



State of rare earth elements in the sediment and their bioaccumulation by mangroves: a case study in pristine islands of Indian Sundarban

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Received: 9 August 2018 / Accepted: 10 January 2019 / Published online: 4 February 2019
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Abstract

The mangrove ecosystems are known to efficiently sequester trace metals both in sediments and plant biomass. However, less is known about the chemistry of rare earth elements (REE) in the coastal environments, especially in the world's largest mangrove province, the Sundarban. Here, the concentration of REE in the sediment and plant organs of eight dominant mangrove species (mainly *Avicennia* sp.) in the Indian Sundarban was measured to assess REE sources, distribution, and bioaccumulation state. Results revealed that light REE (LREE) were more concentrated than the heavy REE (HREE) (128–144 mg kg⁻¹ and 12–15 mg kg⁻¹, respectively) in the mangrove sediments, with a relatively weak positive europium anomaly (Eu/Eu* = 1.03–1.14) with respect to North American shale composite. The primary source of REE was most likely linked to aluminosilicate weathering of crustal materials, and the resultant increase in LREE in the detritus. Vertical distribution of REE in one of the long cores from Lothian Island was altered by mangrove root activity and dependent on various physicochemical properties in the sediment (e.g., Eh, pH, organic carbon, and phosphate). REE uptake by plants was higher in the below-ground parts than in the above-ground plant tissues (root = 3.3 mg kg⁻¹, leaf + wood = 1.7 mg kg⁻¹); however, their total concentration was much lower than in the sediment (149.5 mg kg⁻¹). Species-specific variability in bioaccumulation factor and translocation factor was observed indicating different REE partitioning and varying degree of mangrove uptake efficiency. Total REE stock in plant (above + live below ground) was estimated to be 168 g ha⁻¹ with LREE contributing ~ 90% of the stock. This study highlighted the efficiency of using REE as a biological proxy in determining the degree of bioaccumulation within the mangrove environment.

Keywords Rare earth elements (REE) · Bioaccumulation · Mangrove · Sundarban

Responsible editor: Philippe Garrigues

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Introduction

The series of 17 transition elements, formed by scandium (Sc), yttrium (Y), and fifteen lanthanides (Ln) are collectively known as rare earth elements (REE). These elements exhibit similar chemical properties and tend to occur together in nature. However, light rare earth elements (LREE), i.e., lanthanum (La) to europium (Eu) with densities 2.9 to 5.3 g cm⁻³, are more abundant than heavy rare earth elements (HREE), i.e., gadolinium (Gd) to lutetium (Lu) with densities 6.9–9.8 g cm⁻³. Such enrichment of LREE over HREE (in mg kg⁻¹) is found to occur in different facies, like, upper continental crust (UCC) (157.5 versus 22.3), mean basalt (129.3 versus 26.21) and mean marine sediment (MMS) (173.3 versus 30.9), North American Shale Composite (NASC) (152.8 versus 20.4), and mean shale composite (MSC) (205.2 versus 23.9) (Bowen 1979). However, their ratios (LREE/HREE) differ from one another as MSC > NASC > UCC > MMS > basalt, suggesting, despite their coherent chemical behavior, greater partial fractionation of HREE than LREE by geochemical processes during their riverine transport.

The growing use of REE in mining, refining, and recycling has serious environmental consequences. For instance, application of phosphate fertilizer containing REE in agriculture could elevate REE soil concentrations (Volokh et al. 1990) and could affect plant metabolism, growth, and yield (Hu et al. 2004). Acid drainage mines (AMD) areas often are featured by enrichment in REE (Grawunder et al. 2014), specially Podwiśniówka acid pit lake in south central Poland is among the highest REE rich water bodies worldwide (mean concentration ~ 1000 µg L⁻¹, Migaszewski et al. 2016). Moreover, AMD water affected the Huelva estuary in Spain have even showed REE > 11,000 µg L⁻¹ (Lecomte et al. 2017). Carpenter et al. (2015) demonstrated that phytotoxicity could be a concern to crop grown in REE-contaminated soil. On the other hand, sewage sludge amended soils may be potential REE sources to environment (Hu et al. 2006 and reference hereafter). However, it is also reported that most of the REE in soils is derived from the parent material which are away from REE producing industrial plants.

In addition, the variations of REE is related to complex estuarine-geochemical processes such as removal and fractionation primarily due to estuarine mixing (Sholkovitz 1990; Censi et al. 2005; Santos et al. 2007; Hannigan et al. 2010), redox alteration in the water column (Bau et al. 1997), anthropogenic impacts on sediments (Olmez et al. 1991; Tranchida et al. 2011; Perez-Lopez et al. 2016; Brito et al. 2018b), etc. Iron oxyhydroxides (FeOOH) and organic matter (OM) are known to have strong affinities with REE and play an important role in transfer and immobilization of REE. The stability of complexes between REE

and OM with oxygen donor group such as EDTA⁴⁻ type of ligands increases regularly from La to Lu (Sharpe 1999). In general, processes like dissolution/diffusive transport (Vermeire et al. 2016), adsorption-desorption in oxyhydroxide of Al/Fe/Mn, and complex formation with humic-like OM at varied redox level govern mobility and bioavailability of REE, followed by their inter-horizon distribution in the sediment column (Pourret et al. 2007; Davranche et al. 2011; Rice and Maccarthy 1989; Sonke 2006).

Estuarine and coastal systems, particularly mangroves, are carbon-rich productive ecosystem (Duarte et al. 2005). Clay and OM rich estuarine sediment can serve as repository of REE (Brito et al. 2018a; Zhang et al. 2013; Silva-Filho et al. 2011; Prasad and Ramanathan 2008; Censi et al. 2005). In contrast to estuarine sediment, little is known about the bioaccumulation, distribution, and fractionation pattern of REE within the complex halophytes like mangroves. Bioaccumulation of REE in non-mangrove plant and their physiological responses such as stimulatory effect on plant metabolism, growth, and yield have been reported in different species growing in soils containing low to natural level of the REE (Markert and Li 1991; Hu et al. 2004; Tyler and Olsson 2005; França et al. 2011). REE concentrations in salt marsh halophyte plants have recently been reported by Brito et al. (2018a). However, to our knowledge, toxicological studies on the effects of REE soil contamination on mangrove plants are totally lacking. Do mangrove thrives in favorable REE rich sediment or there is potential risk of phytotoxicity? What is the partitioning of REE within plant organs (leaf, wood, root)? Are there species-specific variations? These are some potential questions that could be addressed in the present study. We hypothesized that bioavailability of REE in mangrove environment is mainly dependent on (1) the sedimentary physicochemical parameters and reactions and, (2) the species-specific REE uptake capacity (bioaccumulation and translocation mechanism).

Towards testing these hypotheses via answering the above-mentioned questions, the present study was carried out in the Indian Sundarban, the largest deltaic mangrove (including Bangladesh part) located at the land-ocean boundary of the Bay of Bengal. This manuscript represents a first quantitative assessment of full set of REE in the mangrove sediment and dominant plants in the Sundarban. The goals of the work presented here were to (1) characterize the distribution and concentration of Y and REE (as YREE) in the mangrove sediment, (2) derive their correlation with other major metal (Mn, Fe, Al), physicochemical properties (Salinity, pH, Eh), and nutrient status of sediment (organic C, PO₄-P), and (3) assess YREE bioaccumulation in eight dominant mangrove plants in the largest mangrove province of India.

Materials and methods

Study area

The Sundarban is a unique bioclimatic zone for its biodiversity of mangrove flora and fauna, located at the estuarine part of the Ganges River and at the land-ocean boundary of the Bay of Bengal (20° 32′–20° 40′ N, 88° 05′–89° 00′ E). The mangrove coverage of the Indian Sundarban is 9630 km², out of which 4264 km² is under reserved forest. The whole mangrove area is dissected by network of crisscrossed channels and creeks, starting from the Hooghly towards the east, Saptamukhi, Thakuran, Matla, and Gosaba. The tide is semi-diurnal with a significant variation in the tidal range from spring tide (5 m) to neap tide (1.5 m or even less). The freshwater input into the mangroves is regulated from the Farakka dam situated 250 km mangrove upstream. Indian Sundarban harbors 34 true mangrove species of which the dominating ones are *Avicennia alba*, *Avicennia marina*, and *Avicennia officinalis*, *Ceriops decandra*, *xylocarpus granatum*, *Aegialitis rotundifolia*, *Bruguiera gymnorrhiza*, *Aegiceras corniculatum*, *Sonneratia apetala*, *Excoecaria agallocha*, etc. The study sites are located within a sedimentary (alluvial) environment formed as a result of extensive fluvial-marine deposits of the river Ganges and the Bay of Bengal. Texturally, sediment is dominated by silt (70–85%) followed by clay (8–15%) and sand (5–15%). The composition of the surface sediment of the Sundarban mangrove is reported elsewhere (Ray et al. 2014).

Sampling, storage, and analytical method

Sampling was carried out during low tide to assess both exposed sediment and surrounding mangrove plants. This was mid of the monsoon period (August–September of 2016) in the north-eastern part of Indian peninsula. Freshly deposited surface sediments were collected from the vegetated littoral zone of two different stations: the Lothian Island (Stn. 1, 21° 41′ 01″ N, 88° 20′ 49″ E) situated in the confluence of the Saptamukhi River and the Bay of Bengal and, the Jharkhali (Stn. 2, 22° 02′ 09″ N, 88° 41′ 55″ E) located at a distance of about 65 km north of the coast (Fig. 1). Deep sediment core or core 1 (up to 70 cm) was collected by using a push-up PVC corer (inner diameter 7.5 cm) from the muddy surface inside the forested part of Stn 1. On the other hand, one core (Core 2, surface to a 6-cm depth) could be retrieved due to the difficulty in pushing PVC corer on the less soft and more compact sediment along with the extensive root network at Stn. 2. Thereafter, the long core and short core were sliced into pieces (in centimeter, core 1: 0–2, 2–4, 4–6, 6–8, 8–10, 10–15, 15–20, 20–30, 30–40, 40–50, 50–60, 60–70; core 2: 0–2, 2–4, 4–6). Sediment subsamples were kept frozen in the laboratory

until further analysis. No rainfall was recorded during sample collection.

A. marina, *A. alba*, and *A. officinalis* are the dominant mangrove species at Lothian and Jharkhali followed by patches of *A. rotundifolia*, *S. apetala*, *A. corniculatum*, *C. decandra*, and *B. gymnorrhiza*. These mangrove trees are 8 to 10 m high and forming forest of 10 ± 2 years old. Samples of fresh leaves, woods, and roots of these eight species were collected ($n = 24$) nearby the areas of sediment sampling sites. Plants samples were washed by jetstream water and transported to the laboratory on ice pending analysis.

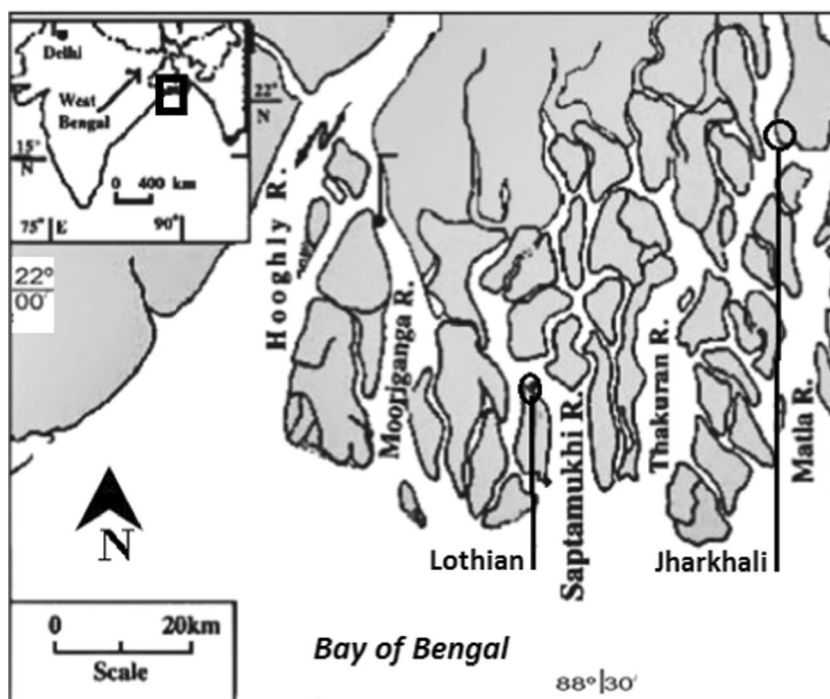
Analyses of physicochemical parameters

Immediate *in situ* measurement of redox potential (Eh) and pH was carried out by gently inserting electrodes into the sediment section (Vischer et al. 1991) (Systronics, micro pH system 362). Salinity (S) was estimated using argentometric method (Grasshoff et al. 1983). Precision of pH and S were ± 0.01 and ± 0.2, respectively. The freeze-dried sediment and plant (leaf, wood, and root) samples were pulverized, homogenized in an agate mortar, and then sieved (63 μm) for the estimation of REE and other metals. For organic carbon (OC) analysis, samples were treated with HCl fumes for 4 h to remove inorganic carbon, encapsulated in Ag cups and then after overnight heating at 40 °C, they were analyzed by CHN carbon analyzer (FLASH-2000), with precision in measurement of ± 0.1% for C. For total inorganic phosphorus (labile), the sediment extract from 75 ml of 2 M KCl solution was analyzed in spectrophotometer at 882 nm wavelength (APHA 1995), with relative error of accuracy ± 2%.

Analyses of REE and trace metals

Samples were acid digested in a microwave (MARS 5 system CEM) in ISO 2 laboratory (Geosciences Environment Toulouse, France) and sample preparation took place in a class A 10,000 clean laboratory. Mangrove samples (0.1 g dry weight each) were mixed in 1 mL H₂O₂ 30% Suprapur® (Merck KGaA, Darmstadt, Germany), 9 mL bi-distilled HNO₃, and 0.2 mL suprapure HF (Merck KGaA, Darmstadt, Germany) in 20 mL Teflon containers (Savilex®). The digestion procedure consisted in a 20-min holding stage at 150 °C, 1600 W, and 100 psi. After cooling, the solution was evaporated at 70 °C for 24 h on a hot plate and the residue was redissolved by sonication in 20 mL of 2% HNO₃. The elemental analysis was carried out by ICP-MS (Agilent 7500ce). The concentration of all the REE and the major metals (Al, Fe, Mn) was evaluated as the mean of 100-times scanned measurements. Every run was also controlled by two blanks, to ensure no contamination during the acid digestion and the concentration of each element in the blank was subtracted to the concentration in samples. The reference standard solution

Fig. 1 Map showing sampling stations, Lothian Island (Stn. 1) and Jharkhali (Stn. 2) in the Indian Sundarban



SRM1646a (NIST, USA) was used (one per 10 sample digestion batch) to certify the accuracy and precision of the analytical procedure. The detection limit for REE was 0.1–1.0 ng L⁻¹, and for Fe, Al, and Mn was > 10 ng L⁻¹.

For plant samples (organic moieties) the acid mixture consisted of 3 mL H₂O₂ 30% Suprapur® (Merck KGaA, Darmstadt, Germany) and 9 mL bi-distilled HNO₃ whereas the microwave digestion protocol followed was the same as the one described above. The BCR-482 lichen standard (EC-JRC-IRMM, Belgium) was used to certify the accuracy of the analysis.

The data quality was assessed by comparing the certified and the measured concentration in the reference standard solution in terms of recovery (%), and by checking the precision of the ICP-MS analysis by the relative percentage differences (RPD) and the relative standard deviation (RSD) among the references material replicates. The recovery for Fe, Al, and Mn were 60%, 82%, and 73%, respectively and between 70% and 98% for REE. The RPD was lower than 20% for all the elements. The precision of the ICP-MS measurements was considered acceptable because of they are within the 10% in terms of RSD.

Enrichment and bioaccumulation factor of REE

In order to estimate the contribution of REE to sediments from other than natural sources, Al-normalized enrichment factors (EF) with respect to the composition of NASC (Haskin et al. 1968; Gromet et al. 1984) are calculated as follows:

$$Enrichment\ Factor\ (EF) = \frac{\left(\frac{REE}{Al}\right)_{sample}}{\left(\frac{REE}{Al}\right)_{NASC}} \tag{1}$$

where, (REE/Al)_{sample} denotes the ratio of the sample and (REE/Al)_{NASC} denotes the corresponding ratio in NASC. Al was selected because it is the second most abundant metal in the earth’s crust with negligible association with anthropogenic contributions (Windom et al. 1989). EF was calculated based on subsurface values of REE and Al for both cores 1 and 2. To show the efficiency of REE phytoextraction, bioaccumulation (BAF), and Translocation (TF), factor values of REE were calculated in mangroves as

$$Bioaccumulation\ Factor\ of\ REE\ (BAF) = REE_{(leaf+wood+root)} / REE_{Sediment} \tag{2}$$

$$Translocation\ Factor\ of\ REE\ (TF) = REE_{leaf+wood} / REE_{root} \tag{3}$$

Here, REE concentrations (in mg kg⁻¹) in leaf, wood, and root were considered to calculate BAF and TF. The BAF > 1 mg kg⁻¹ was categorized as hyper-accumulator and < 1 as hypo-accumulator or excluder of metals, respectively (Cluis 2004). The TF > 1 indicated that translocation of metals efficiently occurred to the shoot from root (Baker and Brooks 1989).

Total REE stock in mangrove plant

REE, LREE, and HREE stocks (in g/ha) in mangrove plant were calculated by multiplying their concentrations and reported values of above-ground biomass (AGB) and live below-ground biomass (LBGB) (mean AGB = 93.72 ton/ha, BGB = 21.69 ton/ha; refers to our previous work—Ray et al. 2011). Total area of Indian Sundarban of 4264 km² was considered to further extrapolate the total REE stock for the entire mangrove system, i.e., AGB-REE and BGB-REE (g/ha) to AGB-REE and BGB-REE (ton).

Ce and Eu Anomalies

Ce and Eu anomalies were calculated following the equations reported by Bau and Dulski (1996) and Migaszewski et al. (2016), respectively:

$$Ce/Ce^* = Ce_{NASC} / (0.5La_{NASC} + 0.5Pr_{NASC}) \quad (4)$$

$$Eu/Eu^* = Eu_{NASC} / (0.5Sm_{NASC} + 0.5Dy_{NASC}) \quad (5)$$

where Ce* and Eu* are theoretical concentrations and La_{NASC}, Pr_{NASC}, and Sm_{NASC}. Dy_{NASC} are the NASC-normalized La, Pr, Sm, and Gd concentrations, respectively. Some references have used Gd in place of Dy in Eq 5 (Hannigan et al. 2010) but due to distinct enrichment of Gd, it is often inadmissible to use this element in calculation of Eu anomaly. Values greater than 1.2 and less than 0.8 are considered positive and negative anomalies respectively while values between that interval indicate the element are not fractionated relative to crustal abundance (Grawunder et al. 2014).

Statistical analysis

Statistical analysis was done using MINITAB (version 13.1) statistical software package. *Q* test was applied to test any doubtful data. Uncertainty in selecting independent variables during stepwise multiple regression was avoided by considering the parameters that gave statistically significant explained variability. The observed variability in the physicochemical parameters and REE were used in VARIMAX rotated factor analysis. Student's *t* test was employed to test differences of data among two stations.

Results and discussion

Features of basic sedimentary properties

Salinity and OC in the sediment were 19.5–22.5 psu and 0.7 to 1.05%, respectively. Mangrove-derived OC in the sediment found to be low which could be due to its tidal flushing (Ray et al. 2018). The sediment pH (7.2–7.5) and Eh (– 80

to – 120 mV) were lower and negative due to water logging leading to anoxic condition.

Distribution of REE in the mangrove sediment

To compare the distribution pattern of YREE, LREE, and HREE, major metals, and other geochemical parameters from the two stations, only subsurface mean values (0–6 cm) are summarized in Table 1. Their mean concentrations YREE, LREE, and HREE were always higher in Stn. 1 (176, 145, 14.2 mg kg⁻¹, respectively) than in Stn. 2 (154, 128, 12 mg kg⁻¹, respectively), also in line with the trends of Al, Mn, and Fe (Stn 1: 69.7, 0.55, 30 g kg⁻¹, respectively; Stn 2: 54, 0.42, 23.7 g kg⁻¹, respectively). Among the Lanthanides, Ce was most abundant with similar concentrations in both stations (Stn.1:

Table 1 Rare earth elements (REE) concentrations (mg REE kg⁻¹ dry sediment), Eu, and Ce anomalies, metalliferous and geochemical parameters in the surface (0–6 cm) mangrove sediments of different locations Stn. 1(Lothian) and Stn. 2 (Jharkhali) in the Sundarban

REE (mg kg ⁻¹)	Lothian		Jharkhali	
	Mean	SD	Mean	SD
La	32.6	1.91	28.9	9.89
Y	16.9	2.24	13.9	4.13
Ce	69.6	8.58	60.5	20.2
Pr	7.72	0.39	7.02	2.26
Nd	28.4	1.64	25.8	8.19
Sm	5.39	0.34	4.94	1.62
Eu	1.05	0.05	0.89	0.29
Gd	5.08	0.32	4.49	1.42
Tb	0.69	0.05	0.59	0.19
Dy	3.77	0.35	3.16	0.97
Ho	0.65	0.08	0.54	0.17
Er	1.88	0.27	1.50	0.42
Tm	0.25	0.04	0.21	0.05
Yb	1.65	0.26	1.29	0.28
Lu	0.22	0.04	0.18	0.04
ΣYREE	176		154	
LREE	144.8		128	
HREE	14.2		11.9	
Eu/Eu*	1.14		1.07	
Ce/Ce*	1.12		1.06	
Other metal				
Al	69746.2	2013.8	54037.8	27302.2
Mn	557.7	63.6	425.4	173.6
Fe	29950.6	353.5	23772.8	7101.7
Metalliferous	0.11x10 ⁻³		0.09x10 ⁻³	
Basic parameters				
	Mean	SD	Mean	SD
S (psu)	19.5	1.5	22.5	2.5
pH	7.5	0.5	7.2	0.8
Eh (mV)	–80	-	–120	-
OC (%)	1.2	0.3	0.7	0.1
PO ₄ -P (µg/g)	0.46	0.1	1.5	0.8

69.6 mg kg⁻¹; Stn.2: 60.5 mg kg⁻¹). The mean Σ REE concentration (HREE + LREE) in the subsurface sediment (149 mg kg⁻¹, ranging 140–159 mg kg⁻¹) was comparable with the Amazonian sediment (217 mg kg⁻¹, Gaillardet et al. 1997), Zhangjiang estuary, China (160–284 mg kg⁻¹, Zhang et al. 2013), salt marshes (146–190 mg kg⁻¹, Brito et al. 2018a), Tagus estuary, SW Portugal (18–210 mg kg⁻¹, Brito et al. 2018b), and Pichavaram mangroves, India (190 mg kg⁻¹ at 0–15 cm sediment, Sappal et al. 2014; 174–230 mg kg⁻¹, Prasad and Ramanathan 2008). The mean REE concentration in the sediment of the Sundarban was comparable with the reported value for marine sediment (156 mg kg⁻¹, Bowen 1979).

Furthermore, LREE in the mangrove sediment were more abundant than HREE in both stations 1 and 2. LREE represented about 91% of the total REE and the rest of 9% was contributed by HREE (LREE/HREE = 10.2–10.7). The enrichment of LREE relative to HREE in the clayey mangrove sediment of the Sundarban is similar to the trend observed for MMS (5.6), UCC (6.9), and NSC (7.5) (Haskin et al. 1966), and common with other studies in mangrove ecosystems (9.0–9.1 by Zhang et al. 2013; 8.2–9.9 by Prasad and Ramanathan 2008). The primary and secondary properties of soils are likely to control the retention and release of REE. Among most important factors are high contents of clay minerals (Dong et al. 2001), presence of secondary REE minerals such as certain phosphates (Åström 2001), and amounts and lability of REE-containing Fe–Mn hydroxy compounds (Cao et al. 2001). Enriched LREE may have been derived from the rocks (granitoids, gneisses, schists) bearing aluminosilicate minerals (e.g., kaolinite) and quartz, both are predominant clay minerals in the Sundarbans (refer to Rajkumar et al. 2012). Among the elements, Al concentration exhibited a maximum in the sediment core at Stn.1 (Al 59,525–75,925 mg kg⁻¹) with subordinate amount of Si (704–1771 mg kg⁻¹, Table 2). Inorganic P content in the mangrove sediment (0.46–1.52 µg g⁻¹) was much lower than the sediment of Bay of

Bengal (687.24 µg g⁻¹, Mohanty et al. 2018). Rajkumar et al. (2012) applied FTIR and SEM-EDS methods and identified Si and Al as the most abundant contributing more than 58 wt% in the Indian Sundarban sediment. Ramesh et al. (1999) suggested that higher LREE than HREE in estuarine sediment of east coast of India could be due to silicate weathering of crustal materials, and a resultant increase in LREE in detritus matter. Zhang et al. (2013) reported LREE enrichment due to intense silicate weathering indicating continental material as the main source for REE in the Zhangjiang estuary.

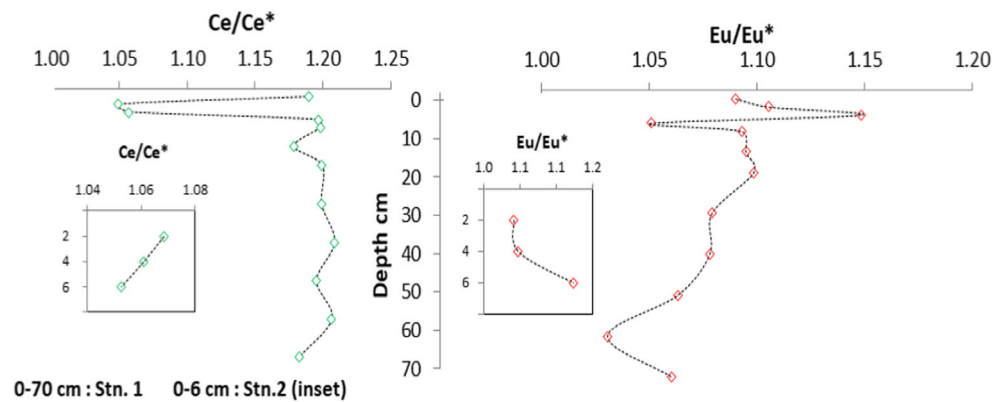
The spatial variation in Σ REE concentrations of surface sediment samples showed increasing trend across the locations from Stn 2 to Stn 1 (Table 1). Preferably, LREE could be scavenged by the flocculated matter in the mixed estuarine zone, contributing to their enrichment in sediment (Zhang et al. 2013) and mangroves root network trapped the flocculated matter suggesting that mangroves could play an indirect role in spatial distribution of REE in the Sundarban sediments.

The redox-sensitive REE, Ce, and Eu can be used to indicate changes in redox conditions in sediments, similar to the Fe–Mn hydroxide abundances (Hannigan et al. 2010). Under the reduced environment in the sediment of the Sundarban mangrove, there was an absence of Ce anomalies in the NASC-normalized REE concentrations (1.06–1.12, at 0–6-cm depth, Table 1). However, there was an indication of slightly positive Ce anomaly at greater depth (1.18–1.21, at 8–70-cm depth, core 1) probably reflecting the variability in redox conditions within the sediment column (Fig. 2). Positive Ce anomaly is common in lithogenic sediments where Ce⁺³ is oxidized by MnO₂ (forming CeO₂) and transported from the sediment to the adjacent overlying water. Ma et al. (2002) observed strong positive Ce anomaly in REE patterns of OM in Southern China, probably because of complexation capacities with the humic acids. In other Indian mangroves, slightly negative Ce anomaly was reported, attributing it to the

Table 2 Sediment profile of REE and major (Al, Mn, Fe, Si) and minor (PO₄-P) elements at Stn.1. Values are presented as mg kg⁻¹

Depth cm	Σ REE	LREE	HREE	Al	Mn	Fe	Si	PO ₄ -P
0–2	174.68	158.93	15.75	71863.7	629.12	30019.6	835.6	0.673
2–4	155.14	141.43	13.71	69519.8	536.66	30264.7	1827.7	0.612
4–6	147.25	134.15	13.09	67855.2	507.34	29567.7	1771.9	0.543
6–8	188.45	171.80	16.65	75925.0	806.13	32327.8	846.1	0.512
8–10	183.82	167.56	16.26	72784.1	718.20	30150.8	899.0	0.487
10–15	187.43	170.91	16.53	71340.3	756.21	29446.7	842.2	0.493
15–20	174.82	158.91	15.91	74330.5	943.65	31510.5	897.7	0.475
20–30	181.95	165.49	16.46	73110.8	764.81	31088.5	946.9	0.422
30–40	149.77	136.62	13.15	59525.3	502.15	24495.7	776.8	0.398
40–50	189.62	172.87	16.75	71684.7	552.65	29134.0	972.1	0.35
50–60	191.00	174.38	16.61	71585.5	728.15	29140.7	785.1	0.321
60–70	185.10	168.76	16.34	72027.7	668.57	29799.4	704.3	0.318

Fig. 2 Depth-wise pattern of Ce and Eu anomaly for both long core of Stn.1. and short core of Stn.2 (inset)



dissolution of Ce^{+4} to Ce^{+3} in the reducing environment (e.g. Pichavaram mangroves, Sappal et al. 2014).

There was almost no anomaly found for Eu with respect to NASC (1.07–1.11, all values less than 1.2) indicating reduced condition of the sediment in both cores. However slightly positive Eu anomaly suggested the oxidizing conditions, particularly during non-monsoon months in the surface sediment; the holes dug by crabs could contribute to the frequent change of redox conditions (Clark et al. 1998). It is noteworthy that Eu anomaly often serves as a proxy of sediment weathering, e.g., high negative Eu anomaly indicates extensive weathering of rocks while positive anomaly refers to moderate weathering (Sholkovitz 1988).

Sediment in these mangroves was quite rich in Al as indicated by the ratio $\text{Al}/(\text{Al} + \text{Fe} + \text{Mn})$ (> 0.69), and the abundance of metalliferous sediment was negligible (metalliferous = $\text{REE}/\text{Al} + \text{Fe} + \text{Mn}$; mean ranging $0.09\text{--}0.11 \times 10^{-3}$, Table 1). Positive and significant correlation among Al and REE in the core of Stn. 1 ($\text{REE} = 0.003 \cdot \text{Al} - 25, r^2 = 0.535, n = 15$ (Table 5) could be due to the adsorption of rare earths onto the Al-bearing minerals such as kaolinite in the Sundarban (Rajkumar et al. 2012). Brito et al. (2018a) observed similar relationship between REE and Al for saltmarshes referring that to presence of REE as insoluble aluminosilicate minerals in the sediment resulting in their insufficient availability for plant uptake.

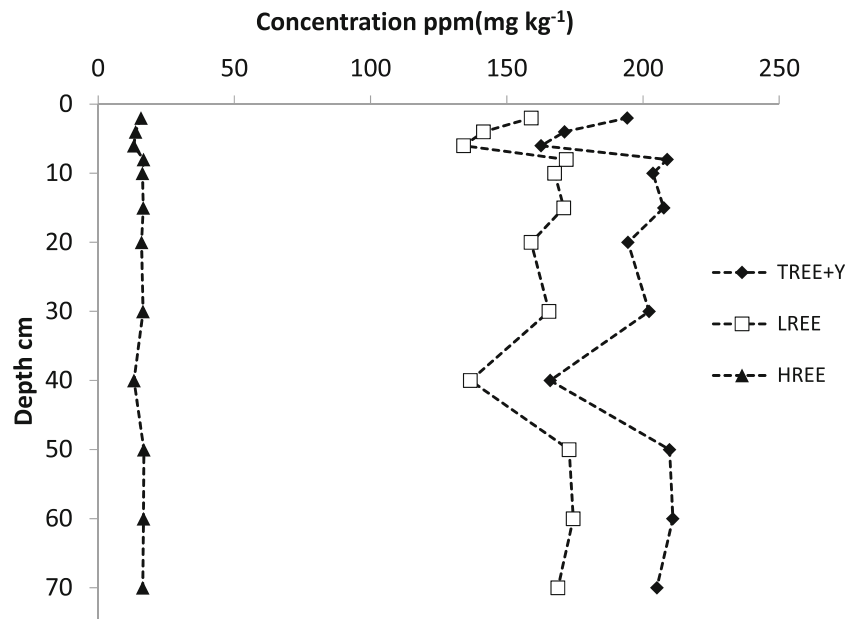
The great diversity of organic compounds produced by microorganisms in litter decomposition is of great importance to the behavior of REE in sediment. Sediment organic matter has many negatively charged groups per unit dry weight and, thereby, a high capacity to adsorb or chelate divalent and trivalent cations (Wu et al. 2001). Das et al. (2014) described major role of phosphate solubilizing bacteria (PSB) and phosphatase activity as a major factor for the variability of phosphate in the Sundarban mangrove sediment. Ray et al. (2017) showed a general decrease of both phosphate and PSB with depth indicating the presence of phosphate-containing minerals as a source of phosphate for PSB in the Sundarban mangrove sediment. Non-mobilized phosphorus buried in the accumulating sediment appeared to consist mostly of stable

minerals such as apatite, because phosphatase enzyme from bacteria (PSB) were capable to solubilize the phosphate-containing minerals (Rodríguez et al. 2006). On the other side, depleted HREE might be linked with soluble complex formation (Millero 1992) with the sedimentary organic matter (SOM) and subsequent export to the Bay of Bengal. Dissolved organic carbon (DOC) is of great importance to the mobility of the REE. DOC accounted for 46–74% of the statistical variability in REE concentrations of the soil solutions (Tyler and Olsson 2002). Humic substances, which are ubiquitous in sediment and estuarine waters in the Sundarban mangrove forest ecosystem, play an important environmental role both in the mobilization and immobilization processes of metal and metalloids (Rice and Maccarthy 1989; Mandal et al. 2013)

Vertical REE distribution along the down-core of Stn. 1 is shown in Fig. 3. The concentration of LREE was found to be greater than that of HREE and exhibited sharp variation compared to HREE, with two minima, one at 4–6 cm and other at 30–40 cm. According to Zhang et al. (2013), spatial heterogeneity could be due to mangrove root activity at the sediment subsurface. The spatial heterogeneity could also be due to the granulometric variation of the sediment. However, the core sample data of $\sum\text{REE}$ concentration in sediment showed the coefficient of variance of 2.9%. Physicochemical parameters such as S, pH, and redox could also be important for the REE variations in the sediment. On the contrary, relatively flat pattern of HREE along the long core suggested that fractionation pattern of heavy rare earths was spatially homogenous. The enrichment factor of REE relative to earth crustal compositions decreased with increasing atomic number for both cores ($\text{EF} > 2$ for LREE decreased to ≤ 2 for HREE, Table 3).

To better characterize the fractionation and enrichment pattern of HREE and LREE in the sediment, the rare earth concentrations were first normalized to their corresponding NASC, UCC, and MMS values to minimize the interferences due to their natural abundance. Results showed that fractionation patterns of NASC, UCC, and MMS-normalized REE mimic at both stations to that of shale with more depletion of HREE relative to LREE (Fig. 4). This indicated that the REE distribution pattern of mangrove sediment was not

Fig. 3 Depth-wise distribution of REE (as YREE black diamond, LREE blank square, and HREE black triangle) in the sediment core of Lothian Island (Stn. 1)



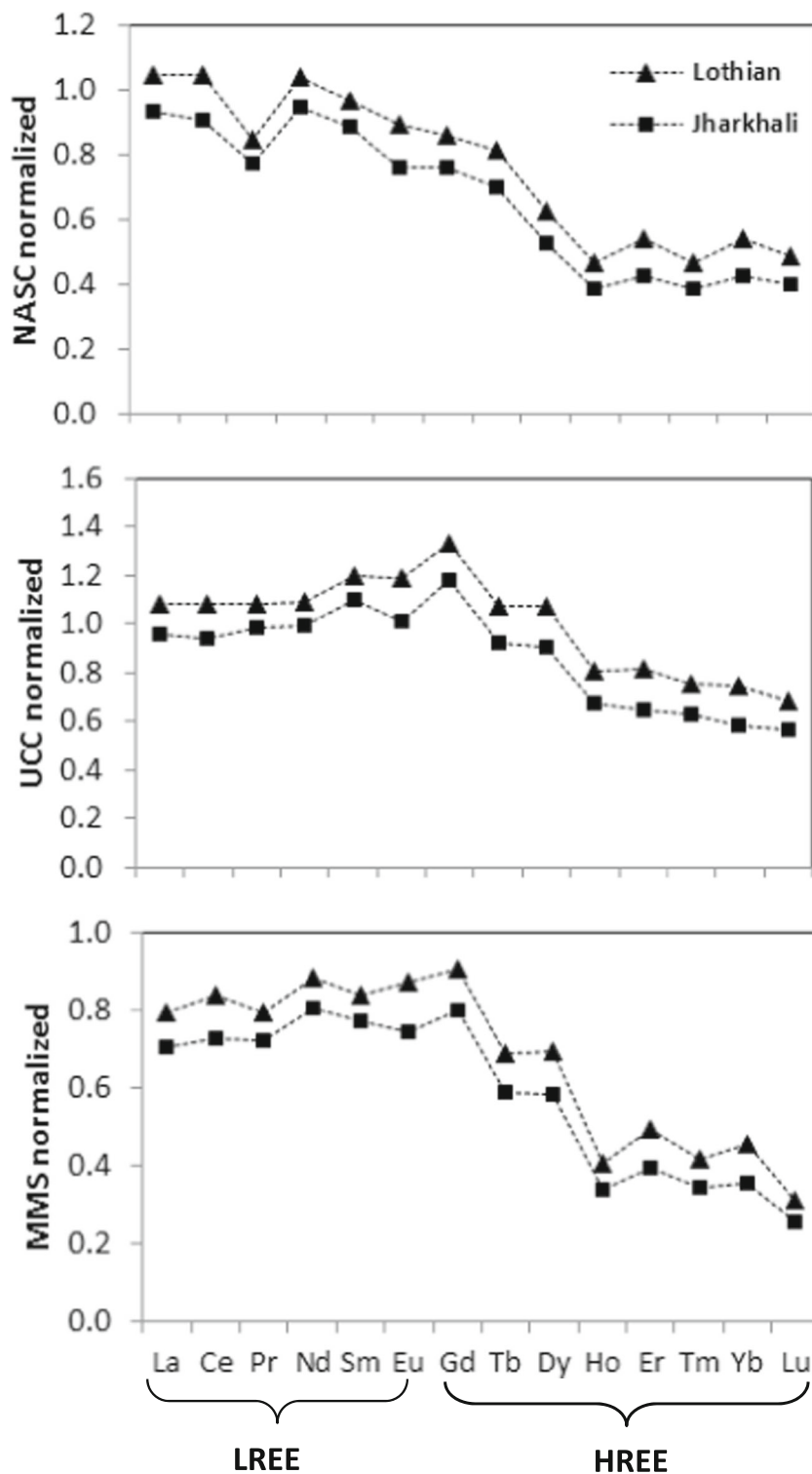
greatly modified during transport from their source. In terms of UCC- and MMS-normalized distribution, the mangrove sediment exhibited a rather distinct LREE plateau. Among REE, La, Sm, and Yb are often chosen as representative LREE, transition REE and HREE, respectively (Migaszewski et al. 2016). A ratio of 1 indicates no fractionation, whereas a value greater than 1 denotes enrichment and less than 1 denotes depletion (Sappal et al. 2014). NASC-normalized values of (La/Yb) and (Sm/Yb) were notably higher for both stations (Stn.1: 1.94, 1.79 respectively; Stn.2: 2.2, 2.09 respectively), indicating predominance of

LREE over HREE in the studied mangrove locations. Similar observation of LREE fractionation was made for the Pichavaram mangroves (Prasad and Ramanathan 2008) referring higher adsorption of LREE onto clay minerals of the mangroves. Furthermore, reducing trend of EF (2.6 to 1.33 for core 1 and 2.2 to 1.0 for core 2, Table 3) along the series of rare earths further confirms abundance of LREE in the sedimentary REE pool. A possible mechanism involves retention of LREE on sediments via adsorption and removal (leaching) of HREE in the form of strong organic complexes (Byrne and Kim 1990).

Table 3 Enrichment factor (EF) for cores 1 and 2, and bioaccumulation factor (BAF) and translocation factor (TF) for REE (AA: *A. alba*, AM: *A. marina*, BG: *B. gymnorhiza*, CD: *C. decandra*, SA: *S. apetala*, AR: *A. rotundifolia*, AC: *A. corniculatum*, AO: *A. officinalis*)

REE	Core		BAF							TF								
	1	2	AA	AM	BG	CD	SA	AR	AC	AO	AA	AM	BG	CD	SA	AR	AC	AO
La	2.68	2.23	0.081	0.013	0.036	0.006	0.028	0.007	0.021	0.012	0.14	0.74	0.72	0.70	0.18	7.25	9.72	4.15
Ce	2.84	2.18	0.070	0.012	0.032	0.005	0.026	0.012	0.025	0.016	0.14	0.72	0.72	0.63	0.30	7.12	7.65	3.79
Pr	2.16	2.85	0.080	0.013	0.037	0.006	0.025	0.006	0.020	0.011	0.13	0.71	0.70	0.64	0.18	6.85	9.76	4.19
Nd	2.64	2.26	0.081	0.013	0.036	0.006	0.028	0.007	0.022	0.012	0.13	0.80	0.72	0.70	0.18	6.49	9.63	3.86
Sm	2.47	2.12	0.087	0.012	0.037	0.006	0.028	0.008	0.023	0.013	0.13	0.77	0.67	0.62	0.17	7.12	9.22	3.52
Eu	2.23	1.81	0.093	0.013	0.039	0.006	0.029	0.009	0.024	0.014	0.11	0.90	0.74	0.81	0.19	5.80	9.17	3.78
Gd	2.22	1.82	0.093	0.014	0.039	0.006	0.027	0.115	0.025	0.015	0.12	0.82	0.70	0.97	0.24	0.05	10.59	3.49
Tb	2.10	1.67	0.094	0.013	0.037	0.094	0.028	0.009	0.025	0.015	0.12	0.85	0.68	1.21	0.20	5.53	8.78	3.90
Dy	1.66	1.26	0.097	0.013	0.039	0.014	0.027	0.010	0.025	0.015	0.12	0.84	0.74	0.91	0.23	4.61	9.46	3.92
Ho	1.24	0.93	0.099	0.012	0.038	0.187	0.025	0.011	0.024	0.016	0.12	0.73	0.70	0.94	0.23	5.65	10.79	3.95
Er	1.41	1.03	0.101	0.013	0.039	0.013	0.024	0.012	0.026	0.015	0.13	0.72	0.68	0.94	0.26	5.14	9.55	3.91
Tm	1.26	0.93	0.098	0.013	0.036	0.222	0.023	0.012	0.023	0.014	0.11	0.69	0.69	0.72	0.30	6.78	9.75	4.74
Yb	1.42	1.01	0.097	0.013	0.037	0.011	0.021	0.012	0.022	0.017	0.13	0.84	0.71	1.00	0.26	4.27	7.83	3.24
Lu	1.33	0.95	0.099	0.011	0.038	0.013	0.022	0.011	0.023	0.015	0.11	0.84	0.66	1.04	0.28	5.14	9.45	4.21

Fig. 4 Plots of NASC, UCC, and MMS-normalized REE data from surface sediment of both stations (0–6 cm) (Stn.1 and 2 as black triangle and square, respectively)



Geochemical control on REE distribution

To identify the major processes controlling REE distributions in the mangrove sediment, as well as to set up a relationship between REE and other observed variables, VARIMAX rotated factor analysis was performed (Table 4). VARIMAX rotated

factor loading matrix shows the communalities of the factor analysis that express the percentage of each element variability explained by each retained factor. Factor loading larger than approximately 0.3 are statistically significant (Heidam 1982). Among ten variables, 98% of total variance was accounted for by five variables. Association of Al, Mn, and Fe with LREE and

Table 4 Varimax rotated table matrix for LREE and HREE in the Sundarban mangrove sediments

Variable	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Communality
LREE	0.949	− 0.117	− 0.159	− 0.198	0.130	0.995
HREE	0.925	− 0.125	− 0.098	− 0.266	0.215	0.997
Al	0.602	0.137	0.016	− 0.752	0.222	0.995
Mn	0.418	0.078	− 0.166	− 0.378	0.802	0.995
Fe	0.302	0.277	0.046	− 0.882	0.208	0.992
S	0.190	− 0.840	− 0.289	0.280	0.042	0.905
pH	− 0.032	0.134	0.980	0.097	− 0.086	0.995
Org C	0.078	0.973	0.076	− 0.038	0.111	0.973
PO ₄ -P	− 0.282	0.659	0.658	− 0.180	0.027	0.980
Eh	− 0.273	0.571	0.665	− 0.315	− 0.173	0.971
Variance	2.581	2.560	1.989	1.816	0.851	9.798
% Var	25.8	25.6	19.9	18.2	8.5	98.0

HREE in factor 1, representing 25.8% of the variance among the elements indicated that they were predominately derived from aluminosilicate weathering. Factors 2, 3, 4, and 5 exhibited no significant association with REE and represented 72.2% of the total variance. Association of organic C and PO₄, S, and Eh in factor 2, and Fe, Al, Mn, and Eh in factor 4, and Mn in factor 5 indicated significant role of redox processes for their variance in the sediment system. Phosphate-containing mineral, apatite is enriched in REE (Wright et al. 1987). P was estimated to be 0.3–0.5 g/kg in the sediment (Stn. 1). In another study, Sundarban mangrove sediment was reported as P sink (Ray et al. 2017). Leucogranites belt of the high Himalaya contain apatite (Ayres and Harris 1997). Therefore, in addition to kaolinite, dissolution of apatite on small scale during weathering of granite (Hannigan and Sholkovitz 2001; Banfield and Eggleton 1989) could also account for the REE sources, mobilization, and fractionation in the mangrove sediment. However, occurrence of P-bearing APS mineral is not ruled out.

The significance of the response of the dependent variable (total rare earth elements, \sum REE) versus independent variables (Al, Mn, Fe, S, pH, Eh, OC, PO₄) was tested by stepwise multiple regression analysis (Table 5). In VARIMAX rotated factor analysis, the observed association of REE with Al, Mn, and Fe in factor 1; S, OC, and PO₄ in factor 2; and pH, Eh, and PO₄ in factor 3 justified their use in stepwise multiple regression analysis as independent parameters. Results indicated that Al, Fe, and Mn accounted for 53.7%, 39.3%, and 1.3% of \sum REE variation, respectively and the other environmental parameters (S, pH, Eh, OC, and PO₄) for another 3.9% (regression equation: TREE = − 86 + 0.007 Al + 0.005 Mn − 0.01Fe + 1.2 S + 11.5 pH + 0.07 Eh + 0.16 OC − 105 PO₄, r^2 = 0.98, p = 0.01, n = 15). Linear term Al and Mn were positive, and Fe was negative with respect to \sum REE variation. Graf Jr. (1977) studied the New Brunswick iron formations and observed that REE correlated positively with the aluminosilicate minerals and negatively with the amount of

Fe oxides. Caccia and Millero (2007) suggested that Fe and Al minerals were the primary carrier phases for REE in Florida Bay. Enrichment of LREE in the Sundarban mangrove sediment could be due to their scavenging on the surface of particles such as Mn–Fe oxyhydroxides and clay minerals, or precipitation as REE phosphates (Byrne and Kim 1990) from water. Depletion of HREE from sediment could occur through the formation of both dissolved inorganic and organic strong complexes in water (Millero 1992). The mangrove sediment in the Sundarban had high silt plus clay concentration and OM (Ray et al. 2011, 2014) and these conditions were known to contribute considerably to the retention of REE in mangrove sediments due to strong interaction of REE with clay and OM (Wan and Liu 2006).

Bioaccumulation of REE in mangroves

To our knowledge, the present study represents a first quantification of REE accumulation in mangrove plant organs. We demonstrate that six out of eight mangrove species, i.e., *Avicennia alba* (AA), *A. marina* (AM), *Bruguiera gymnorhiza* (BG), *Ceriops decandra* (CD), *Sonneratia. apetala* (SA), *Aegialitis rotundifolia* (AR) accumulated higher concentration of REE in the root than leaves and wood, while *Aegicerus corniculatum* (AC) and *Avicenna officinalis* (AO) contained higher REE in wood relative to leaves and root. High REE accumulation in roots has been found in several previous reports on other plants (Fu et al. 1998; Tyler and Olsson 2005; Thomas et al. 2014; Carpenter et al. 2015). Nakanishi et al. (1997) also reported accumulation of REE mainly in the roots of seven tropical tree species. However, total REE concentration in the plant biomass was lower than that in sediment pool. The average concentrations of \sum REE in leaf, wood, root of all species and two sediment cores were 0.58 ± 0.2, 1.21 ± 1.1, 3.32 ± 2.5, and 149.5 ± 18 mg kg^{−1}, respectively (Tables 1 and 6). Many studies (e.g., Li et al. 1998; Cao et al. 2000;

Table 5 Multiple regression analysis with a stepwise variable. Dependent variable: total rare earth elements (Σ REE), Independent variables: aluminum (Al), manganese (Mn), iron (Fe), salinity (S), pH, redox potential (Eh), organic carbon (Org C), phosphate ($\text{PO}_4\text{-P}$)

Equations	r^2	p	N
$\Sigma\text{REE} = -25.1 + 0.003 \text{ Al}$	53.7	0.007	15
$\Sigma\text{REE} = -6.1 + 0.002 \text{ Al} + 0.019 \text{ Mn}$	55.0	0.028	15
$\Sigma\text{REE} = -32 + 0.009 \text{ Al} + 0.005 \text{ Mn} - 0.015 \text{ Fe}$	94.3	0.001	15
$\Sigma\text{REE} = -45.4 + 0.008 \text{ Al} + 0.004 \text{ Mn} - 0.014 \text{ Fe} + 0.54 \text{ S}$	94.4	0.001	15
$\Sigma\text{REE} = 16.9 + 0.009 \text{ Al} - 0.0006 \text{ Mn} - 0.015 \text{ Fe} - 0.15 \text{ S} - 6.92 \text{ pH}$	95.4	0.001	15
$\Sigma\text{REE} = 91 + 0.010 \text{ Al} + 0.008 \text{ Mn} - 0.018 \text{ Fe} + 1.4 \text{ S} - 18.6 \text{ pH} + 0.104 \text{ Eh}$	96.1	0.002	15
$\Sigma\text{REE} = 32 + 0.009 \text{ Al} + 0.002 \text{ Mn} - 0.017 \text{ Fe} + 2.2 \text{ S} - 14.3 \text{ pH} + 0.072 \text{ Eh} + 0.052 \text{ Org C}$	96.6	0.009	15
$\Sigma\text{REE} = -86 + 0.007 \text{ Al} + 0.005 \text{ Mn} - 0.010 \text{ Fe} + 1.2 \text{ S} - 11.5 \text{ pH} + 0.072 \text{ Eh} + 0.165 \text{ Org C} - 105 \text{ PO}_4\text{-P}$	98.2	0.015	15

Wen et al. 2001) showed a decreasing REE concentrations in plant organs following the order: root > leaf > stem. LREE concentration was consistently 9–10 times higher than HREE in all plant organs. The transfer of REE from soil to plant is low, and the tendency of decreasing BAF with increasing atomic mass could be due to decreasing ionic radius (Lanthanide contraction) of the HREE (Morrison and Cleland 1983). Tyler and Olsson (2002) observed the variability of concentrations of REE proportional to the ionic radius in non-fertilized Australian soils solutions of 30 forest Cambisols. Similar trend of higher LREE and REE accumulation in root was observed for *Spartina maritima* and *S. fruticososa* marshes (Brito et al. 2018a). Total REE concentration ($\Sigma\text{REE} = \text{HREE} + \text{LREE}$) in leaf, wood, and root was highest in AA (0.8, 0.8, 6.0 mg kg⁻¹) followed by BG (0.4, 2.2, 3.6 mg kg⁻¹), SA (0.2, 0.5, 3.9 mg kg⁻¹), AC (0.5, 2.9, 0.4 mg kg⁻¹), AM (0.1, 0.3, 1.2 mg kg⁻¹), AO (0.7, 1.0, 0.4 mg kg⁻¹), and AR (0.6, 0.2, 0.6 mg kg⁻¹) (Fig. 5). Accumulation of REE in the above-ground and below-ground (live) biomass were estimated to be 168 ± 52 g ha⁻¹ and 72 ± 23 g ha⁻¹, respectively, with LREE contributing ~90% in both biomass pool. Total storage of REE in the forest biomass of the Sundarban mangrove was estimated to be 102.4 ton (AGB-REE + BGB-REE = 71.7 + 30.7 ton) (Table 6).

The bioaccumulation and translocation factors (as BAF and TF, respectively) showed a variety of trends indicating different partitioning of REE within the plant organs. BAF varied significantly among mangrove species with decreasing order of AA >

BG > SA > AC > AR > (CD/AM/AO) (Table 3). All values were less than 1, suggesting these mangroves are hypo-accumulator of REE (Chuis 2004). The BAF > 1 was also reported in vascular plants of Japanese forests (Yoshida and Muramatsu 1997). However, relationships between total REE concentrations in plants and substrate soils are usually weak. Translocation factor (TF) was highest in AC (4.3–10.8) and lowest in AA (0.11–0.12). Except for AC, AO, and AR, the TF values observed for other species were always less than 1. This indicates that the transfer of REE from root to the shoot occurred less effectively for six other mangroves despite the REE enrichment in their root biomass. Such species-specific variabilities in BAF and TF could be attributed to the varying degree of REE root uptake efficiency and recycling by the plant. Pearson's correlation revealed that species-wise correlation between TF and BAF was not significant ($r^2 = 0.08$) except slightly in AA and SA ($r^2 = 0.55$). REE sequestration specific to mangrove plant might be related to environmental factors other than physiological requirements and accumulation (Analuddin et al. 2017).

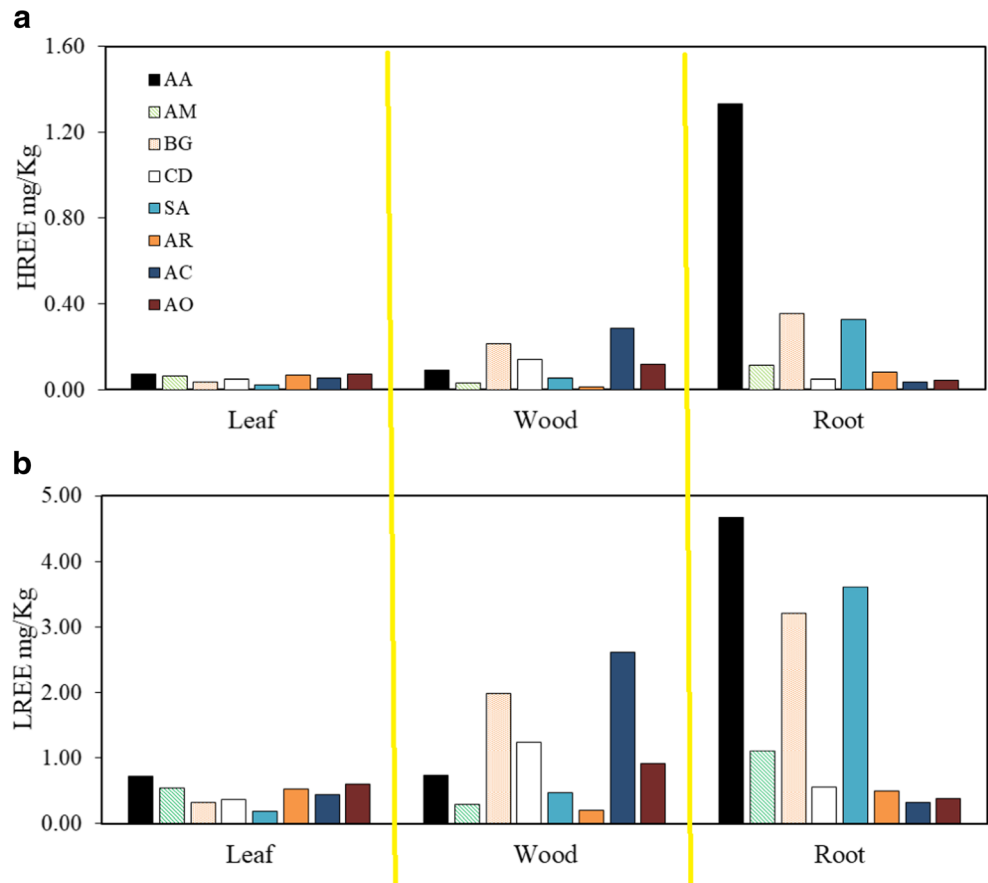
This study revealed that REE was absorbed, mobilized, and partitioned within the mangrove plants growing in sediments with natural levels of REE and mangrove root activity could likely to alter vertical REE distributions in the core samples. Likewise, França et al. (2011) observed the higher concentration of REE in both the roots and shoots than other plant organs in variety of different tropical plant species. High concentrations of REE in the root could be due to replacement of

Table 6 Stock of total rare earth elements (Σ REE), light rare earth elements (LREE), and heavy rare earth elements (HREE) within above-ground biomass (AGB) and live below-ground biomass (LBGB). Here, mean AGB = 93.72 ton DW/ha, BGB = 21.69 ton DW/ha; both values are

REE	Leaf mg kg ⁻¹	Wood mg kg ⁻¹	Leaf + wood mg kg ⁻¹	AGB-REE g ha ⁻¹	AGB-REE ton (total)	Root mg kg ⁻¹	LBGB-REE g ha ⁻¹	BGB-REE ton (total)
ΣREE	0.58 ± 0.2	1.21 ± 1.1	1.8 ± 1.3	168. ± 52	71.7	3.32 ± 2.5	72. ± 23	30.71
LREE	0.53 ± 0.2	1.10 ± 1.0	1.6 ± 1.2	153 ± 47	65.2	3.02 ± 2.1	65. ± 19	27.90
HREE	0.05 ± 0.02	0.11 ± 0.1	0.2 ± 0.1	15 ± 5	6.5	0.30 ± 0.05	6.6 ± 4	2.81

taken from Ray et al. (2011). DW denotes dry weight. Total area of Indian Sundarban of 4264 km² is considered to extrapolate AGB-REE and BGB-REE (g ha⁻¹) to AGB-REE and BGB-REE (ton, in total). Values are as mean ± SD

Fig. 5 Accumulation of (a) HREE and (b) LREE (in mg kg⁻¹) in eight most abundant mangrove plants in the Sundarban (AA: *A. alba*, AM: *A. marina*, BG: *B. gymnorhiza*, CD: *C. decandra*, SA: *S. apetala*, AR: *A. rotundifolia*, AC: *A. corniculatum*, AO: *A. officinalis*)



calcium molecules by REE given the similarity of their ionic radii (Pickard 1970; Hu et al. 2004), resulting in a number of physiological processes involving proteins and enzymes, including root growth, and photosynthesis (Xiaoqing et al. 2009). However, the extent of bioaccumulation from sediment with 140–159 mg REE kg⁻¹ DW is regarded as slightly high for the mangroves and in range of the inhibition concentration (IC25) reported for the native species (*Asclepias syriaca* L., *Desmodium canadense* (L.), *Panicum virgatum* L.) at 100 to 300 mg REE kg⁻¹ DW (Inhibition concentrations causing 25% reductions in plant biomass (Carpenter et al. 2015)).

Other studies in non-mangrove plants showed no sizeable correlation between REE concentrations in soil and plants (Tyler 2004; Wiche et al. 2016). On the contrary, Carpenter et al. (2015) and Mleczek et al. (2018) showed that phytoextraction of REE increases in plant organs (especially in roots) with an increase of their concentration in soil. The mutual relationship between REE, as well as the influence of other elements present in soil, could be a factor that controls the degree of phytoextraction of particular REE (Olivares et al. 2014). Differences between results could be due to the amount of bioavailable forms of REE and also the pH and Eh of soils which significantly influenced REE phytoextraction (Cao et al. 2000, 2001). Mleczek et al. (2018) observed the soil pH of 6.00–6.05 with sizeable uptake of REE confirmed

by BAF > 1. Thomas et al. (2014) found clear differences in the phytoextraction of selected REE (Ce, La, Y) by native Canadian plant species and commonly used crop species in terms of different pH values (4.08 and 6.74). In acidic soils, REE are more toxic to most plant species, and generally inversely correlated with soil pH so that a higher pH value was related to a generally lower phytoextraction of REE (Thomas et al. 2014). The Sundarban sediment is generally neutral to alkaline and reducing in nature (pH 7.2–7.5; Eh – 80 to – 120 mV, Tables 1 and 5) which provides quite low geochemical mobility of REE and their availability to mangrove plants. A small change in soil pH and Eh may strongly modify the degree of REE phytoextraction (Wiche et al. 2016; Khan et al. 2017). The diverse efficiency of phytoextraction of REE could also be an effect of the changes in the physiology of these plants, such as the biosynthesis of selected low molecular weight organic acids (LMWOAs), especially oxalic, acetic, and citric acids (Wiche et al. 2017). The dissolution of REE-bearing phosphate minerals may occur by phosphate solubilizing bacteria (PSB) via phosphatase activity. A low concentration of REE in soil could stimulate plant growth, in contrast to the negative influence of high REE concentrations (Zhang et al. 2013). However, the diverse factors affecting phytoextraction potential of individual plant species are not yet fully identified (de Oliveira et al. 2015). As a result, the use

of solely BAF values for comparison of phytoextraction and phytoremediation potential among different plants species is unwarranted (Kötschau et al. 2014).

Conclusions

This study represents a first quantitative assessment of full set of REE in the mangrove sediment and dominant plants in the Sundarban (India). Although significant spatial differences in total REE concentration between two stations was observed, mangrove plants did not show significant difference of REE enrichment factor, suggesting relationships between total concentrations in plants and in their substrate sediments are weak. There was a tendency of decreasing BAF with increasing atomic mass (and decreasing ionic radius) of the REE. However, considerable species-specific differences in the degree of REE uptake requires further work to quantify plant-available REE pool in the Sundarban mangrove sediments.

Acknowledgements RR is indebted to LabexMER International Postdoctoral Program for providing fellowship (FNP150009-DOCTR-AY). AGG thanks to the Laboratoire d'Excellence LabexMer (ANR-10-LABX-19) and the Postdoctoral program from the Universidad de Las Palmas de Gran Canaria. The authors sincerely thank the Sundarban Biosphere Reserve for giving permission to undertake this study inside the mangrove forest. We thank the editor and reviewer for their comments that helped much improving the manuscript.

Funding information SKM received minor research project grant from the University Grant Commission, New Delhi (No. F, PSW-076/13-14, ERO).

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