Environ Earth Sci (2011) 64:1257–1267
DOI 10.1007/s12665-011-0942-y

ORIGINAL ARTICLE

Origin of rare earth element anomalies in mangrove sediments, Sepetiba Bay, SE Brazil: used as geochemical tracers of sediment sources

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Received: 18 May 2010 / Accepted: 24 January 2011 / Published online: 12 February 2011

Abstract Elemental contents were determined in two mangrove habitats along Sepetiba Bay, SE Brazil, an area impacted by local industrial activities, as well as hinterland water diversion networks. This study demonstrates how specific REEs (La, Ce, Nd, Sm, Eu, Tb, Yb and Lu) may be used as a sediment source tracer to mangrove-dominated coastlines. From the two stations studied, a pair of cores was collected, one in the mangrove forest and the other in the tidal flat. Station 1 results show a general enrichment in most of the fractioned patterns of the REEs normalised by Post-Archean Australian Shale. The relatively light rare earth elements are similarly enriched in the generally more polluted Station 1. Despite the probable difference in background sediment characteristics, a common sharp increase in mud contents patterns in the upper part of the mangrove sediment core was related to a lower REE content as well as Eu anomalies. With existing knowledge of clockwise water circulation in the bay, these patterns can be explained by man-made water diversion from the São Francisco and Guandu rivers, initiated more than 30 years ago, whereby suspended matter with relatively large contents of REEs and material originating from industrial sources accumulate in the eastern sector of the bay. This is the first comprehensive assessment of REEs as sedimentary tracers in a mangrove ecosystem in Brazil.

Keywords Rare earth elements · Mangrove · Sedimentary tracers

Introduction

As REEs have specific geochemical characteristics, they can serve as powerful tracers at various scales in marine environments, including specific estuarine traits, ocean circulation patterns and used to determine hydrothermal mixing along freshwater–oceanic gradients, including groundwater within mangrove forests. The high productivity and low ratio of sediment respiration to net primary production gives mangrove sediments the potential for long-term sequestration of pollutants before reaching the coastal ocean (Valiela and Cole 2002), commonly associated with depositional stratifications along mangrove-dominated estuarine gradients (Sanders et al. 2008), which may be indicated by anomalies in sedimentation patterns (Sanders et al. 2006). A variable equilibrium between the processes described in this study indicates that mangrove sediments play an important role as either temporary sources or longer lived sedimentary carbon and pollutant sinks (Bouillon et al. 2008; Sanders et al. 2006; Alongi 1998) or may register anomalies associated to natural or anthropogenic impacts (Machado et al. 2008). As such balances are sensitive to climatic change and/or anthropogenic perturbations (e.g., Chapman and Wang 2001), a detailed knowledge of recent sedimentary processes in mangroves systems is essential in evaluating the potential implications of local environmental disruptions, ultimately

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indispensable in defining the significance of how mangrove ecosystems may contribute to global processes.

Geochemical tracers have been successfully utilised to study the transport processes and fate of numerous pollutants, and are well documented in the pristine systems (see recent comprehensive overviews by Oliveira et al. 2007 and Xu et al. 2009, for examples). As REEs have specific geochemical characteristics, given in bulk sediment and will be implied as such from here forward, they can serve as powerful tracers at various scales in marine environments, including specific estuarine geochemical characteristics. Occurrences of anomalous patterns in REEs, commonly reflected in impacted areas, such as changes in hydrogeochemical sediment sources. (Hoyle et al. 1984; Elderfield et al. 1990; Sholkovitz 1993; Bertram and Elderfield 1993; Klinkhammer et al. 1994; German et al. 1995; Nozaki et al. 1999; Sherrell et al. 1999; Tachikawa et al. 1999; Leybourne et al. 2000; Lacan and Jeandel 2004; Santos et al. 2007).

Re-suspended matter may influence depositional rates found along Sepetiba Bay's coastline, such conditions are considered an important process in this dynamic system (Quevauviller et al. 1992; Barcellos et al. 1997; Marques et al. 2006). The coastal region of Sepetiba Bay has been experiencing an exponential population growth, triggered by industrialisation and subsequent urbanisation, particularly within the previous few decades. Freshwater input into the bay has been modified through changes in the watershed, in particular the Paraiba do Sul River, considered the major source of fresh water to Sepetiba Bay. One such development was the construction of a relatively large harbour in the early 1970s, to support the increasing industrialisation in the area. The population increase in the region became significant beginning in the 1970s, increasing from 600,000 to 1.2 million today. Being so, the bay has gone through serious consequences due to high pollutant discharge from industries and subsequent inhabitants, having inadequate infrastructure to support the population growth (Barcellos and Lacerda 1994; Mendes and Moreira 1976; Machado et al. 2008; Gomes et al. 2009).

This study investigates the distribution and fractionation patterns of REEs in sediments of differing mangrove forests and adjacent tidal flats within Sepetiba Bay, and to interpret these potential tracers in terms of possible hinterland and local sources of suspended material including pollutants. Anomalies in the sediment distribution are hypothesised to indicate changes in the flux of differing fresh water sources. This is the first comprehensive assessment of REEs as sedimentary tracers in a complex mangrove ecosystem in Brazil. To note, the authors were unable to find, for comparative reasons, assessments of REEs as sedimentary tracers in mangrove ecosystems as presented in this work.

Study area

Sepetiba Bay is on the southeastern coast of Brazil, about 60 km southeast of Rio de Janeiro city (Fig. 1a). The construction of a large harbour in the early 1970s made the area attractive for industrial development, concentrated in the eastern sector of the bay. The development mentioned has contributed to significant pollution of the bay, principally due to unplanned urban development (Barcellos and Lacerda 1994; Barcellos et al. 1997).

Nine rivers drain in the eastern sector, considered a large source of freshwater input, reaching an annual flow of 5.7–7.6 $\times$ 10^9 m^3. The São Francisco River, with an annual flow of $\sim$5.5 $\times$ 10^9 m^3, is responsible for over 86% of the total freshwater runoff flow and 73% of the total suspended solid inputs to the bay (Rodrigues 1990). There are no significant seasonal variations in fluvial discharge to the bay. The constant flow of the São Francisco River to the bay is primarily due to the constant flux from the nearby Guandu River (feeding the São Francisco River), which is artificially controlled by an upstream water treatment plant, within a heavily industrialised area (FEEMA 1989; Rodrigues 1990). Once reaching the bay, suspended matter is associated with river flow and is distributed through active tidal currents within the bay, creating accumulation areas along its eastern coast (Lacerda et al. 1987; Marins et al. 1998; Barcellos et al. 1997).

Materials and methods

Sampling

Four sediment cores were hand sampled, with PVC tubes and immediately sliced into 3 cm intervals from the two sampling stations in Sepetiba Bay (Fig. 1). Each site is within distinct regions (see below). Two sediment cores were sampled at station 1, one from within the mangrove forest (core 1), 85.5 cm in depth and a second from the tidal flat (core 2) 28.5 cm in depth. Two sediment cores were also collected at a second station, again within the mangrove forest (core 3) 58.5 cm in depth and at the tidal flat (core 4) 61.5 cm in depth. The samples were stored in polyethylene bags and cooled to 4°C, and immediately thereafter, transported to the laboratory where they were maintained at −20°C until analysis (Wasserman and Lavaax 1991). Station 1 is within a large mangrove forest, which is ubiquitous in the eastern part of the bay. This region of the bay is the most affected by metal contamination (Barcellos and Lacerda 1994). The clockwise circulation of the bay creates depositional conditions that characterise the eastern part of the bay as a strong geochemical barrier for pollutants that would otherwise likely

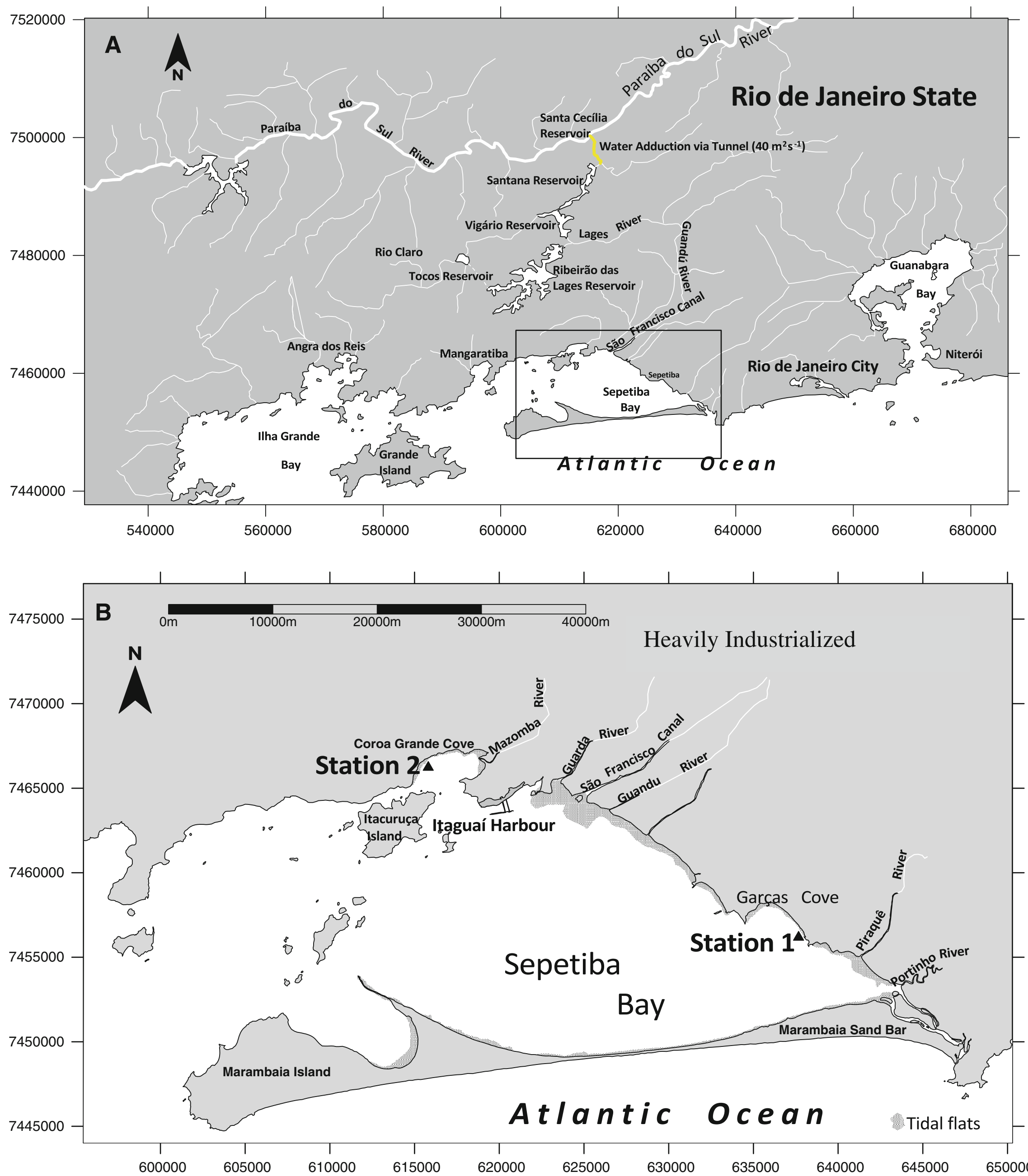


Fig. 1 **a** General location of Sepetiba Bay in the State of Rio de Janeiro, also showing the major source of freshwater input to the bay via the Paraiba do Sul–Guandu river network (simplified). **b** More detailed map of semi-enclosed Sepetiba Bay, showing the two sampling stations. Note the many rivers (nine in all) draining from the more heavily industrialised sector east of the harbour. Highest inflow is from the Guandu River, its waters reaching the bay partly via two man-made canals, the larger being the São Francisco Canal (*SFC*)

reach the continental region. Station 2 is in the more preserved region of the bay and is near the mouth of a small creek that is fed by neighbouring mountains.

Analytical procedures

The samples were subdivided into two aliquots, one for granulometric analysis and the other for geochemical analyses. In the former aliquots, mud contents were determined by wet sieving through a nylon 63-μm sieve, followed by drying and weighing the mud (<63 μm) and sand fractions. The second aliquots were dried in a ventilated oven at 40°C for 3 days, then carefully ground and stored in sealed polyethylene bags until geochemical analysis.

Approximately 100 mg of each aliquot (bulk sediments) was weighed in polyethylene vials. Elemental synthetic standards were prepared by dissolving their respective oxides or salts (analytical grade) with adequate amounts of inorganic acids, and diluting with distilled water. Subsamples of these solutions were pipetted onto 1-cm^2 pieces of Whatman No. 40 filter paper, evaporated to dryness under an infrared lamp, and sealed in polyethylene envelopes.

Subsamples and standards were irradiated for 8 h at a thermal neutron flux of 10^{13} cm^{-2} s^{-1}, at the IEA-R1 nuclear reactor of the Instituto de Pesquisas Energéticas e Nucleares (IPEN-CNEN/SP), Pinheiros. Measurements of induced gamma-ray activity were carried out by means of a GMX20190 hyper-pure Ge detector (CANBERRA) at a resolution (FWHM) of 1.90–1,332 keV activity ^{60}Co, in two series of counting: the first was 5 days after irradiation, the second 15 days after irradiation, with counting times of 1–2.5 h. Gamma-ray spectra were processed with the SAMPO90 gamma-ray software, which locates peak positions and calculates the activities of net areas. Accuracy and precision were verified by analysis of the reference materials *Buffalo River Sediment* (NIST SRM 2704) and *Estuarine Sediment* (NIST SRM 1646a). Results obtained for these standard reference materials, as well as certified and proposed values and detection limits (3σ) are reported elsewhere (Larizzatti et al. 2001; Wasserman et al. 2001; Oliveira et al. 2007). Reproducibility and precision were tested by means of six replicate analyses of random samples, showing relative errors of 0–10% and standard deviations of less than 15%.

Results

At the more polluted site (station 1) in the eastern sector of Sepetiba Bay, the down core profiles in mud contents show values of 21–94 dry wt% in the mangrove sediment core (1), and 73–89 wt% in the tidal flat, sediment core 2, as shown in Fig. 2 a. At less polluted station 2, in the western sector, the values measured were from 0 to 48 dry wt% of mud in the mangrove sediments of core (3), and 9 to 77 wt% in the tidal flat sediments in core (4) are shown in Fig. 2b. Overall, mud contents decreased down core in cores 1 and 3. In cores 2 and 4, in the tidal flat areas, mud content peaked immediately below the surface layers and remained relatively homogeneous down core.

Enrichment levels (mg kg^{-1} dry wt bulk sediments) of REEs, Sc and Th in the four cores collected at stations 1 and 2 are reported in Tables 1 and 2. The down-core range in the Th values is 19–143, 20–43, 9–27 and 4–26 in stations 1, 2, 3, and 4, respectively. The LREEs mean contents are higher in core 1 than in core 2 as shown in Table 1. This is not the case for station 2, which shows essentially no difference in LREE content from sediment cores 3 and 4.

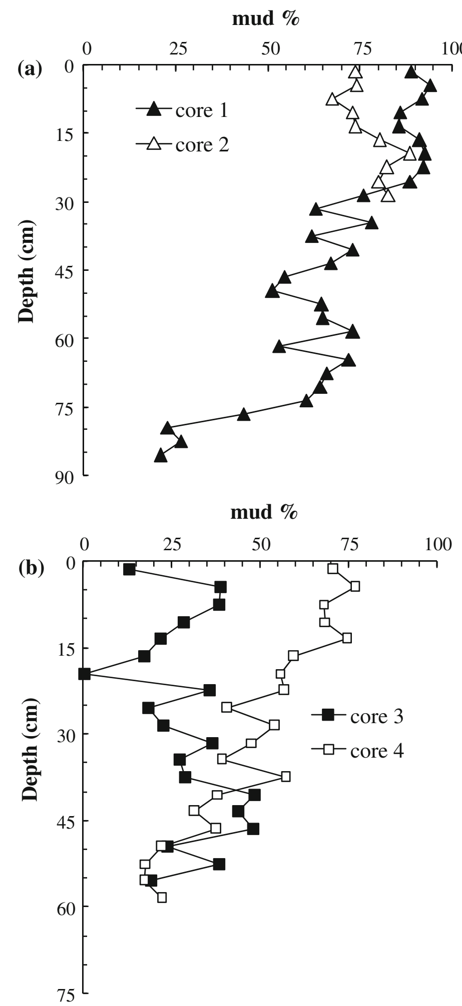


Fig. 2 Down-core patterns of mud contents (<63 μm fractions, dry wt% of bulk sediments): **a** more polluted station 1: *core 1* mangrove forest, *core 2*, adjacent tidal flat; **b** less polluted station 2: *core 3* mangrove forest, *core 4*, adjacent tidal flat

Station 1 results show a general enrichment in most of the fractioned patterns of the REEs, La, Ce, Nd, Sm, Eu, Tb, Yb and Lu, normalised by Post-Archean Australian Shale (PAAS) of 5.6, 9.3, 1.9, 0.6, 0.3, 1.4, 5.3 and 0.4 times greater in the mangrove forests and 1.5, 2.1, 1.0, 14.6, 1.1, 1.6, 2.1 and 2.0 times higher in the tidal flats, respectively. The LREEs are similarly enriched in the more polluted station. These differences are pronounced in the bottom sediments, which may be related to the site-specific lithology. Figures 3 and 4 show the vertical distribution patterns of Th, Sc and $\sum$REE in stations 1 and 2, respectively.

The distribution profiles of REEs normalised to PAAS show a slight LREE enrichment and a strong negative Eu anomaly, at station 1 (Fig. 5). On the other hand, Fig. 6 shows that there is heavy rare earth elements (HREE) impoverishment at station 2 and a slight positive Eu anomaly.

Table 1 Th, Sc and REE contents (mg kg^{-1} dry mass bulk sediments) in two cores from station 1 in the more polluted eastern bay sector

Depth (cm)	Mud (dry wt%)	Th	Sc	Rare earth elements							
				La	Ce	Nd	Sm	Eu	Tb	Yb	Lu
Core 1, mangrove forest											
1.5	89	23	14	71	133	66	9.3	1.7	1.4	2.2	0.4
4.5	94	19	14	60	118	64	8.2	1.6	1.1	1.9	0.4
7.5	92	25	15	76	147	64	10	1.8	1.1	2.9	0.4
10.5	86	36	16	101	196	89	14	1.9	1.3	3.0	0.5
13.5	86	35	15	98	189	81	13	1.9	1.5	2.9	0.5
16.5	91	34	15	97	189	82	13	1.9	1.5	3.4	0.5
19.5	93	30	15	85	160	86	11	1.9	1.3	2.4	0.4
22.5	92	33	15	91	174	80	12	1.8	1.5	2.6	0.4
25.5	89	33	15	93	178	84	13	1.9	1.5	2.4	0.4
28.5	76	74	11	170	331	122	22	1.8	1.9	3.6	0.8
31.5	63	117	11	256	509	183	32	2.1	3.4	6.4	1.5
34.5	78	40	13	106	206	79	14	1.9	1.5	3.3	0.7
37.5	62	95	11	206	404	147	25	1.9	2.5	4.4	1.0
40.5	73	46	12	115	223	84	15	1.7	1.5	2.8	0.7
43.5	67	69	9.9	167	320	137	20	1.6	1.4	3.2	0.5
46.5	55	84	12	200	377	158	24	1.8	1.9	3.7	0.7
49.5	52	80	10	184	350	154	22	1.8	1.5	3.3	0.5
52.5	65	80	12	179	340	150	23	1.9	2.0	4.2	0.6
55.5	65	98	11	219	413	155	26	1.9	1.8	3.3	0.6
58.5	73	57	12	144	268	112	1.8	1.8	1.5	3.0	0.5
61.5	53	117	11	268	495	201	31	1.9	2.1	3.2	0.5
64.5	72	102	11	234	418	179	24	2.0	1.9	2.8	0.5
67.5	66	88	11	196	374	155	24	1.7	1.9	3.8	0.7
70.5	65	76	11	179	335	140	23	1.8	1.7	3.5	0.6
73.5	61	93	10	201	390	140	24	1.7	1.8	3.4	0.6
76.5	44	132	7.0	189	541	187	23	1.5	2.2	4.2	0.7
79.5	23	143	7.1	201	570	199	24	1.4	2.8	6.2	1.2
82.5	27	92	3.7	134	376	128	15	1.0	1.5	2.9	0.5
85.5	21	114	4.6	153	445	157	18	1.0	1.9	3.0	0.5
Mean	70	76	11	167	335	137	20	1.8	1.5	3.2	0.5
Core 2, tidal flat											
1.5	74	52	11	109	284		18	1.7		5.5	1.2
4.5	74	43	11	95	243		16	1.8		3.2	0.7
7.5	68	38	12	84	212		13	1.6		3.0	0.7
10.5	73	38	11	76	214		12	1.9		3.5	0.7
13.5	74	32	11	75	195	52	10	1.5	1.2	3.5	0.7
16.5	81	31	11	63	189	42	9.0	1.5	1.2	3.3	0.4
19.5	89	22	10	50	137	40	10	1.4	1.0	2.8	0.5
22.5	83	20	11	48	129	36	6.4	1.4	1.0	2.7	0.4
25.5	80	26	12	54	169	33	10	1.5	1.1	2.5	0.4
28.5	83	28	13	64	187	44	10	1.6	1.0	2.4	0.5
Mean	78	32	11	70	192	41	10	1.6	1.1	3.1	0.6

Table 2 Th, Sc and REE contents (mg kg^{-1} dry mass bulk sediments) in two cores from station 2 in the less polluted northwestern bay sector

Depth (cm)	Mud (dry wt%)	Th	Sc	Rare earth elements							
				La	Ce	Nd	Sm	Eu	Tb	Yb	Lu
Core 3, mangrove forest											
1.5	13	15	9.8	2	42	94	36	6.4	1.3	0.7	1.4
4.5	39	13	7.0	5	28	62	26	4.7	1.2	0.5	1.2
7.5	38	9	5.4	8	24	51	21	4.0	1.0	0.4	1.0
10.5	28	12	5.9	11	27	61	24	4.4	1.0	0.5	1.1
13.5	22	18	5.9	14	38	82	32	5.6	1.0	0.6	1.3
16.5	17	27	4.5	17	27	56	23	4.8	0.9	0.5	1.2
19.5	0	19	5.0	20	48	94	41	7.1	1.0	0.6	1.4
22.5	36	10	4.3	23	25	46	21	4.1	1.0	0.5	1.1
25.5	19	14	5.2	26	40	76	34	5.7	1.1	0.5	1.1
28.5	23	12	4.2	29	28	55	24	4.9	1.1	0.5	1.5
31.5	36	16	7.6	32	41	84	36	6.5	1.2	0.7	1.6
34.5	27	11	6.7	35	33	65	27	5.1	1.2	0.6	1.5
37.5	29	12	7.0	38	33	66	28	5.1	1.1	0.6	1.4
40.5	48	12	7.5	41	36	75	32	5.7	1.2	0.6	1.2
43.5	44	13	8.2	44	37	77	34	5.8	1.3	0.6	1.3
46.5	48	11	6.6	47	40	74	33	5.6	1.1	0.5	1.2
49.5	24	16	12	50	51	101	44	8.4	1.5	0.8	1.9
52.5	39	15	11	53	45	86	40	7.3	1.4	0.7	1.6
55.5	19	14	9.7	56	39	74	35	6.5	1.2	0.6	1.6
Mean	28	13	6.6	30	36	74	32	5.6	1.1	0.6	1.3
Core 4, tidal flat											
1.5	71	20	13	60	120	50	9.2	1.7	0.8	1.9	0.3
4.5	77	19	12	64	123	51	10	1.7	0.9	1.8	0.3
7.5	68	26	13	77	148	67	12	1.8	0.9	1.9	0.3
10.5	68	20	14	67	131	56	10	1.8	0.9	1.9	0.3
13.5	74	17	11	58	105	52	9.1	1.5	0.8	1.8	0.3
16.5	60	18	11	56	115	48	8.5	1.6	0.8	1.8	0.3
19.5	56	16	11	52	103	46	8.0	1.5	0.7	1.7	0.3
22.5	57	16	11	47	93	41	7.3	1.5	0.7	1.6	0.3
25.5	41	17	10	54	106	48	7.0	1.5	0.8	1.7	0.3
28.5	54	13	9.8	46	88	41	6.9	1.4	0.7	1.5	0.3
31.5	48	16	10	47	92	41	6.8	1.4	0.7	1.4	0.2
34.5	39	17	11	51	104	46	7.7	1.6	0.8	1.8	0.3
37.5	57	15	12	48	98	42	7.3	1.5	0.8	1.3	0.3
40.5	38	12	9.1	47	73	41	7.0	1.4	0.7	1.0	0.2
43.5	32	14	9.5	41	83	35	4.4	1.4	0.6	1.3	0.2
46.5	38	12	8.7	36	73	33	5.7	1.4	0.5	1.4	0.2
49.5	22	12	7.1	31	61	27	5.0	1.2	0.4	1.4	0.2
52.5	18	13	6.0	39	73	33	5.7	1.2	0.4	1.2	0.2
55.5	17	18	4.4	34	67	30	5.5	1.0	0.4	1.0	0.2
58.5	22	7.6	5.2	22	41	21	3.8	1.0	0.3	1.0	0.2
61.5	9	4.4	2.9	11	16	11	1.8	0.6	0.2	0.4	0.1
Mean	48	15	10	47	91	41	7.0	1.4	0.7	1.5	0.3

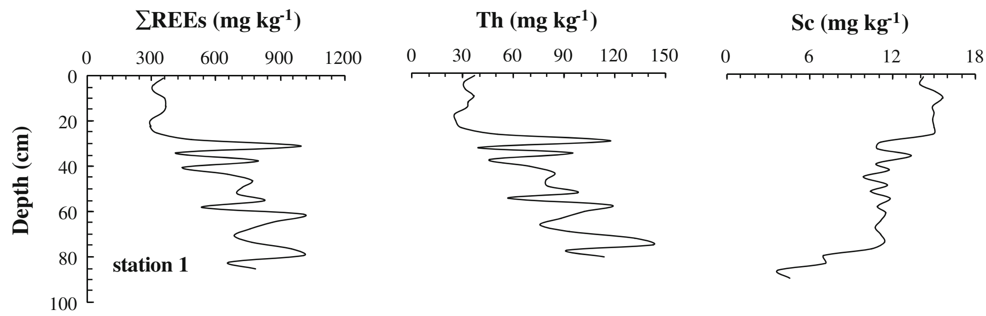


Fig. 3 Down-core patterns of ∑REE, Th and Sc contents (mg kg^{-1} dry bulk sediments) at station 1 in the more polluted eastern sector of Sepetiba Bay, unvegetated tidal flat, core 2

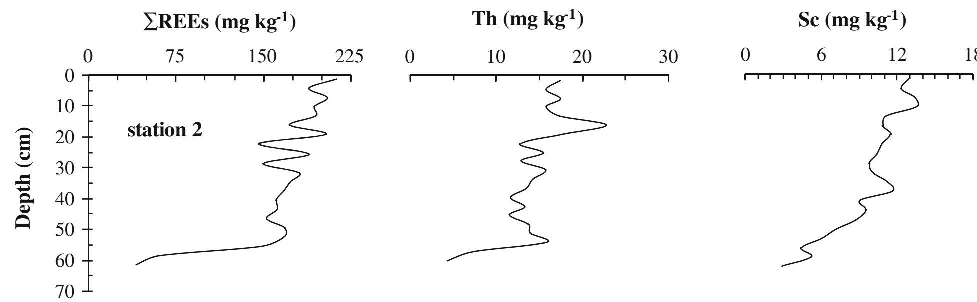


Fig. 4 Down-core patterns in ∑REE, Th, Sc contents (mg kg^{-1} dry bulk sediments) at station 2 in the less polluted western sector of Sepetiba Bay, unvegetated tidal flat, core 4

Discussion

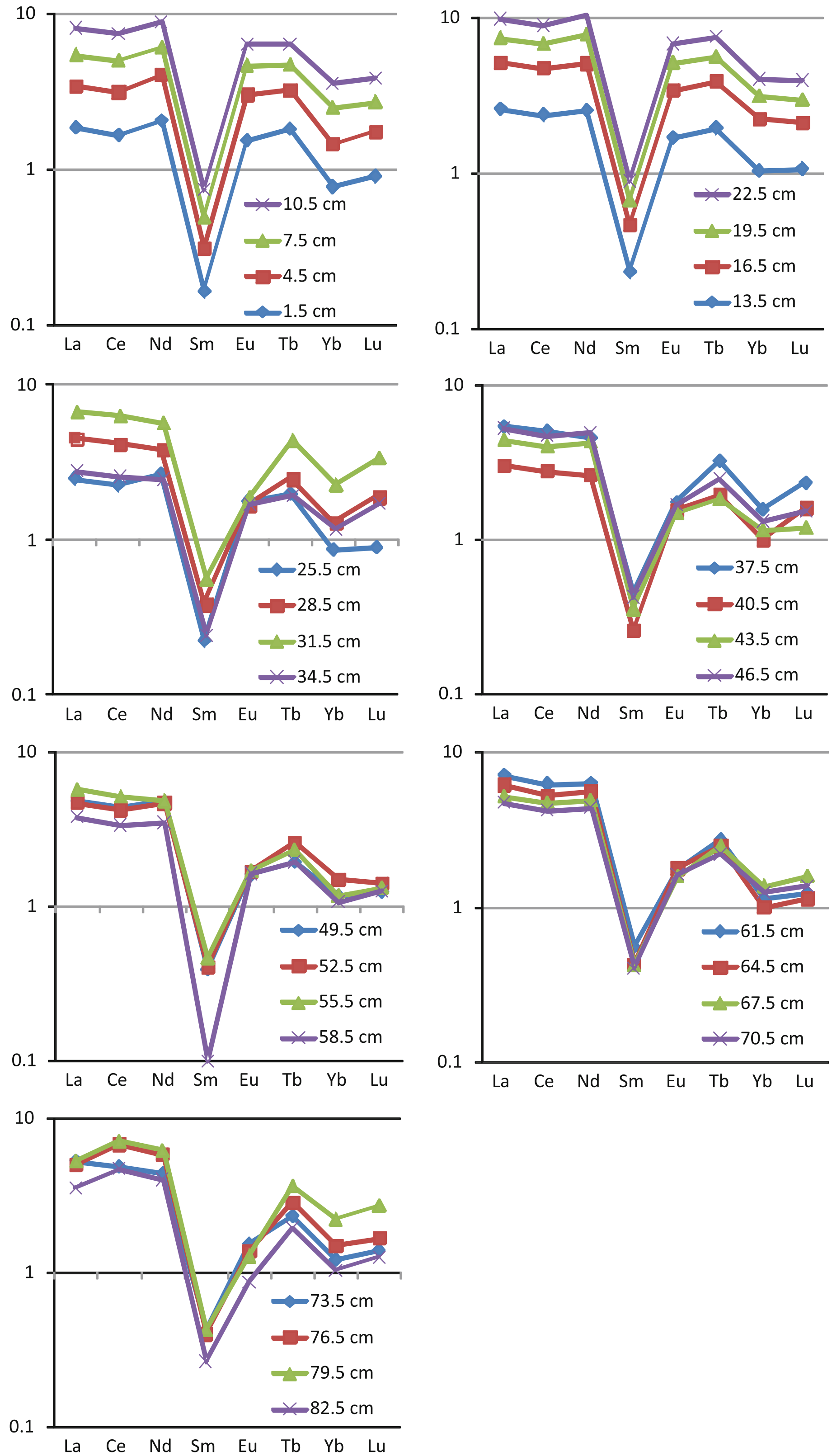
At the east side of the bay (station 1) granites dominate, 70% K-feldspar and quartz and minor amounts (0.5–1%) of accessory minerals (sphene, allanite, titanomagnetite, monazite, apatite and zircon), whereas granodiorite are prevalent at the northeast side (station 2), is composed essentially of plagioclase (30–65%), hornblende and biotite and minor amounts of alkaline feldspar and quartz, but rich in accessory minerals (sphene, titanomagnetite, apatite and zircon). The mean content of Sc at station 1 is similar to the Upper Continental Crust (UCC 11.0 mg Kg^{-1}), though slightly lower in station 2. The mean Th content in station 1 is significantly higher than those in the UCC (10.70 mg Kg^{-1}) and similar in station 2. Enrichment factors (EFs) relative to earth crustal composition were calculated based on the elements mean concentration reported by Wedepohl (1995). Mean crustal Sc level was used as a reference. The data obtained for station 2 (cores 3 and 4) show that all the elements studied are slightly enriched ($0.7 < EF < 3.9$) with Yb and Lu presenting the lowest values. As for station 1, besides the lower depths, core 2 presents EFs similar to cores from station 2. Moreover, core 1 shows higher EFs (1.5 Lu < FE > 9.8 Th) on average. These higher EFs were observed below 30 cm depth.

As has been noted in previous studies (Zhu et al. 1997; Yang et al. 2002, 2003) granulometric trends exert limited effects on the REEs content, due to their relatively low reactivity. Therefore, the distribution profile of granulometry and REEs most likely suggest a change in source (Hoyle et al. 1984; Klinkhammer et al. 1994; McLennan 1989; Oliveira et al. 2007; Xu et al. 2009).

The association between Th, Sc and REEs in station 2 (Fig. 4) suggests that these elements may have the same provenance. Thorium and REEs do not show association with Sc in station 1 (Fig. 3) and present an inverse distribution profile compared to station 2, with lower contents above the 30 cm depth. The presence of allanite and monazite, minerals rich in REEs and Th (Compton et al. 2003), may explain the higher contents of these elements in station 1. However, it does not explain the sharp change in the distribution profile above the 30 cm mark.

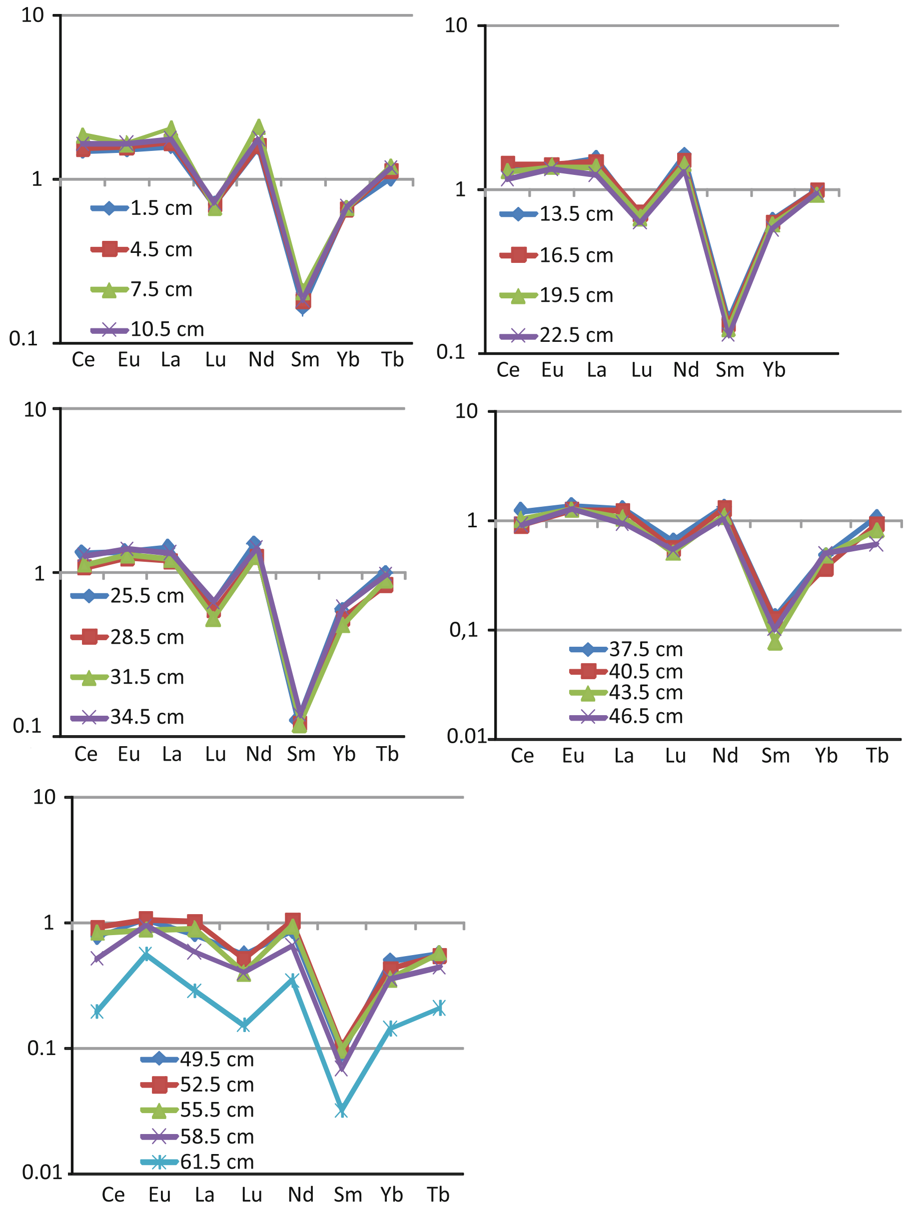
According to Compton et al. (2003) relative enrichment from LREEs in altered granites is a result of HREEs preferential scavenging, which has a higher mobility in poor carbonate environments. The fractioning between LREEs and HREEs is better visualised with La/Y ratio (Calvert et al. 1987, Murray et al. 1992). In suspended sediment derived from weathered rocks, the La/Yb ratios are lower than older samples (Goldstein and Jacobsen 1988). The La/Yb ratios are similar among cores 2, 3 and 4 (Fig. 7) when compared to the superior layers of core 1 (above 30 cm depth). However, below the 30 cm mark, core 1 shows a significant increase in La/Yb ratios (superior to 3.8) revealing a stronger fractioning between LEERs and HREEs.

Fig. 5 Down-core PAAS-normalised REE patterns in bulk sediments at station 1



Moreover, core 1 is well distinguished due to the Eu anomalies below 30 cm depth (Fig. 8a). The Eu impoverishment caused by fast plagioclase alteration in granites would explain the lower values of Eu at these depths (White et al. 2001), resulting in a positive Eu anomaly at station 2 explained by differing lithology between stations.

Fig. 6 Down-core PAAS-normalised REE patterns in bulk sediments at station 2



The question that remains is if Eu anomalies could occur after regional modifications. In general, crustal material shows REEs homogeneous distribution with a slight negative Eu anomaly due to deep crust retention. In principle, the changes in Eu valences are impossible under temperature normal conditions (Henderson and Pankhurst 1984). The Eu anomalies observed in some of the sediment profiles could be a result of plagioclases hydrolysis along alteration processes (Probst et al. 2000).

The authors suggest that the increase in the mud content above 30 cm in the mangrove forests is most likely associated with the input of a differing geological material. According to Molisani et al. (2006), sediment load into Sepetiba Bay has increased 28% since the water diversion from Paraiba do Sul River. The changes (from 30 cm to the top) in the REEs, fractionation as well as the Eu anomaly coincide with the period of water transposition of Paraiba do Sul River (in 1950). This evidence implies that sediment is detained within the five large reservoirs (Molisani et al. 2006) of the Paraiba do Sul drainage system and may play an important role in the fate of nutrient and pollutant in the Sepetiba Bay environment.

Data from sedimentation rates in this coastal environment vary greatly, from 0.2 to 1.03 cm year^{-1} (Smoak and Patchineelam 1999, Marques et al. 2006). According to Marques et al. (2006) these apparent discrepancies on sedimentation rate are attributed to inputs of different geological materials associated with water diversion wells as the sedimentary dynamics within an estuarine environment and/or mangrove system (Sanders et al. 2008). As

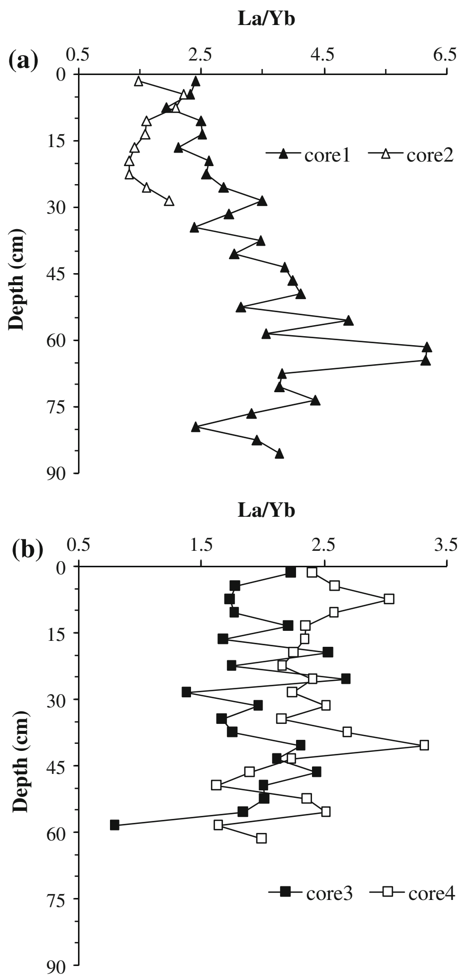


Fig. 7 REE fractionation ratios (La/Yb) in bulk sediments: **a** more polluted station 1: *core 1* mangrove forest, *core 2* adjacent tidal flat; **b** less polluted station 2: *core 3* mangrove forest, *core 4* adjacent tidal flat

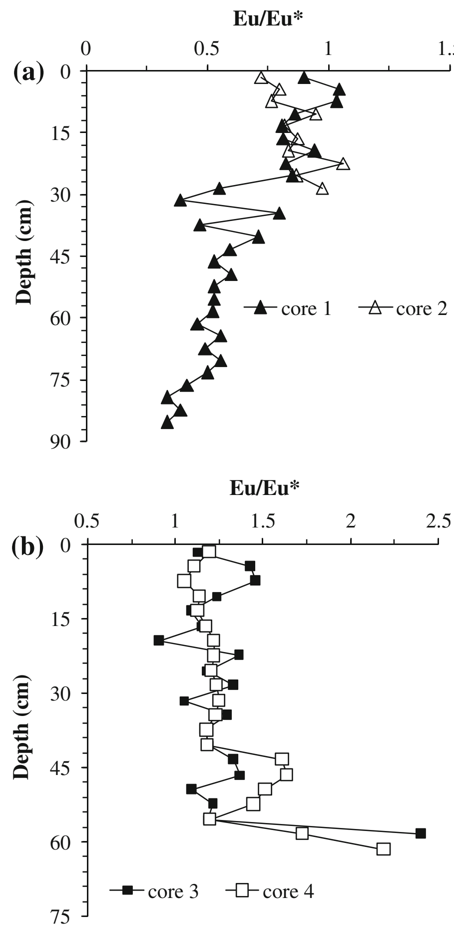


Fig. 8 Eu anomalies in bulk sediments: **a** more polluted station 1: *core 1* mangrove forest, *core 2* adjacent tidal flat; **b** less polluted station 2: *core 3* mangrove forest, *core 4* adjacent tidal flat. Eu/Eu* = Eu (norm)/(Sm (norm) × Tb (norm)$^{0.5}$

noted in Marques et al. (2006) and in this study, a higher mean content in the elements from station 1 compared to station 2 are most likely related to the differing lithology.

Conclusions

This study shows how REEs may be used as geochemical tracers of sediment sources in mangrove-dominated coastlines. The results of four sediment cores show how differing fractionating patterns of REEs normalised to PAAS are more enriched in one region and at specific depths. Evidence in this study suggests that sediment is detained within the five large reservoirs of the Paraiba do Sul drainage system and may play an important role in the fate of nutrient and pollutants to Sepetiba Bay. These changes coincide with the spatial and temporal water diversion from São Francisco and Guandu rivers. The modifications in the REEs distribution pattern within the upper 30 cm of the sediment cores studied suggest that fine-grained sediments discharged by diversions in the water systems, well preserved in the mangrove forest, have affected the sedimentation dynamics of Sepetiba Bay.

Acknowledgments This work is part of the Instituto do Milênio (CNPq/420050/2005-1) and INCT-TMCOcean (573-601/2008-9), with FAPERJ support, Grant (E-26/101.952/2009), to Christian J. Sanders.

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