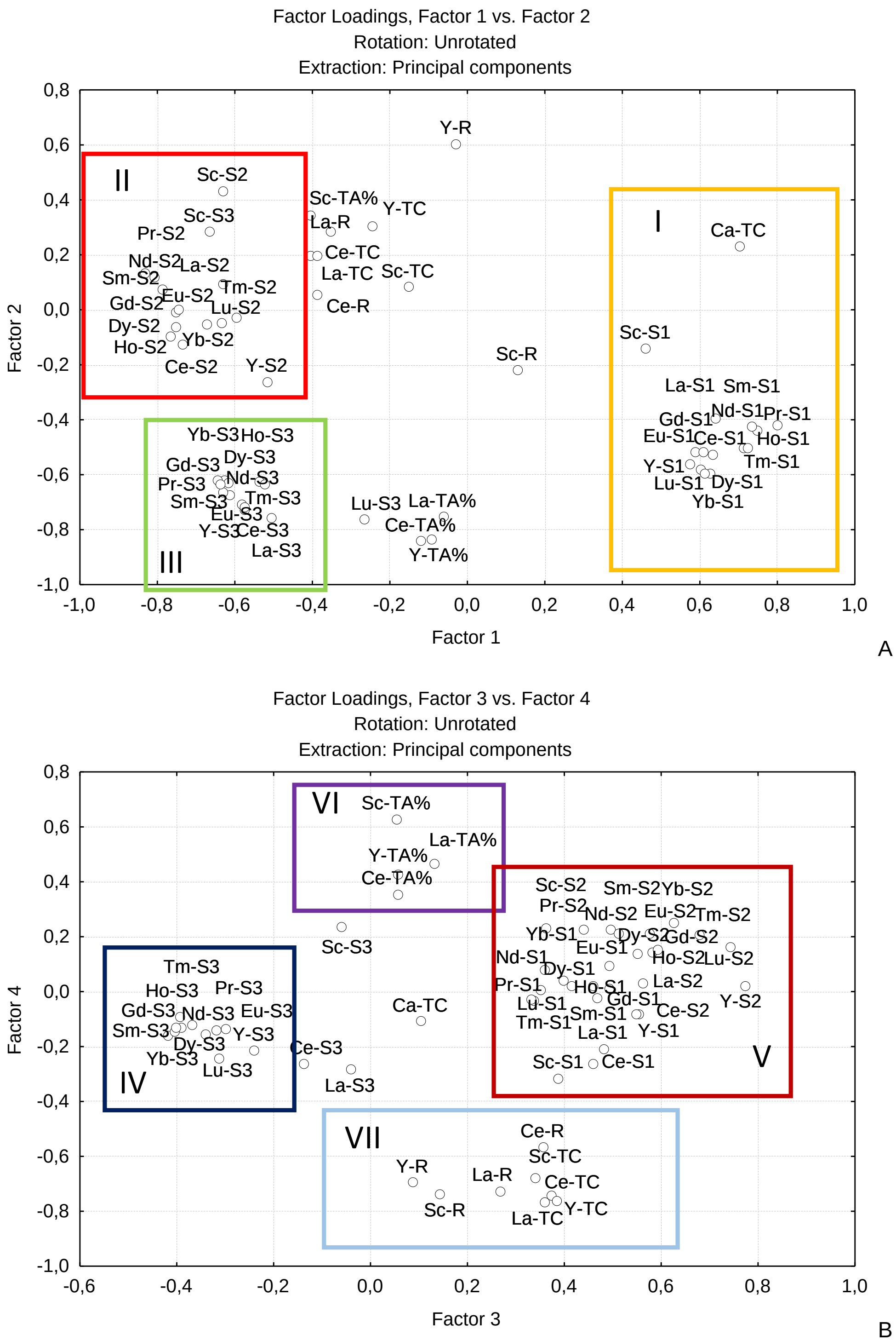

Fig. 4. PCA analysis based on the REE available concentrations in S1, S2 and S3 as well total concentrations (TC), residual concentrations (R) and percentage of total available concentrations (TA%) of Ce, La, Sc and Y. The plot of the first factorial plan (Factor 1 x Factor 2) is presented in (A) and the Factor 3 against the Factor 4 is presented in (B).

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Tab. 2. Maximum (Max), minimum (Min) and average (Aver) values of the analyzed variables according to the results of the Q-mode CA of Figure 7. Legend: SMGS – sediment mean grain size; Sort – sorting; Qtz – quartz; K-Flds – K feldspars; Plag – plagioclase; Calc – calcite; Phyl – phyllosilicates; Pyr – pyrite; III – Ilite; Kaol – kaolinite. Residual (R) and percentage of availability (TA%) of Ce, La, Sc and Y as well as the REE in S1, S2, S3 and TA also are presented.

Clusters/Sub-clusters		**1.1**			**1.2**			**2**		
Variables		**Max**	**Min**	**Aver**	**Max**	**Min**	**Aver**	**Max**	**Min**	**Aver**
EH	mV	-12.0	-55.3	**-29.2**	-18.0	-72.0	**-34.2**	134.0	-41.5	**-0.9**
pH		7.7	6.8	**7.1**	8.9	7.0	**7.4**	7.4	4.2	**6.6**
SMGS	μm	368	18.4	**66.2**	255.3	18.8	**56.4**	356.6	18.6	**110.7**
Sort		4.9	1.5	**3.7**	4.7	2.1	**3.8**	5.7	1.5	**3.9**
Qtz	%	44	21	**30.2**	44.0	15.0	**31.0**	42.3	19.3	**31.5**
K-Flds	%	7.3	1.2	**3.65**	7.65	1.24	**3.58**	7.3	1.9	**4.1**
Plag	%	34.3	0.0	**7.9**	8.2	2.5	**5.2**	25.8	2.8	**6.2**
Calc	%	6.9	1.1	**2.7**	5.4	0.0	**0.9**	3.6	0.0	**1.5**
Phyl	%	54.4	21.7	**42.7**	68.0	29.9	**47.3**	53.6	30.2	**42.1**
Pyr	%	4.6	0.7	**2.0**	3.9	1.3	**2.2**	3.3	0.6	**1.4**
Ill	%	82.8	50.9	**72.3**	84.0	51.4	**72.0**	82.0	58.9	**71.6**
Kaol	%	49.1	10.9	**24.8**	41.0	10.9	**24.6**	41.1	10.6	**26.4**
Kubler Index		0.5	0.2	**0.37**	0.50	0.30	**0.38**	0.70	0.20	**0.41**
TOC	%	7.4	0.1	**2.7**	3.5	0.2	**2.2**	4.0	0.3	**1.6**
Ca-TC	%	2.4	0.3	**0.76**	0.63	0.27	**0.36**	1.56	0.20	**0.68**
Ce-TC	mg kg^{-1}	115	31	**57**	95	50	**64**	71	30	**45**
La-TC	mg kg^{-1}	54	15	**26**	45	24	**30**	33	12	**20**
Sc-TC	mg kg^{-1}	12	4	**6**	7	5	**6**	8	4	**5**
Y-TC	mg kg^{-1}	28	7	**11**	15	10	**11**	13	6	**8**
Ce-R	mg kg^{-1}	672	307	**456**	717	443	**581**	691	292	**434**
La-R	mg kg^{-1}	29	11	**19**	30	19	**24**	23	9	**15**
Sc-R	mg kg^{-1}	10.5	0.9	**4.0**	6.0	3.0	**5.0**	6.4	2.8	**4**
Y-R	mg kg^{-1}	23	0.5	**7**	11	4	**6**	7	0.5	**3**
Ce-TA%	%	3.1	0.8	**1.4**	2.3	0.8	**1.8**	3.1	1.2	**2.4**
La-TA%	%	32.3	6.5	**14.6**	20.3	6.5	**15.9**	32.3	10.2	**23.6**
Sc-TA%	%	76.3	10.3	**34.6**	49.5	14.6	**19.8**	30.4	10.3	**20.7**
Y-TA%	%	92.3	18.9	**38.8**	59.2	25.5	**49.8**	92.6	29.0	**67.4**
REE-S_1	mg kg^{-1}	9.5	2.0	**3.76**	5.96	2.90	**3.84**	10.9	3.2	**5.87**
REE-S_2	mg kg^{-1}	27.6	3.8	**15.3**	21.7	8.3	**13.0**	19.5	7.2	**11.4**
REE-S_3	mg kg^{-1}	19.4	0.2	**8.1**	20.7	8.0	**17.9**	21.0	4.6	**15.1**
REE-TA	mg kg^{-1}	39.2	12.4	**27.2**	39.4	23.7	**34.7**	51.5	18.0	**32.4**

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4. Discussion

Total concentrations of Ce, La, Sc and Y reach higher values in the Ria de Aveiro than in several kinds of continental materials, such as in the Bulk Continental Crust and Upper Continental Crust (Rudnick and Gao, 2003), World Shale Average (Piper, 1974), the European Shale (Haskin and Haskin, 1966), and Portuguese granites (Neiva et al., 1990; Gomes and Neiva, 2002; Martins et al., 2009) (Table 3). However, the highest and mean REE values in the study area are slightly lower than in the NW Iberia Continental Shelf sediments (Araujo et al., 2007), namely in the Holocene Galician Muddy Deposits (Table 3). The highest total concentration of REE in the Douro Muddy Deposit are slightly lower than those found in surface sediments of Ria de Aveiro, but the average values in the Holocene strata of this continental shelf sedimentary body are higher (Table 3).

The NW Iberian margin is a high-energy environment (McCave and Omex partners, 2000) which is reflected in the sedimentary cover, composed mostly of sand and gravel sediments, interrupted at water depths of around 100–120 m by siliciclastic muddy deposits facing the Douro estuary and the Galician rias (Dias et al., 2001; 2002 b, c). In both these muddy areas, the highest sedimentation rates (varying between 0.05 and 0.40 cm yr^{-1}) were recorded around the 100m bathymetric contour, facing the Douro estuary, and also near the Galician rias to the north of the NW Iberian continental shelf (Jouanneau et al., 2002). These muddy deposits were formed over the last 2500 years (Drago, 1995) and were nourished by sediments provided by the river discharges onto the northern Portuguese Continental Shelf, particularly those from the Douro River (Araujo et al., 2002; Dias et al., 2002 b, c). The Galician muddy deposit is composed of finer-grained sediments than the Douro deposit (Dias et al., 2002 c), which also may explain its higher concentrations of REE.

4.1. Total and residual concentrations of REE against their availability

The statistical results of this work show that the total concentration and R concentrations of Ce, La, Sc and Y follow similar patterns of distribution (Fig. 4b) and are also essentially related to fine-grained sediments and to kaolinite and pyrite content. Kaolinite is a common soil 1:1 type clay mineral in tropical or subtropical areas, formed by the decomposition of feldspar-bearing rocks (Chamley, 1989). It is known that clay minerals may play an important role in REE adsorption and fractionation processes (Awwiller and Mack, 1991; Zhao et al., 1992), however kaolinite has no interlayer surfaces, thus has much less surface area and constant negative charges, and less capacity for adsorbing ions than smectite, for example (Zhao et al., 2011), which is a rare mineral in the Aveiro Lagoon (Martins et al., 2015a). Moreover, pyrite content in sediments is essentially a result of the breakdown of organic matter by decaying and sulfate-reducing bacteria in an anaerobic environment or microenvironment (Schallreuter, 1984; Wilkin et al., 1996). Since its preservation also requires anoxic conditions, both kaolinite and pyrite, which tend to co-occur in the study area, are preferentially found in confined areas.

Murtosa Channel, which is where the highest concentrations of REE are recorded, is directly connected with the Antuã River that flows in its inner zone (Fig. 1). According to Lopes et al. (2006), this river gives a negligible contribution in terms of water and sediment input to the lagoon, except near its mouth, and to Murtosa Channel. The right arm of the northern end of Ovar Channel receives the input of water and sediments of several small rivers, such as Caster, Fontela and Gonde Rivers, but the fresh water run-off and sediment contribution to the left arm of this channel is much less. The rivers' influence in suspended sediment concentrations is commonly more important near their mouths, but tides may have a great importance in the distribution of fine-grained sediments throughout the lagoon (Lopes et al., 2001, 2006; Dias et al., 2003; Lopes and Dias, 2007). The suspended sediment concentrations in the lagoon are, in general, much higher during the spring tide and during the ebb period, due to the higher intensity of the currents. This effect can be observed both in Murtosa Channel and in the southern zone of Ovar Channel (Lopes et al., 2006). The northern parts of the Ovar Channel seem to have a small exchange of sediments with the rest of the lagoon, due to their shallowness and weak currents (Lopes et al., 2006).

The Vouga is another river that can deliver relatively high suspended sediment concentrations (Lopes et al., 2006), and represents the most important drainage into the Ria de Aveiro (Moreira et al., 1993). Its influence is, however, mainly restricted to the Espinheiro, an estuarine tidal channel of this lagoon (Vaz and Dias, 2008). The total concentration and R concentrations of REE are intermediate near the Vouga River mouth, along the Espinheiro Channel and in the small channels located in the central lagoonal area connected with it. However the Vouga River, as well as the Caster, Fontela, Gonde and Antuã Rivers that drain into the northeast and central regions of the lagoon cut areas with similar lithology, mainly composed of Precambrian homogenous series of

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alternating greywacke and shale - greywacke complex, and patches of granitic rocks, mostly of Variscan origin (Teixeira, 1981). The Vouga River basin crosses vast areas of unconsolidated Cenozoic alluvial deposits (conglomerates and sands, with large quartz predominance), which probably dilute the contribution of minerals enriched in REE released by the source rocks.

The relatively lower total concentration and R concentrations of REE in the zone under the direct influence of the Vouga River is likely due to its outflow being rather deflected northward and southward into the complicated and ramified structure of channels, islands. Several intertidal zones also may reduce the signal and dilute the fingerprint of this river in the lagoon.

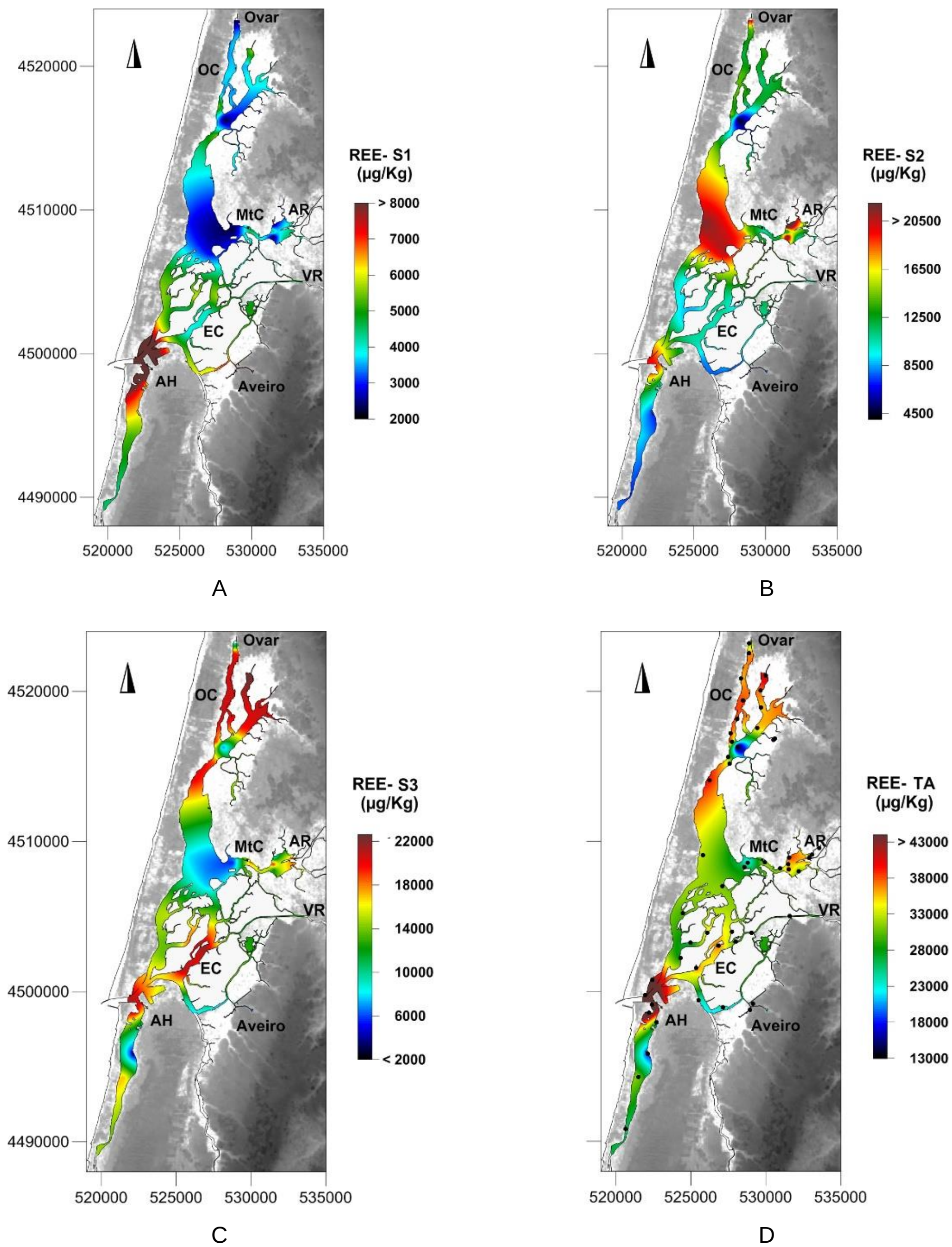

Fig. 5. The general view of available concentrations of REE distribution in: (A) S1; (B) S2 and; (C) S3 extracted phases; as well as (D) global sum of it (TA).

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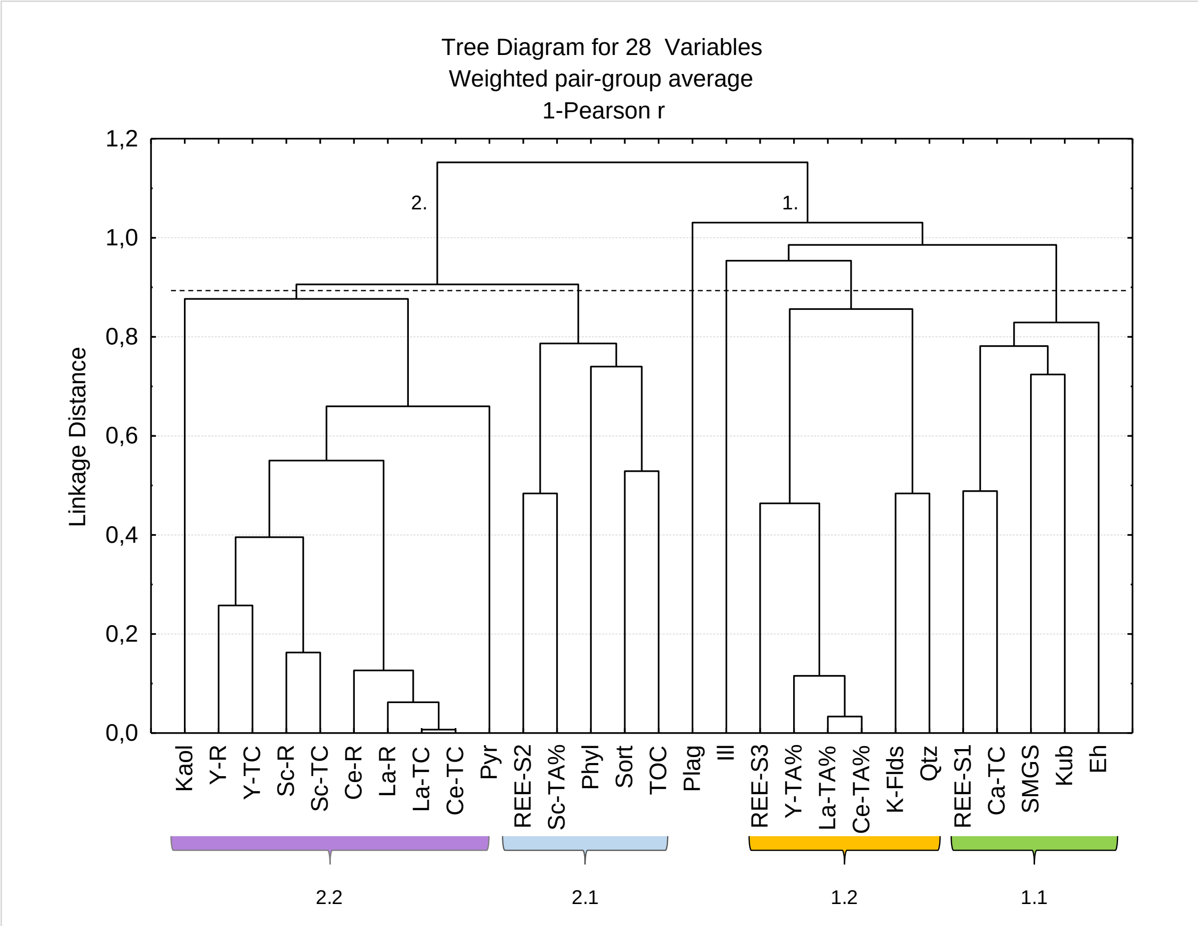

Fig. 6. Results of R-mode CA based on the total concentrations (TC) of Ca, Ce, La, Sc and Y as well as residual (R) and percentage of total available concentrations (TA%) of Ce, La, Sc and Y. The REE in S1, S2 and S3 also were considered as well as the following variables: Eh – potential redox; Kub – Kubler index; SMGS – sediment mean grain size (µm); Plag – plagioclase (%); Qtz – Quartz (%); K-Flds – K-feldspars; III – ilite; TOC (%); Sort – sorting; Phyl – phyllosilicates (%); Pyr – pyrite (%) and; Kaol – kaolinite (%).

The strong currents of the Espinheiro Channel, with tidal velocities reaching values higher than 2 ms^{-1} (Vaz and Dias, 2008), may also contribute to the dispersion of the sediments in the central area of the lagoon, and to sediment transport through the Espinheiro and the S. Jacinto channels to the ocean. Some of those sediments also are likely to be deposited in the protected areas of the outer sector of the lagoon, such as harbors.

Total and R concentrations of Ce, La, Sc and Y increase in three main zones: at the northern part of Ovar Channel, along the Murtosa Channel, and even more so near the Antuã River mouth and close to the lagoon inlet and harbor protected areas close to the lagoon entrance. Intermediate total concentration and R values occur along the Espinheiro Channel, located near the zone of highest influence of the Vouga River.

These conditions suggest that total and R concentrations are not only related to the sources of the sediments supplied to the lagoon, but also to current speed, as seen in the nearby continental shelf environments.

On the other hand, statistical results show that total and R concentrations of Ce, La, Sc and Y follow opposite patterns than those the TA% of those elements, through the Ria de Aveiro (Figs. 4, 6).

These findings suggest that the labile fraction portion of REE also depends on other factors, which are not likely restricted to the supply processes or redistribution of sediments due to tidal current action.

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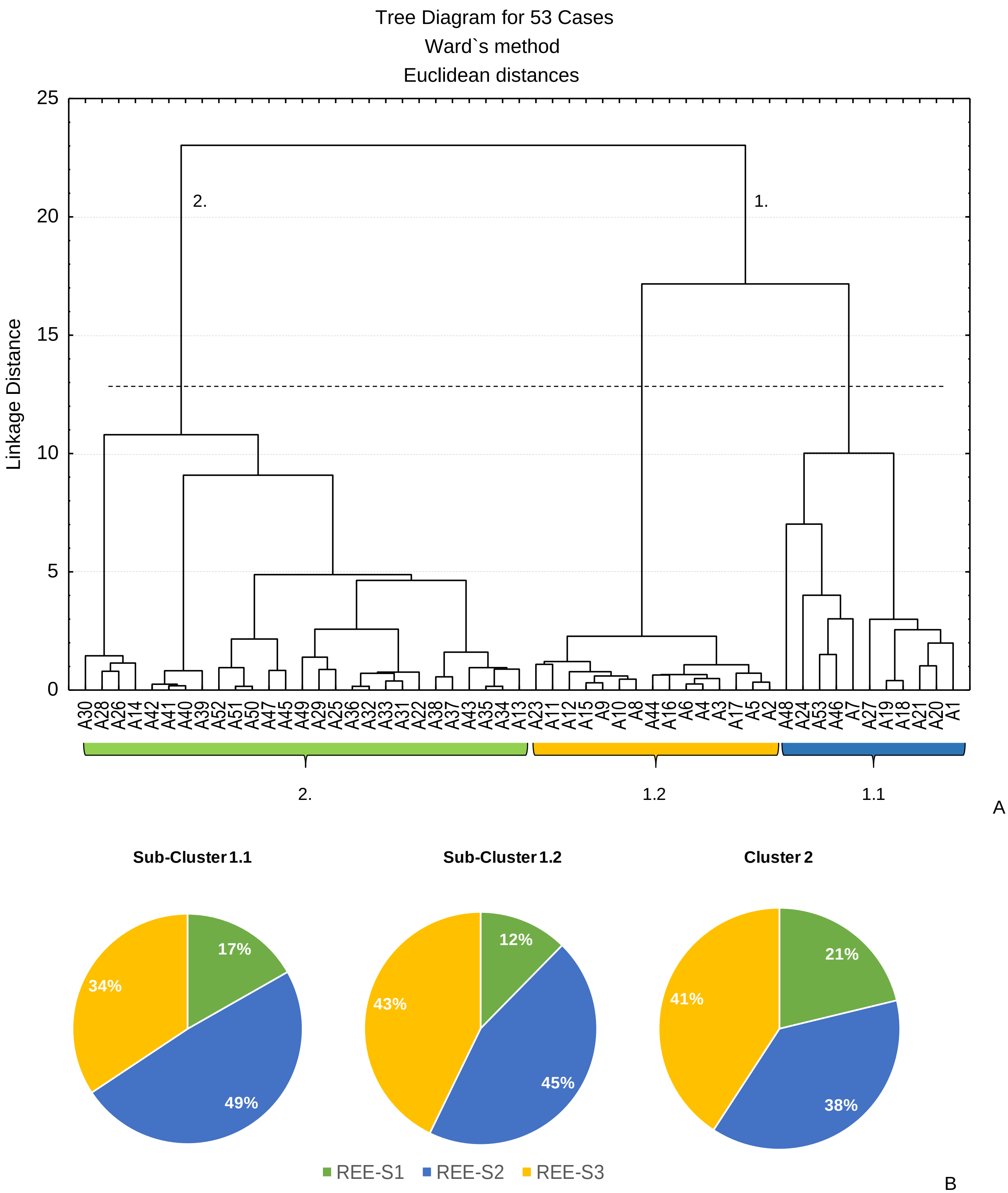

Fig. 7. (A) Results of Q-mode CA based on residual (R) and percentage of availability (TA%) of Ce, La, Sc and Y as well as the REE in S1, S2 and S3. (B) The proportion of REE in S1, S2 and S3, in each cluster/sub-cluster.

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4.2. Availability of REE distribution in Ria de Aveiro

The highest REE-TA are located in four main areas: the extremities of Ovar and Murtosa channels, the Espinheiro Channel and the outer sector of the lagoon, however not necessarily in the same sites in which high total and R concentrations of Ce, La, Sc and Y were found. The analyses of REE-S1, REE-S2 and REE-S3 content, which contribute to the overall REE-TA, confirms that these sedimentary phases have dissimilar patterns of distribution (Fig. 5) and co-vary with different sedimentological variables. The highest concentrations of REE-S2 (adsorbed by organic matter) are reached in association with fine grained and extremely poorly sorted sediments (reflecting the asymmetry of the tidal currents), characterized by high phyllosilicates and TOC content, as evidenced by the results of R-mode CA (Fig. 6). The higher available concentration in S2 are associated with relatively low pH values in different areas: in the interconnection of the S. Jacinto/Ovar and Murtosa channels, in the inner extremity of Murtosa and Ovar channels, and also in confined zones near the lagoon entrance (Fig. 5b). Except in the inner sector of Murtosa Channel, linked directly with the Antuã River, the other areas are not under the direct influence of the rivers.

This indicates that siliciclastic sediments, once introduced into the lagoon, are subjected to changes which contribute to REE partition. Typically, the mobility of REE is greater in acidic than in neutral or alkaline waters (Verplanck et al., 2004), and the mobility is enhanced with lower pH (Ferreira da Silva et al., 2009). Thus, processes related to organic matter accumulation and degradation seem to play a very important role in the availability and retention of REE in confined areas of the lagoon.

Tab. 3. Concentrations of Ce, La, Sc and Y in several kind of lithological materials.

Lithological Materials	**References (sources of data)**	**Ce** $\mu g\ g^{-1}$	**La** $\mu g\ g^{-1}$	**Sc** $\mu g\ g^{-1}$	**Y** $\mu g\ g^{-1}$
Composition of the upper Continental Crust	Rudnick and Gao (2003)	63	31	14	21
Composition of the bulk continental crust.	Rudnick and Gao (2003)	43	20	21	19
World Shale Average	Piper (1974)	83	41	*	*
European Shale	Haskin and Haskin (1966)	81.3	41.1	*	*
Portuguese granites	Neiva (2002)	13-53	5-20		6-17
Portuguese granites	Gomes and Neiva (2002)	26-55	11-26	6-8	42-46
Portuguese granites	Martins et al. (2009) Neiva et al. (1990)	48-73	24-39	4-7	27-48
N Iberia Continental Shelf	Araujo et al. (2007)	67-145	32-70	*	*
N Iberia Continental Shelf (Galicia Muddy Deposit)	Not published data from core KSGX40 from these authors	62-141 (87)	28-67.6 (42)	4-12.4 (6.9)	10-16 (12)
N Iberia Continental Shelf (Douro Muddy Deposit)	Not published data from core W90 from these authors	55-99 (67)	25-52 (32)	7-14 (9)	10-16 (11)
Ria de Aveiro	This work	30-115 (52.2)	12.4-53.5 (23.8)	4-12 (5.5)	5.9-28.2 (9.6)

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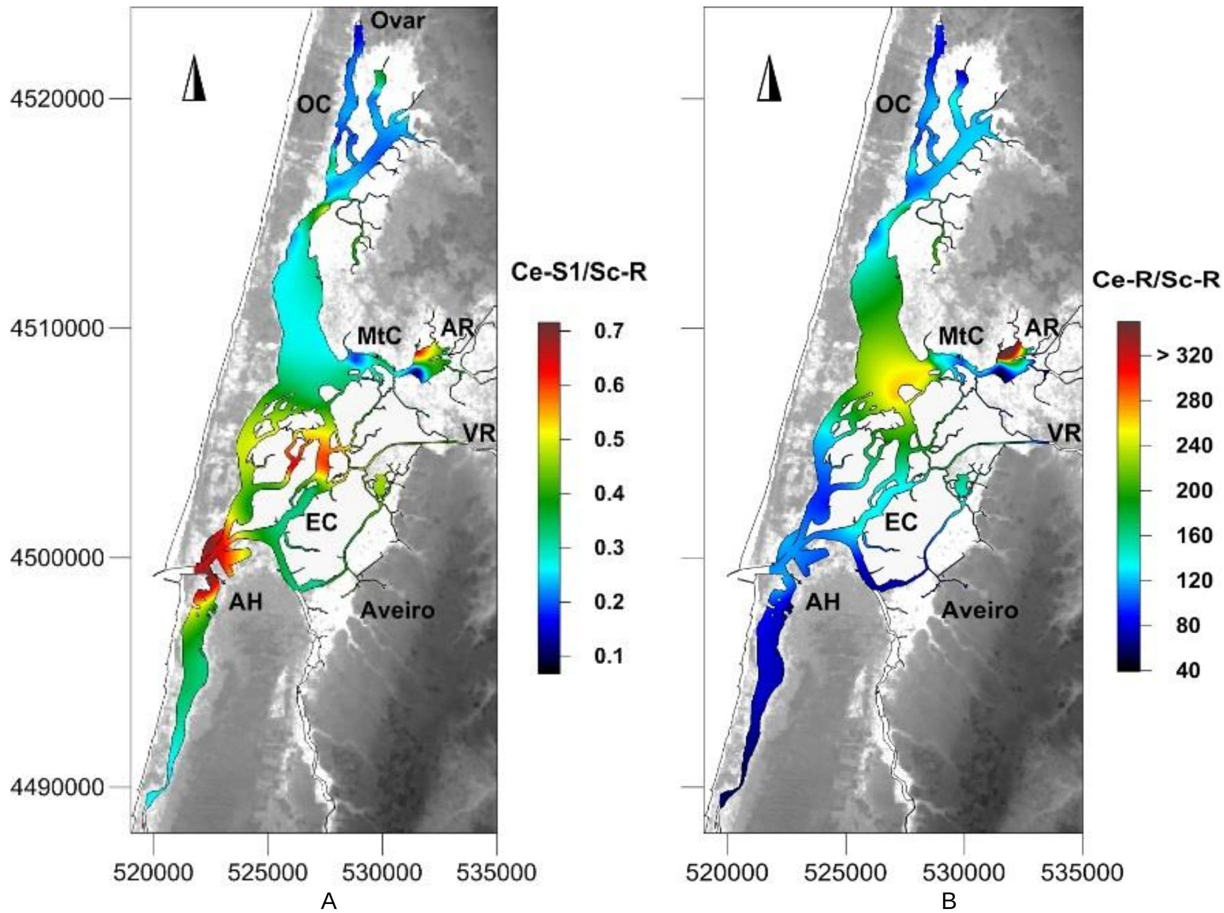

Fig. 8. Maps of distribution of the ratios: (A) Ce-S1/Sc-R and; (B) Ce-R/Sc-R.

The capture of REE by amorphous Mn hydroxides (S3) seems to be almost as effective, or even more so (lower maximum values, but the average value is greater) than by organic matter. The highest concentrations of REE-S3 are in general opposite to those of REE-S2 (Fig. 5 b, c). Three main areas have the highest concentrations of REE-S3: the Ovar Channel, the Espinheiro Channel and the outer sector of the lagoon. REE-S3 are also associated with increasing Ce-TA%, La-TA% and Y-TA% in sites characterized by relatively coarser sediments composed of higher amounts of quartz and feldspars.

These results are indicative that active biogeochemical processes acting on surface sediments may induce significant changes in their composition, associated with the production of amorphous Mn hydroxides in the lagoon. These processes were also analysed by Martins et al. (2015a), who verified that biogeochemical processes also affect the availability of potentially toxic metals in this polluted lagoon. Thus, distribution patterns of both REE-S2 and REE-S3 concentrations (stations of cluster 1.1 and 1.2, respectively; Fig. 7) and their relationship with other sedimentary variables suggests that they are at least in part related to biogeochemical processes affecting surface sediments in the lagoon, and are not related only to the source areas of the sediments supplied to the lagoon.

REE content in S1 phase (adsorbed by clay and co-precipitated with carbonates) displays the lowest concentrations in Aveiro Lagoon. REE, or the lanthanides, comprise a group of elements with similar geochemical properties, with trivalent state and ionic radii ranging from 0.87 Å (Sc^{3+}) to 1.16 Å (La^{3+}), similar to that of Ca^{2+}, which allow them to be easily absorbed onto clays during hydrothermal or weathering processes (Bau, 1999; Nasraoui et al., 2000). The highest REE-S1 concentrations are restricted to the lagoon mouth area (Fig. 5a). These values show decreasing gradients towards the end of the main channels. The largest decreases are mainly observed in Ovar, Murtosa and Espinheiro channels, and close to river

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mouths. REE-S1 distribution is related to coarser-grained sediments, with highest values of Ca total concentration, Kubler Index and Eh values (Fig. 6). Coarser-grained sediments, higher Ca total concentration, and Eh values are characteristic features of the outer sector of the Ria de Aveiro (Martins et al., 2014), related to the direct or indirect influence of current activity. The strong currents of this sector do not favour the accumulation of high amounts of organic matter, which contributes to much better oxygenation (indicated by relatively high values of Eh) than muddy substrates, and favours carbonate preservation. The highest values of Kubler Index are indicative of the occurrence of illite with relatively low crystallinity, which means more degradation of its crystallochemical arrangement (Roberts et al., 1990). Since the highest values of Kubler Index are restricted to the lagoon entrance zone, they may be indicative of a major transportation from source areas far away, which are likely the far mouth of the river that flows into the lagoon, or oceanic materials introduced through the inlet.

In addition, Ce-S1/Sc-R (Fig. 8a), La-S1/Sc-R and Y-S1/Sc-R values increase significantly not only near the lagoon entrance but also near the Antuã and Vouga River mouths, whereas those of Ce-R/Sc-R (Fig. 8b), La-R/Sc-R and Y-R/Sc-R display the highest values mostly in zones close to Antuã River mouth and along the Murtosa Channel, the zone under the highest influence of this river. These results seem to indicate that those values are clearly related to sediments provided from different sources to the Ria de Aveiro.

4.3. Sediment sources to Aveiro Lagoon

The sources of the sediments that are supplied to the Ria de Aveiro are diverse. The amount of solid flow drained by the river system to the lagoon is on average approximately 250,000 m^3 per year, of which 50,000 m^3 is sand and 200,000 m^3 is fine sediments (silt and clay) (Teixeira, 1994, 1995). The Vouga and Antuã rivers provide the largest contribution of sediments to the lagoon (Teixeira, 1994, 1995). This contribution is revealed by suspended cohesive sediments in the lagoon water column, which reach the highest concentrations when the rivers display their maximum discharge capacity during winter, the rainiest season in the region, during spring tides, and during ebb tidal phases (Lopes et al., 2001, 2006; Lopes and Dias, 2007). However, geochemical fingerprints of these two rivers are different, as indicated by the distribution of Ce-S1/Sc-R and Ce-R/Sc-R ratios (Fig. 8 a, b). This difference may be related to current speed, or to the fact that the Antuã River is able to supply minerals and materials more enriched in REE than the Vouga River.

Other sedimentary sources of siliciclastic materials include erosion of intra-lagoonal terrains; resuspension of sediments from channel bottoms and intertidal plains, by tidal currents or by dredging navigable canals in order to ensure the depth necessary to keep Aveiro Port operational; and runoff from banks and adjacent farmlands. The transfer of sediments from the shoreline to the lagoon across the sand bar, or wind transport and coastal flooding events, due to storms and the destruction of natural coastal defenses (dunes) are certainly less important contributions compared with lagoonal river contributions (Teixeira, 1994).

However, other rivers, such as the Minho and Douro, to the North, and the Mondego, located to the South of the study area, may also influence sedimentation in the lagoon, especially the slow current zones of the lagoon entrance. The influence of the Douro River through littoral drift is likely higher in the region than that of the Minho River, which is much more distant, or that of the Mondego River, which acts as a sediment trap and discharges a relatively small amount of sediments into the estuary (Dias et al., 2002 a). The Douro River is first in catchment area in the Iberian Peninsula (97,682 km^2), with a mean output of 22.4x10^6 m^3 $year^{-1}$ (Loureiro et al., 1986). This river can supply the ocean system with about 1.8 million m^3/year of sediments in its natural regime, according to a report of Instituto da Água (2001) making it a substantial source of sediment for the continental shelf (Dias et al., 2002 b). Yet the Douro River seems to be the main continental source of fine sediments being deposited on the northern Portuguese shelf (Araujo et al., 2002). Hydrodynamic forces act on the sediments introduced in the littoral system, carrying sands southwards via the littoral drift (Dias et al., 2002 c), which may then reach the Aveiro region (Abrantes and Rocha, 2007; Martins et al., 2012).

The spatial and temporal variability of the Douro estuarine plume was studied by Mendes et al. (2014) by using long-term ocean color satellite data (2003–2011), and concurrent *in situ* wind, tidal and river discharge data. According to this study, the Douro estuarine plume propagation is forced and influenced by the magnitude of the river discharge, tide and wind intensity and direction. Wind patterns determines the swell and the direction of surface currents on the continental shelf and also influence the plume pathway. N-NW winds, prevailing during the spring-summer period, are the major forcing for a general N-S coastal circulation (Fiúza, 1983), favoring sediment transportation from northern continental shelf areas, through the southward littoral drift (Dias et al., 2002 b, c). Winds blowing from the North, and north- westerly in upwelling favorable conditions, originate a continuous coastal turbid band, with approximately 25 km wide, along the shore, in a southward direction. Eventually, some fine-grained sediments reach the Aveiro region and are introduced in the Ria de Aveiro during tidal flood phases (Martins et al., 2011 a).

The higher values of the REE-S1 in the lagoon entrance area seem to be a good tracer of the Douro River influence in the Ria de Aveiro. Measurements of suspended sediment concentrations in the external sector of this lagoon showed that fine-grained sediments are supplied from the adjacent continental shelf and are introduced into the lagoon (Martins et al., 2011a). These imported sediments are deposited in protected areas near the lagoon entrance, where current activity declines (Martins et al., 2011 b). Cluster 2 of the CA (Fig. 7a) incorporates stations where this influence is at the highest. However, not all stations that are part of this group seem to be related to sediments imported from the ocean system and deposited in the lagoon. The highest values of Ce-S1/Sc-R ratio (Fig. 8a), around the islands of the central zone of the lagoon, also suggest that sediments provided from the erosion of these deposits are also leaving a geochemical fingerprint. Since this evidence is similar to that found in the lagoon entrance area, it may be hypothesized that sediments supplied from the Douro and Antuã River may have contributed to the construction of these islands in the past.

According to the results of this work, total concentration, R and REE-S2 concentrations are mostly related to river inflow and circulation in the lagoon, with stations A1-A17 located in a low circulation zone, stations A19-A30 located in an inner zone influenced by the Antuã River inflow, stations A33-A47 located in a central portion, and stations A39-A42 and A45-53 related to an open area of the outer sector of the lagoon. REE-S3 concentrations are related to biogeochemical processes inside the lagoon. The most interesting labile phase as a sediment tracer seems to be REE-S1, which could discriminate an external source of sediments to the lagoon, from a continental shelf source through littoral drift.

5. Conclusions

Our results demonstrated that REE sediment content of Ria de Aveiro, as well as that of continental shelf settings, are controlled by grain size, and consequently by current conditions. Thus, the distribution of available concentrations of REE provides a supplementary contribution to discriminate sources of sediments that are supplied to the Ria de Aveiro. Whereas total and R concentrations of REE are mainly related to deposition of fine-grained sediments, the extracted phases S2 and S3 are most likely related to sedimentary processes inside the lagoon itself. The pattern of distribution of REE-S1 concentrations are indicative of a contribution of sediments from northern rivers of Portugal by littoral drift. These sediments enter the lagoon during tidal flooding phases, and are deposited in protected areas near the lagoon entrance. Increases of Ce-S1/Sc-R around the central lagoonal islands suggest that the construction of these islands was not only due to local river contributions, but probably also received supplies from the northern rivers of Portugal, including the Douro River. The distributional pattern of Ce-R/Sc-R allows us to consider the Antuã River as the main local contributor of materials provided from erosion of ancient hard rocks, rather than the other rivers flowing into the Ria de Aveiro at present. Results of this work emphasize the importance of the use of REE available concentrations analyses, in order to be able to discriminate different sources of sediments in modern sedimentary processes.

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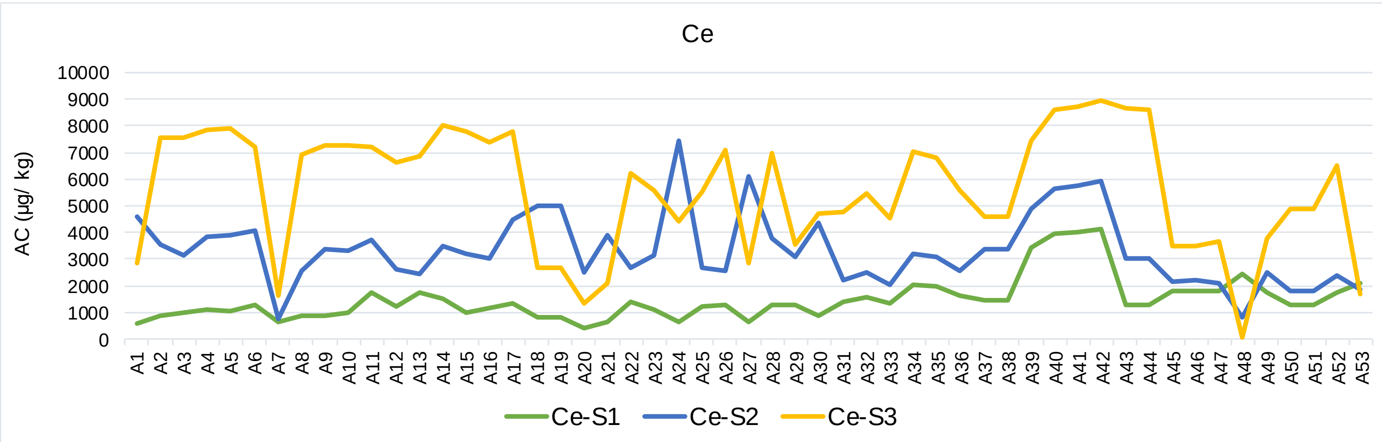
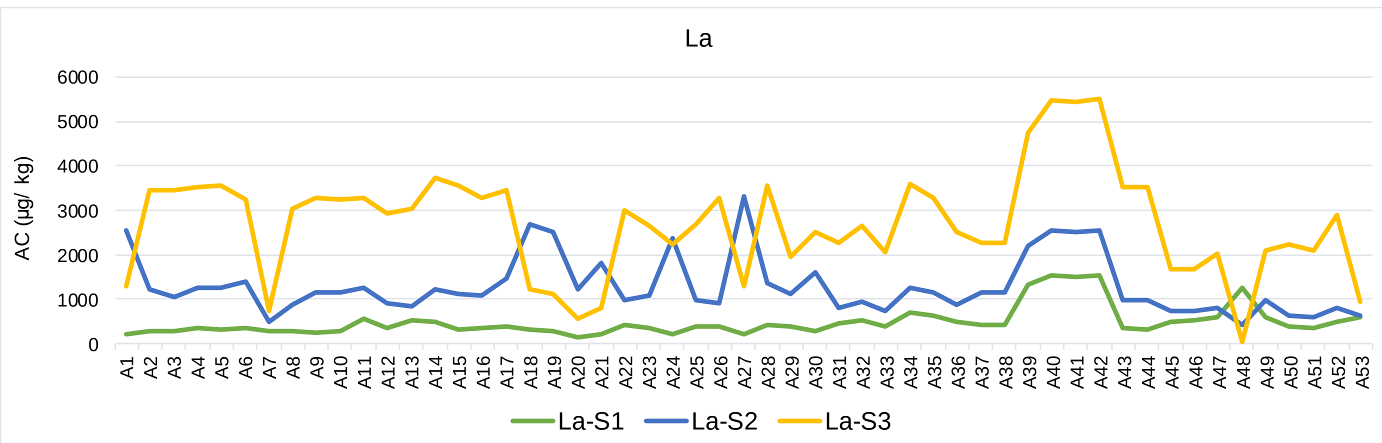
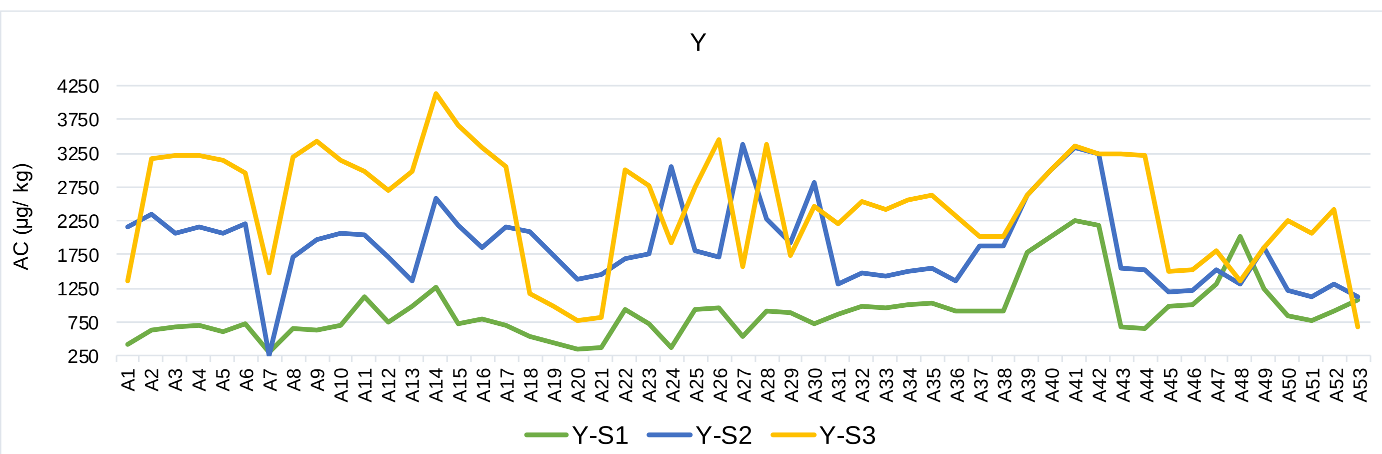
Supplementary material 1. Distribution of each analyzed REE available concentrations in S1, S2 and S3 in the studied sites (A1-A53).







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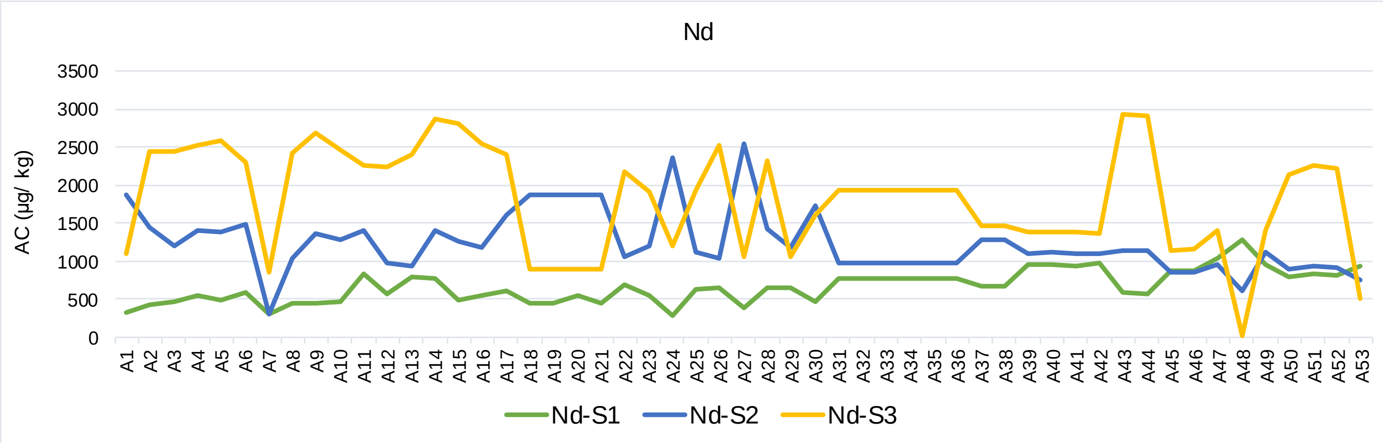

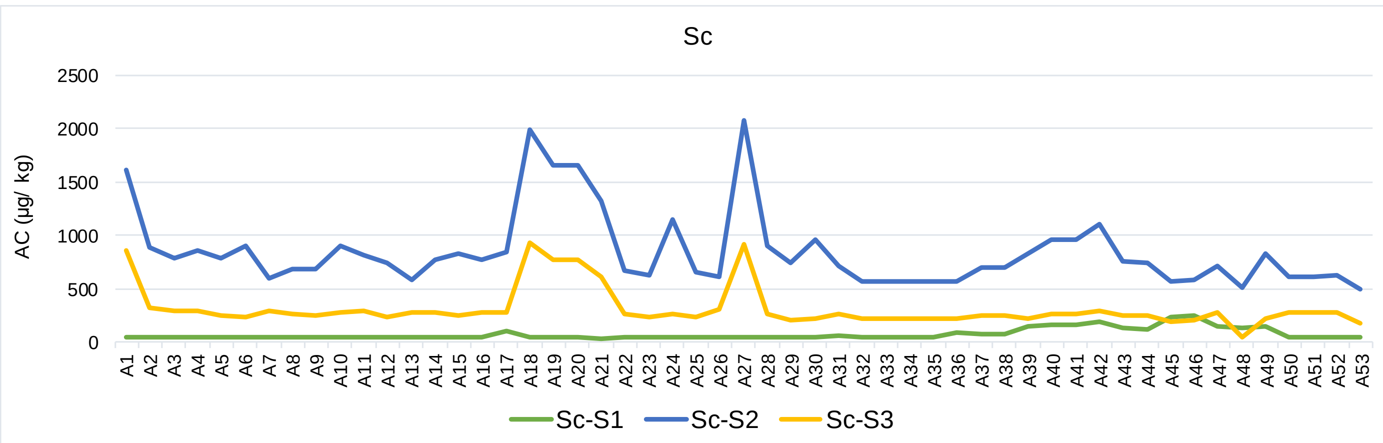

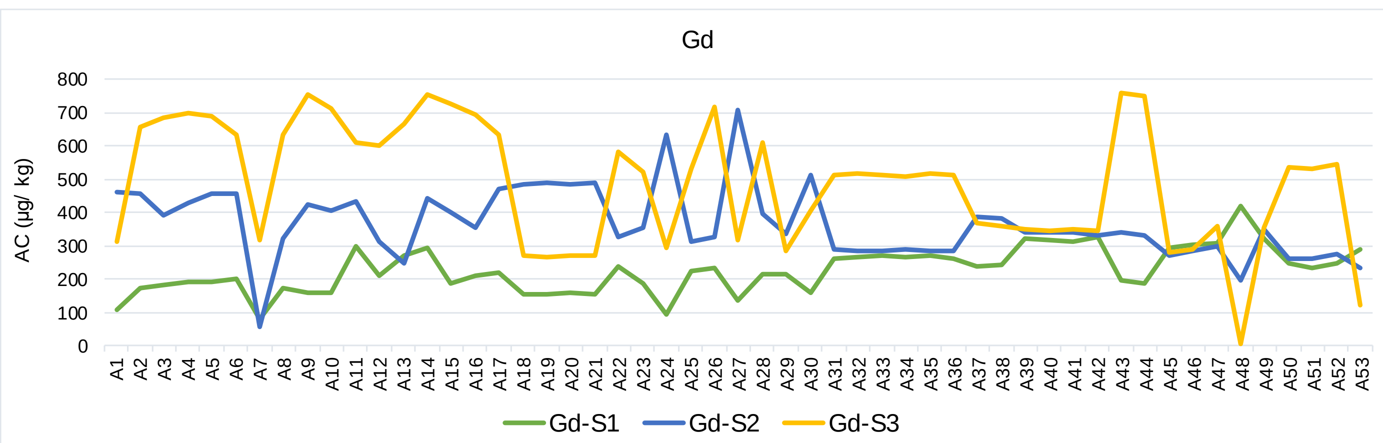

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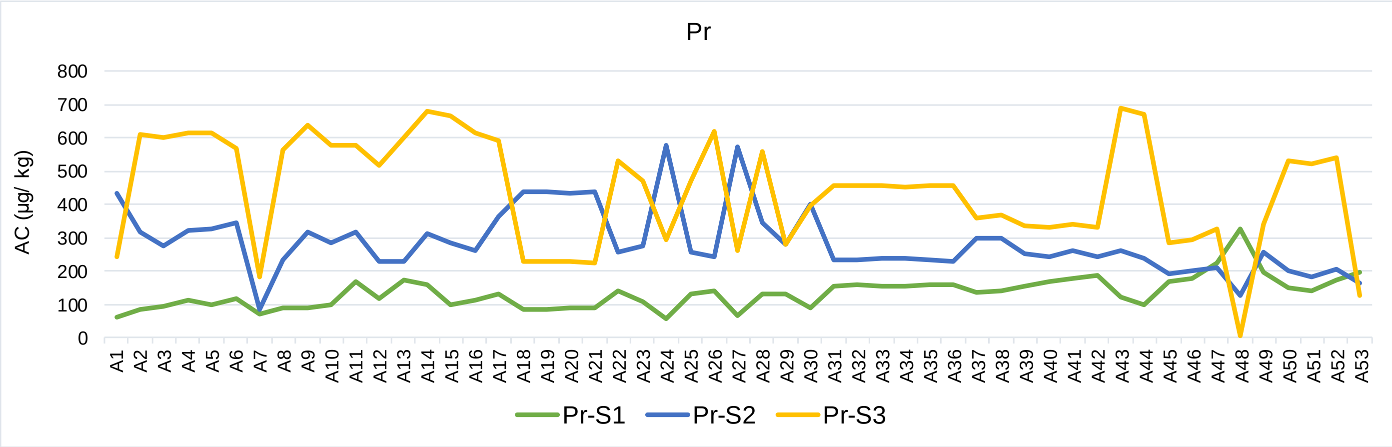
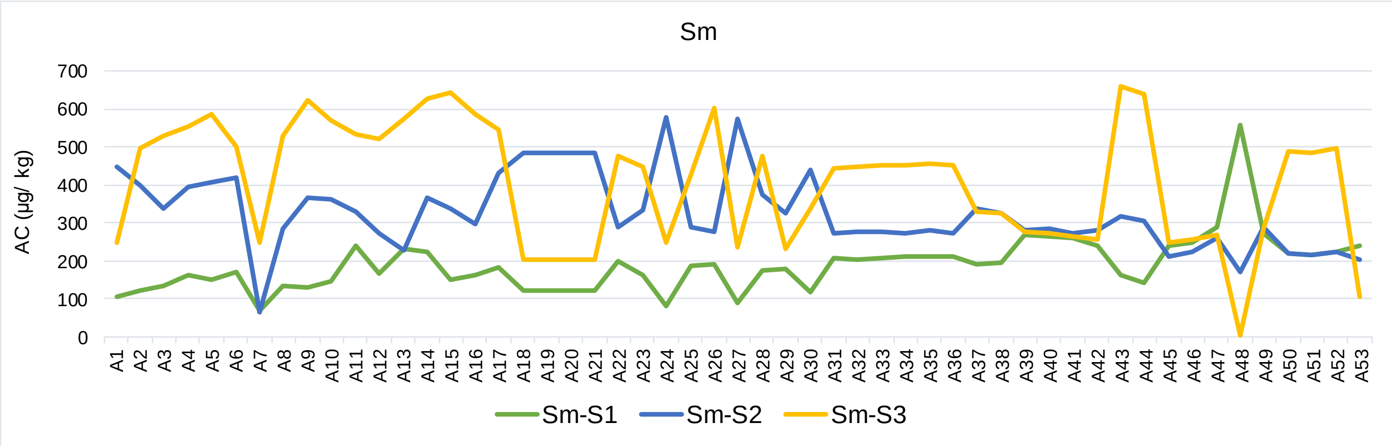
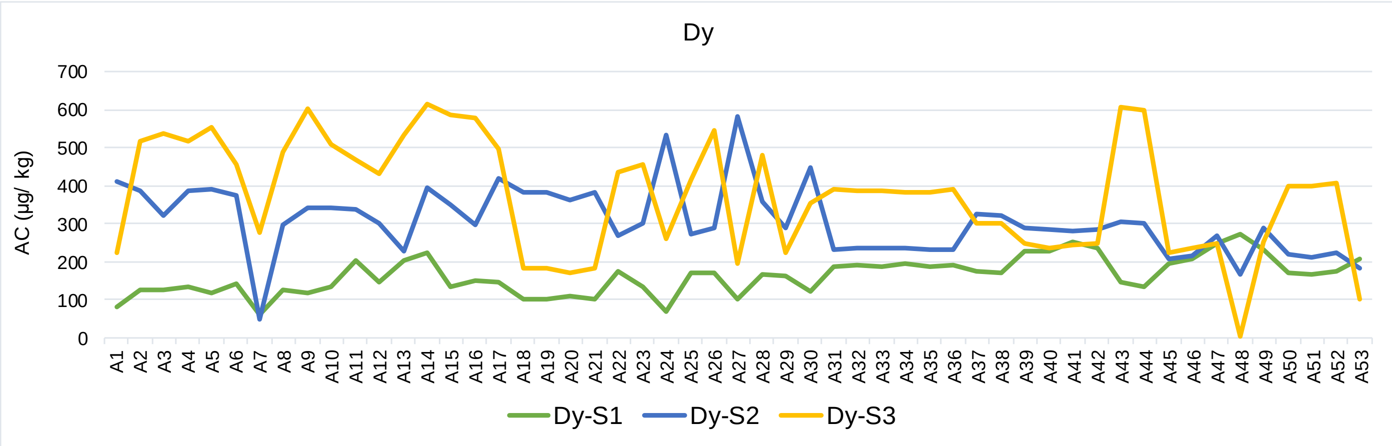
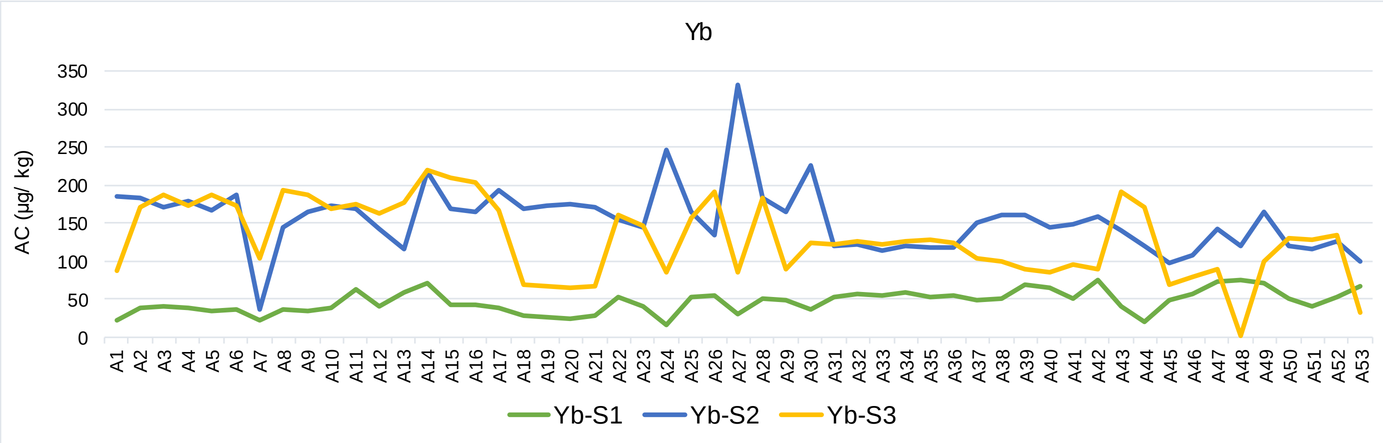
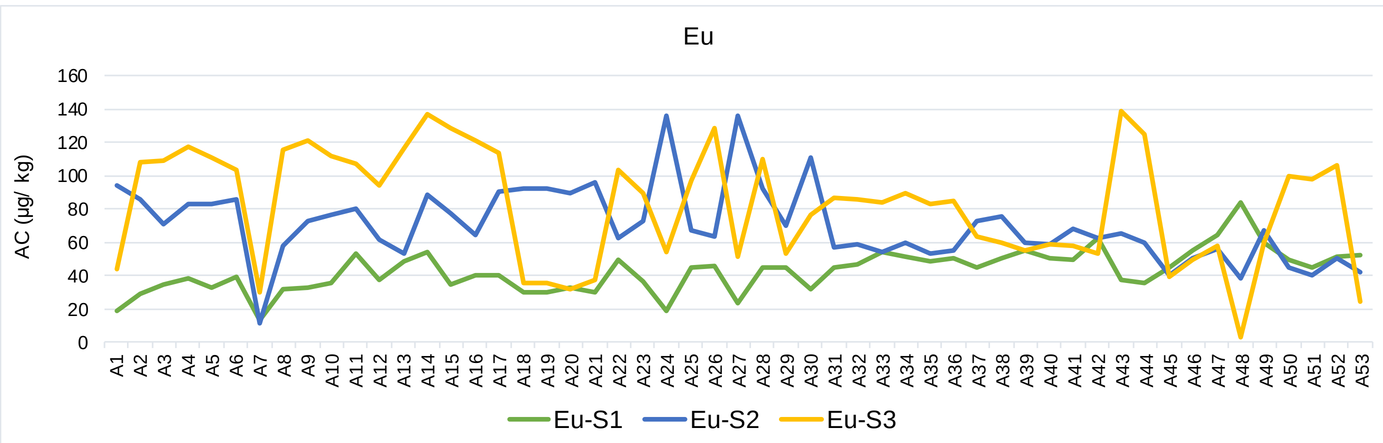







Yb
AC (µg/ kg)
350
300
250
200
150
100
50
0
A1 A2 A3 A4 A5 A6 A7 A8 A9 A10 A11 A12 A13 A14 A15 A16 A17 A18 A19 A20 A21 A22 A23 A24 A25 A26 A27 A28 A29 A30 A31 A32 A33 A34 A35 A36 A37 A38 A39 A40 A41 A42 A43 A44 A45 A46 A47 A48 A49 A50 A51 A52 A53
Yb-S1
Yb-S2
Yb-S3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AC (µg/ kg)
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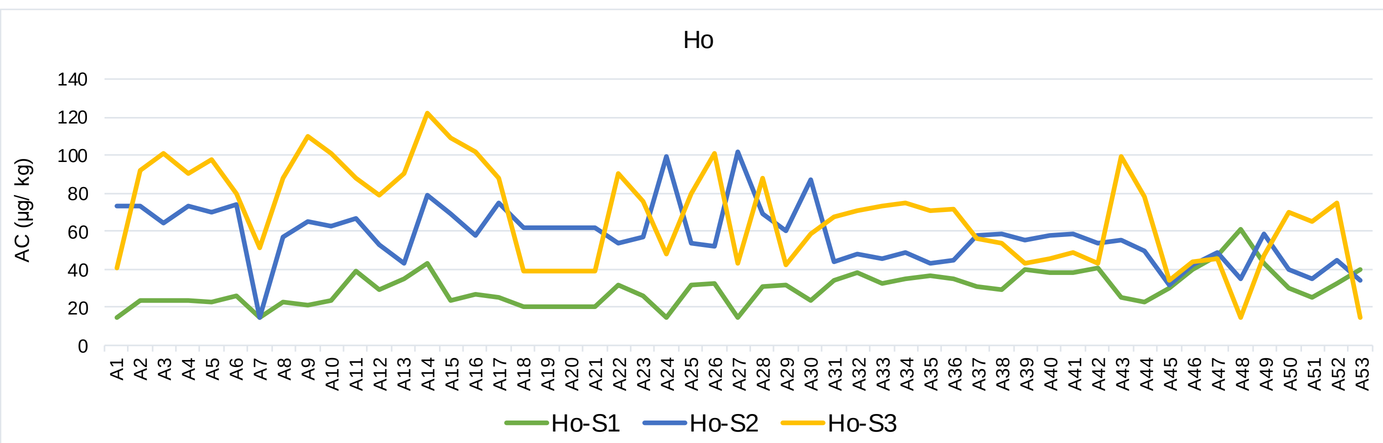
Eu-S1
Eu-S2
Eu-S3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Ho-S1
Ho-S2
Ho-S3

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