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Rare earth elements and heavy metal distribution in estuarine sediments of east coast of India

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Abstract

Bed sediment samples collected from the Hoogly, Godavari, Krishna and Cauvery estuaries on the east coast of India were analyzed for rare earth elements (REEs), mainly lanthanides (La–Lu), Y, a number of metals (V, Cr, Co, Ni, Zn, Ag, Cd and Pb), using Thermal Ionization Mass Spectrometry. Continental weathering plays an important role in the distribution of REEs and metals. However, metals showed wide variation in concentration among estuaries, mainly due to varying salinity, which controls complex estuarine processes, and partly to anthropogenic inputs. Factor analysis of elemental data identified two major groups of elements: (i) LREEs, HREEs, Cd, Pb and Ag, revealing an association with detritals brought in by the rivers; and (ii) V, Cr , Co, Ni and Zn, indicating complex estuarine processes and human input. LREEs are more enriched than HREEs (LREE/HREE ratio varied between 12 and 40) reflecting silicate weathering of crustal materials, and a resultant increase in LREEs in detritals. We conclude that the estuarine system constitutes 70% of LREEs and 30% of HREE flux to the Bay of Bengal.

Introduction

Rare earth elements (REEs), and especially the lanthanides (La–Lu), have received a great deal of attention over the last few decades because their unique chemical behaviour allows them to be used as tracers of a variety of geochemical processes (Henderson, 1984). The role of sediments as carriers and potential sources of rare earth elements and metals is well established and these materials in the aquatic systems will affect surface ecosystems when dispersed by geochemical processes. Land-derived sediments, freshwater and metals all enter the coastal zone at point inputs, the river mouths. Fractionation of REEs and metals occurs predominantly in the solid phase during transport in river systems. Despite a similarity in chemical behaviour, metals and REEs can be partially fractionated, one from the other, by geochemical processes operating in various aquatic environments and can be used as a pointer to their genesis. The coastal zone acts as an ultimate sink for all the elements derived from river systems. Further, it is well established that estuaries regulate the amount of river-borne metals and REEs entering the coastal environment and ultimately the deep ocean (Milliman & Syvitski, 1992). Hence, the study of REEs and metal concentration and their distribution in estuaries becomes essential and can be used to understand low temperature geochemical processes (Sholkovitz, 1995).

Limited information is available on Indian estuaries and deltaic regions. The heavy metal distribution in the Gangetic delta region was briefly studied by earlier researchers (Subramanian et al., 1985; 1987). Naidu (1966) studied the bed sediments of the deltaic region of the Godavari river. Borole et al. (1982) were the first to study chemical aspects of suspended sediments in the estuaries of the Narmada, Tapti, Mahanadi and Godavari rivers. Based on single time sampling

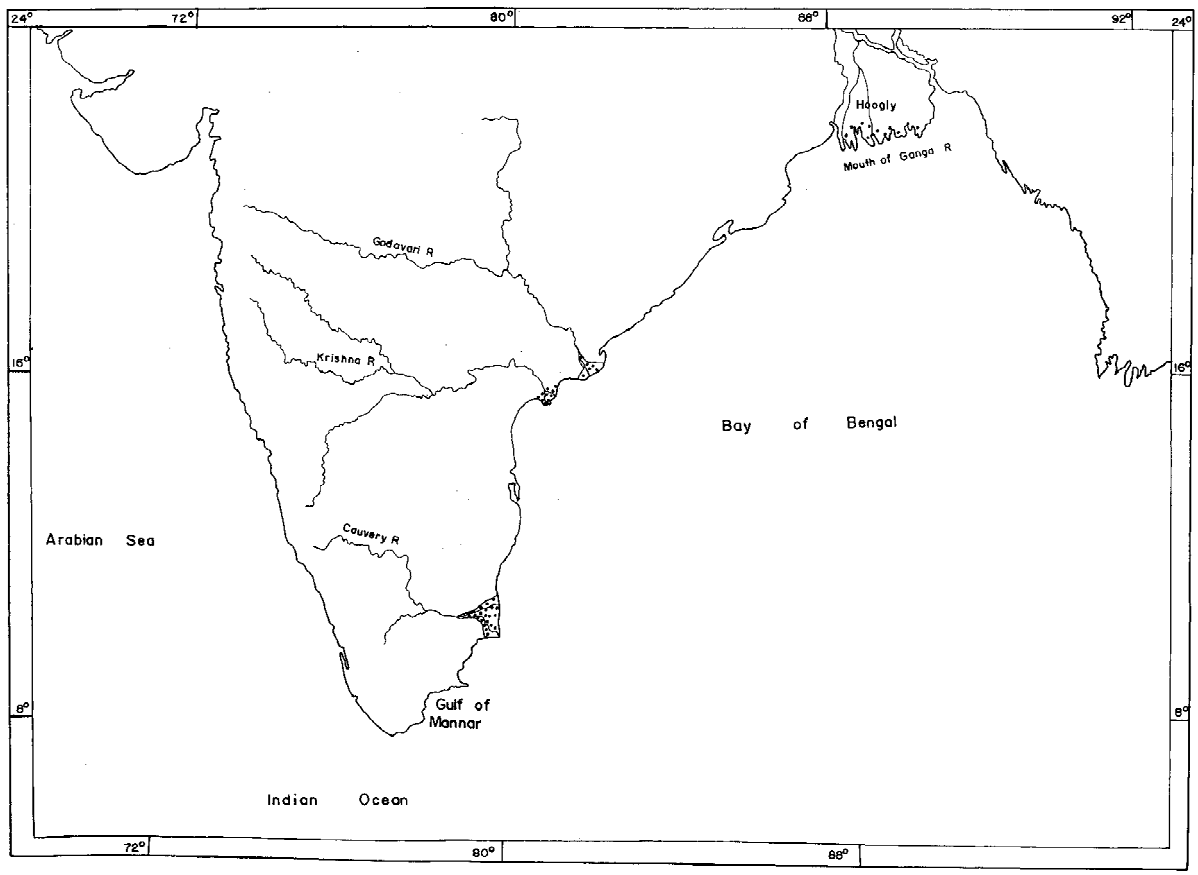

Figure 1. Location map of the major estuaries of the east coast of India, showingthe sites where sediment samples were collected.

(monsoon season), Seralathan & Seetharamaswamy (1982, 1987) reported on the clay mineralogy and trace element chemistry of the Cauvery delta. Later, Ramanathan et al. (1988, 1993) discussed the geochemical characteristics of the Cauvery delta. Most of these authors' works deal with elemental distribution in these estuaries, while trace metals such as V, Ag, Cd and Co were not reported on earlier. Virtually no work has been reported on REE distribution in any of the Indian estuaries and deltaic regions. This paper forms the baseline study for the Hoogly, Godavari, Krishna and Cauvery estuaries (Figure 1). For the first time we are presenting REE distribution in estuarine sediments along the east coast of India and their relation to metal enrichment.

Study area

The study area (8° E to 24° E and 70° N to 81° N) is of importance due to urbanization and agricultural activities, and the Cauvery, Krishna, Godavari and Hoogly estuaries form part of the Peninsular Shield and Bengal Basin. These estuaries formed over the surface of an area that emerged from the sea. Emergence caused rivers to drain further east, resulting in the formation of estuaries. All are well mixed and shallow. Unlike the large Amazon system (discharge 6340 km^3 yr^{-1}), representing a single drainage network, Indian rivers cover different climatological, geographical and geological formations. Rocks in these estuaries range in age from Archaean crystallines (granite, charnokite, gneiss, quartzite) to quaternary sediments (Krishnan, 1982). In addition, the Godavari and Krishna rivers drain Deccan basalts and Gondwanas. The Ganges passes through sedimentary and metasedimentary terrain and subsequently

through quaternary sediments. Archaeans are overlain by Cretaceous, Gondwanas (Mio-Pliocene) and Quaternary sediments. All the estuaries along the east coast of India have alluvial sediments on their surface. The Godavari, Krishna and Cauvery basins together account for over 60% of tropical Indian rivers. They originate in the Western Ghats and flow about 1000 km before discharging to the Bay of Bengal. The climate of the region is semi-arid, where the NE monsoon (Krishna and Cauvery estuary) and the SW monsoon (Godavari and Hoogly estuary) dominate. In the last decade, the population increase in these regions was about 50% (Census, 1991) indicating a growing urbanization and related pollution problems. Land use in areas surrounding the estuaries is dominated by agriculture.

Materials and methods

Figure 1 shows the major estuaries of the east coast of India and the location of the sampling sites. Freshly deposited bed sediments from wet portions of the estuaries were collected from 48 locations, which include the major estuaries – Hoogly, Godavari, Krishna and Cauvery. Bed sediment samples were collected by simple scooping with a plastic spade, care being taken not to lose the fines, and transferred to pre-cleaned plastic bags, sealed and brought to the laboratory, where they were kept at 4 °C until analysis. Prior to sample preparation for ICP–MS analysis, the samples were air-dried. The dehydrated samples were then crushed to a homogeneous powder using mortar and pestle. All samples were prepared in a flux mixture consisting of 100 mg sample, 100–150 mg Li-metaborate ($LiBO_2$, M.P. 845 °C), 100–150 mg Li-tetraborate (LiB_4O_7, M.P. 920 °C).

The samples were then heated at 1050 °C, past the melting point of the flux, in an inert, heat-resistant graphite crucible. Heating was maintained and the crucible regularly agitated, until the sample had completely dissolved in the molten flux. At this point, the melt was poured into a 50 ml aqueous solution of 5% HNO_3. This solution required considerable agitation via shaking and magnetic stirring to get the flux to dissolve with sample into the acidic solution. Each sample was prepared for Plasmaquad analysis by taking 1.5 ml of this dilution, adding 0.1 ml internal standard of 9.997 mg l^{-1}Indium and 8.4 ml deionized water. This preparation yielded an aqueous solution with a whole sediment sample dilution of $\sim$3300 $\times$ and In concentration of 99.97 μg l^{-1}. The extracted samples were analyzed for rare earth elements and metal concentration, using VG thermal ionization mass spectrometer and expressed in μg g^{-1}. The accuracy was checked using two certified sediment samples, BCSS-1 and MESS-1 from the National Research Council, Canada. The results were within the 95% confidence limits of the recommended values given for these two certified materials. Overall analytical precision was $\pm$ 3% for trace metals and REE analyzed.

Results and discussion

The important processes controlling metal cycling are: (i) adsorption/ precipitation/ dissolution (exchange between aqueous and solid phases); and (ii) complexation (conversion among various dissolved forms of the metal). In this, aqueous suspension is the major mechanism for metal movement from land to the coastal environment. In estuaries with a large amount of heavy metal input due to pollution, the bottom sediments bind the heavy metals from the water column acting as a sink for contaminants. Table 1 shows the average REEs and metal composition (in μg g^{-1}) and their range in estuarine sediments of the east coast of India. In general, metals were most enriched most in the Krishna estuary followed by the Cauvery, Hoogly and Godavari estuaries. In the Krishna, V, Ni, Cr and Zn concentrations were higher than in other estuarine sediments. Concentrations of Ag, Cd and Pb were uniformly distributed in all estuarine sediments (1–10% change in standard deviation Table 1), while other metals showed a heterogeneous distribution (10–60% change in standard deviation). For Co and Ag, geological control over their distribution seemed to be remote because their concentration was uniform in all estuarine sediments. Even though the Krishna and the Godavari have an almost similar geological setup, there was a wide variation in their metal distribution, indicating the possible addition of metals by anthropogenic input.

In the Cauvery estuary, all metal concentrations were relatively higher than in the other estuaries and were uniformly distributed, indicating a predominantly geogenic origin. The Hoogly estuarine sediments had a lower metal concentration than the peninsular estuaries, again suggesting geological control. In general, there was enrichment of all metals (particularly Cd and Pb) in comparison to average continental

Table 1. Range, mean (in μg g^{-1}) and standard deviation of rare earth and trace elements in estuarine sediments along the east coast of India

Element	Range	Hoogly (n=11)*	Godavari (n=6)	Krishna (n=9)	Cauvery (n=22)
Salinity	Min–Max	5.50–20.50	0.27–1.12	0.36–3.68	5.5–33.6
	Mean ± SD	9.55 ± 4.56	0.59 ± 0.32	1.03 ± 1.06	20.17 ± 9.57
La	Min–Max	6.68–33.67	15.92–94.38	3.16–18.41	6.44–29.50
	Mean ± SD	21.4 ± 7.18	11.51 ± 6.33	8.3 ± 4.84	18.92 ± 6.65
Ce	Min–Max	12.65–54.41	30.93–167.86	6.02–36.43	11.46–62.71
	Mean ± SD	41.89 ± 14.30	23.38 ± 13.26	17.02 ± 9.52	34.98 ± 14.29
Pr	Min–Max	1.61–7.93	3.63–21.5	0.86–4.34	1.44–7.26
	Mean ± SD	5.03 ± 1.71	2.96 ± 1.59	2.06 ± 1.09	4.41 ± 1.69
Nd	Min–Max	5.28–24.58	11.59–67.31	3.29–13.15	5.19–27.29
	Mean ± SD	15.89 ± 5.2	11.15 ± 5.86	6.84 ± 3.12	18.31 ± 6.63
Sm	Min–Max	0.97–4.74	3.30–13.05	0.78–3.09	1.38–7.98
	Mean ± SD	3.21 ± 1.07	2.27 ± 1.21	1.61 ± 0.74	4.8 ± 1.73
Eu	Min–Max	0.37–0.70	0.43–1.58	0.28–0.53	0.47 -2.44
	Mean ± SD	0.58 ± 0.12	0.38 ± 0.19	0.42 ± 0.10	1.43 ± 0.55
Gd	Min–Max	1.48–4.96	2.45–12.71	0.94–3.23	1.19–7.72
	Mean ± SD	3.53 ± 1.07	2.09 ± 1.02	1.84 ± 0.73	4.64 ± 1.71
Tb	Min–Max	0.19–0.65	0.33–1.54	0.12–0.39	0.17–1.05
	Mean ± SD	0.45 ± 0.13	0.29 ± 0.12	0.24 ± 0.09	0.66 ± 0.23
Dy	Min–Max	1.59–3.97	2.35–9.77	0.88–2.93	0.71–6.46
	Mean ± SD	2.91 ± 0.73	1.58 ± 0.82	1.64 ± 0.66	3.43 ± 1.48
Ho	Min–Max	0.36–0.93	0.53–2.04	0.22–0.66	0.17–1.91
	Mean ± SD	0.66 ± 0.17	0.36 ± 0.21	0.38 ± 0.15	0.77 ± 0.37
Er	Min–Max	0.86–2.09	1.31–4.81	0.46–1.74	0.69–4.11
	Mean ± SD	1.49 ± 0.36	1.23 ± 0.72	0.91 ± 0.43	2.19 ± 0.92
Tm	Min–Max	0.13–0.34	0.14–0.29	0.07–0.33	0.09–0.80
	Mean ± SD	0.23 ± 0.06	0.14 ± 0.08	0.15 ± 0.08	0.44 ±
Yb	Min–Max	0.69–2.06	1.17–4.27	0.44–2.21	0.71–4.42
	Mean ± SD	1.39 ± 0.38	0.92 ± 0.60	0.92 ± 0.55	2.41 ± 0.94
Lu	Min–Max	0.11–0.33	0.19–0.68	0.06–0.39	0.09–0.54
	Mean ± SD	0.23 ± 0.06	0.12 ± 0.07	0.16 ± 0.10	0.37 ± 0.14
Y	Min–Max	9.98–26.12	14.63–41.92	5.65–20.52	4.85–27.66
	Mean ± SD	18.55 ± 4.79	8.77 ± 5.16	10.54 ± 4.92	12.25 ± 5.19

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Table 1. Continued

Element	Range	Hoogly (n=11)*	Godavari (n=6)	Krishna (n=9)	Cauvery (n=22)
LREE	Min–Max	5.4–27.38	2.68–16.58	2.84–15.08	5.18–25.45
	Mean ± SD	17.48 ± 5.88	10.26 ± 5.63	7.16 ± 3.85	16.28 ± 5.94
HREE	Min–Max	0.68–1.9	0.39–1.48	0.41–1.49	0.48–3.08
	Mean ± SD	1.37 ± 0.37	0.84 ± 0.43	0.78 ± 0.34	1.86 ± 0.66
V	Min–Max	42.32–106.29	19.59–108.36	133.21–1037.7	25.35–75.06
	Mean ± SD	71.69 ± 24.39	52.01 ± 42.43	536.75 ±323.89	43.01 ± 14.15
Cr	Min–Max	24.89–96.55	16.08–140.03	71.6–297.92	8.37–116.7
	Mean ± SD	61.46 ± 22.82	50.88 ± 47.9	148.46 ± 66.18	73.39 ± 27.62
Co	Min–Max	4.5–15.54	2.44–14.39	16.16–61.84	3.79–14.69
	Mean ± SD	10.76 ± 4.06	6.04 ± 4.65	37.8 ± 14.16	9.49 ± 4.49
Ni	Min–Max	16.88–58.28	11.47–48.63	58.64–122.22	15.57–66.57
	Mean ± SD	37.5 ± 12.91	23.55 ± 15.62	94.67 ± 21.36	34.16 ± 14.01
Zn	Min–Max	27.23–95.16	8.93–58.91	43.32–379.48	15.58–192.82
	Mean ± SD	64.38 ± 23.91	27.28 ± 22.95	171.12 ± 97.19	49.36 ± 46.54
As	Min–Max	0.04–0.14	0.03–0.11	0.03–0.43	0.09–0.71
	Mean ± SD	0.08 ± 0.02	0.05 ± 0.03	0.14 ± 0.11	0.35 ± 0.17
Cd	Min–Max	0.11–0.69	0.06–0.38	0.11–4.21	0.17–1.26
	Mean ± SD	0.45 ± 0.17	0.18 ± 0.13	0.99 ± 1.24	0.73 ± 0.32
Pb	Min–Max	6.83–14.21	8.08–13.05	3.81–6.01	6.93–22.04
	Mean ± SD	10.49 ± 2.26	10.15 ± 2.11	4.81 ± 0.066	15.12 ± 4.1

*n = Number of samples.

soil (V 90 μg g^{-1}; Cr 70 μg g^{-1}; Co 8 μg g^{-1}; Ni 50 μg g^{-1}; Zn 90 μg g $^{-1}$; As 6 μg g $^{-1}$; Cd 0.35 μg g $^{-1}$; Pb 35 μg g $^{-1}$; Martin & Whitfield 1983). This again indicates input of metals into the estuaries through anthropogenic sources. Besides this, all the estuarine sediments showed metal enrichment in comparison to sediments upstream of the rivers (Subramanian et al., 1985; Ramesh et al., 1989; Ramesh et al., 1990; Biksham et al., 1991 and Vaithiyanathan et al., 1993). At the freshwater/seawater interface, complex physical-chemical processes (flocculation, desorption-adsorption, etc.) take place, which in turn enhance the metal concentration in these estuarine sediments. In addition, estuaries receive urban effluents and agricultural runoff, which further enhance metal concentration in sediments. The results obtained in this study confirm observations on many Indian rivers, such as the Krishna (Ramesh et al., 1989; Ramesh et al., 1990), Ganges-Brahmaputra (Subramanian et al., 1987) and Cauvery river (Vaithiyanathan et al., 1993), all with a downstream increase in heavy metal content.

REE abundance in estuarine sediments provides insight as well into the marine cycling of REEs as the abundance of these elements in the continental crust. It also provides information on sediment-water interaction and redox reactions talking place in surface environments. Table 1 shows the REE abundance and distribution in the estuarine sediments of the east coast of India. REE are divided into two groups: light rare earth elements (LREEs) from La to Sm, and heavy rare earth elements (HREEs) from Gd to Lu (Henderson,

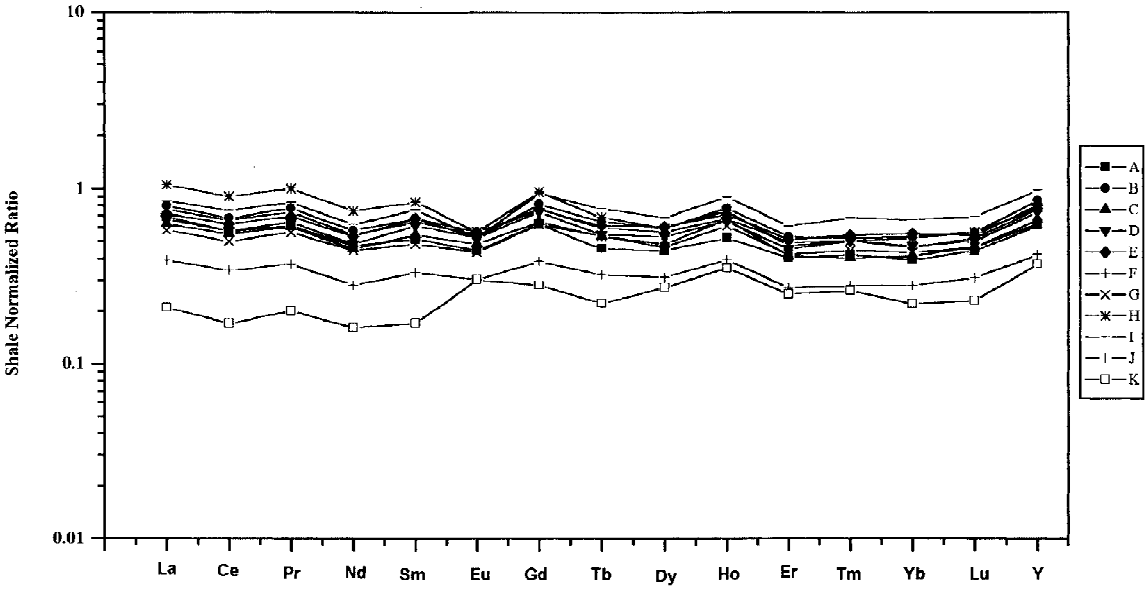

Figure 2. Shale normalized ratios for REEs at various locations from the Hoogly estuary.

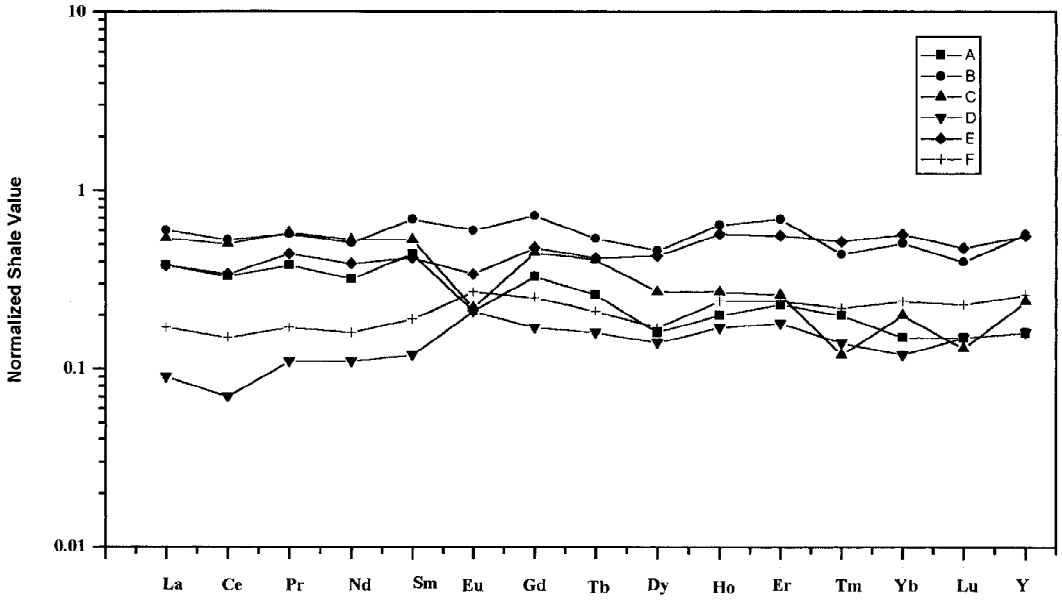

Figure 3. Shale normalized ratios for REEs at various locations from the Godavari estuary.

1984). In general, LREEs are enriched in all estuaries in comparison to HREEs. La is the dominant element, followed by Dy, Yb, Tb, Ho, Er, Eu, Tm and Lu. Y is also abundant and behaves similar to LREEs.

Several researchers (Henderson, 1984; Ravichandran, 1996) recommend the North American Shale Composite (NASC) for normalizing REE concentrations in sediments. These NASC concentrations are: La: 32 mg l^{-1}; Ce: 73 mg l^{-1}; Pr: 7.9 mg l^{-1}; Sm: 5.7 mg l^{-1}; Th: 0.85 mg l^{-1}; Dy: 4.0 mg l^{-1}; Ho: 1.04 mg l^{-1}; Er: 3.4 mg l^{-1}; Tm: 0.5 mg l^{-1}; Yb: 3.1 mg l^{-1} (Haskin et al., 1968). The NASC normalized REE patterns of the estuarine sediments are plotted in Figures 2 to 5. REEs are dominant in the following order: Godavari > Cauvery > Hoogly > Krishna. LREE/ HREE ratios vary by a factor of 12 to 40 in all estuaries other than the Krishna. LREE enrichment reflects the intense silicate weathering of

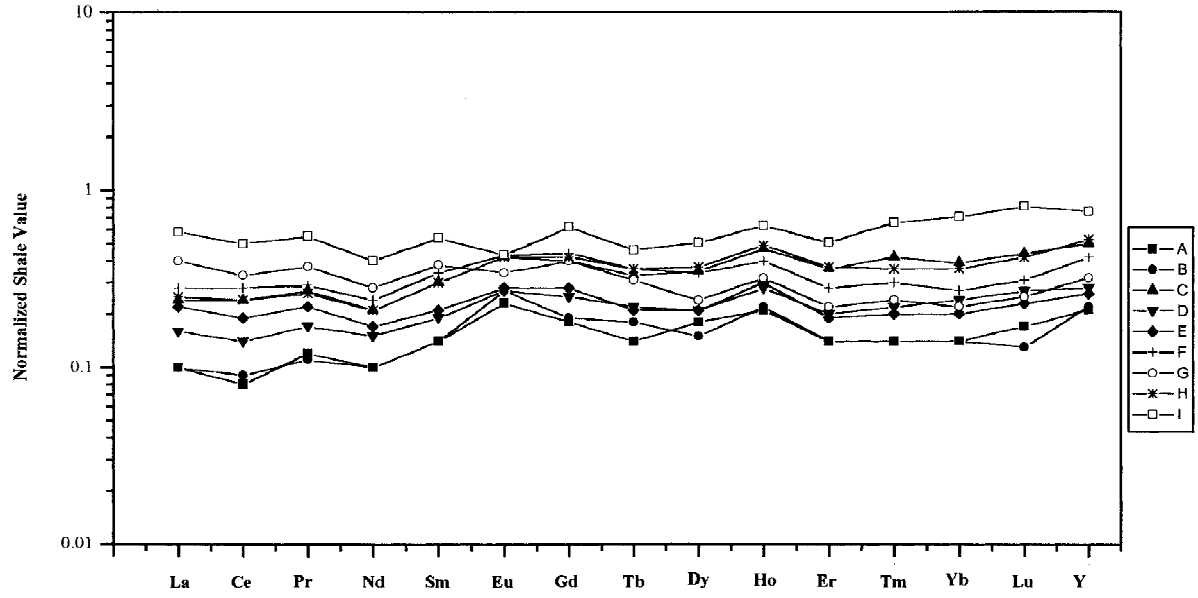

Figure 4. Shale normalized ratios for REEs at various locations from the Krishna estuary.

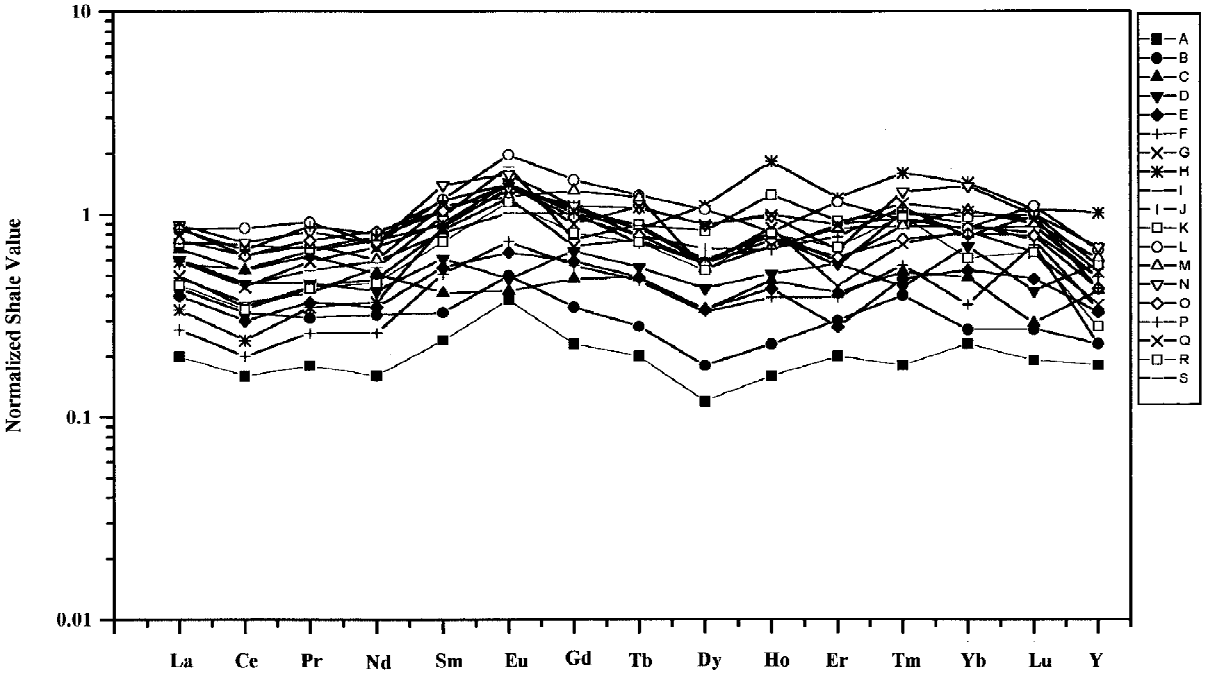

Figure 5. Shale normalized ratios for REEs at various locations from the Cauvery estuary.

crustal materials, and a resultant increase in LREEs in detritals.

The Hoogly and Cauvery estuarine samples were collected exclusively in the high salinity zone and are hence subject to complex physical-chemical processes (adsorption-desorption, flocculation etc.) which in turn enhance the deposition processes. For a few samples there is a slight depletion of LREEs compared with HREEs in the high salinity waters (Figures 2 and 5). This appears to be due to greater mobilization of the LREEs, as suggested by the studies of Goldstein & Jacobsen (1988) and Elderfield et al. (1990). Since

Table 2. Correlation matrix for the major estuaries along the east coast of India (n=48)

	LREE	HREE	V	Cr	Co	Ni	Zn	Ag	Cd	Pb
LREE	1.00									
HREE	0.72	1.00								
V	−0.27	−0.25	1.00							
Cr	−0.01	−0.02	0.81	1.00						
Co	−0.18	−0.14	0.93	0.86	1.00					
Ni	−0.15	−0.12	0.87	0.85	0.96	1.00				
Zn	0.12	0.06	0.81	0.82	0.85	0.81	1.00			
Ag	0.37	0.71	−0.09	0.16	−0.01	−0.02	0.71	1.00		
Cd	0.18	0.33	0.54	0.67	0.56	0.44	0.63	0.50	1.00	
Pb	0.63	0.80	−0.52	−0.25	−0.43	−0.40	−0.27	0.71	0.10	1.00

Table 3a. Correlation matrix for the Hoogly estuary

	LREE	HREE	V	Cr	Co	Ni	Zn	Ag	Cd	Pb
LREE	1.00									
HREE	0.93	1.00								
V	0.43	0.47	1.00							
Cr	0.28	0.29	0.96	1.00						
Co	0.35	0.36	0.98	0.95	1.00					
Ni	0.27	0.31	0.96	0.96	0.97	1.00				
Zn	0.43	0.43	0.96	0.88	0.95	0.92	1.00			
Ag	0.36	0.49	0.55	0.48	0.46	0.56	0.46	1.00		
Cd	0.77	0.68	0.67	0.57	0.67	0.57	0.64	0.26	1.00	
Pb	0.30	0.29	0.78	0.80	0.80	0.74	0.71	0.13	0.74	1.00

Table 3b. Correlation matrix for the Godavari estuary

	LREE	HREE	V	Cr	Co	Ni	Zn	Ag	Cd	Pb
LREE	1.00									
HREE	0.73	1.00								
V	0.44	0.94	1.00							
Cr	0.22	0.74	0.86	1.00						
Co	0.50	0.90	0.92	0.59	1.00					
Ni	0.46	0.92	0.97	0.72	0.98	1.00				
Zn	0.43	0.93	0.99	0.91	0.87	0.94	1.00			
Ag	0.16	0.39	0.41	0.01	0.61	0.52	0.32	1.00		
Cd	0.59	0.93	0.91	0.89	0.74	0.83	0.94	0.23	1.00	
Pb	0.34	0.37	0.34	−0.04	0.60	0.47	0.26	0.52	0.05	1.00

they drain crystalline and sedimentary terrains, they are dominated by detritals rich in quartz and feldspars. Hence LREEs were used as the best approximation of the continental weathering process and the composition of the modern continental surface. Further, it is also observed from the above discussion that 70% of REE supply (flux) by these rivers via estuaries to the Bay of Bengal is made up of LREEs, and the remaining is made up of HREEs.

Table 3c. Correlation matrix for the Krishna estuary

	LREE	HREE	V	Cr	Co	Ni	Zn	Ag	Cd	Pb
LREE	1.00									
HREE	0.90	1.00								
V	0.77	0.90	1.00							
Cr	0.88	0.93	0.84	1.00						
Co	0.83	0.93	0.91	0.94	1.00					
Ni	0.74	0.86	0.92	0.85	0.96	1.00				
Zn	0.85	0.87	0.80	0.99	0.93	0.84	1.00			
Ag	0.72	0.73	0.59	0.86	0.69	0.56	0.86	1.00		
Cd	0.82	0.85	0.68	0.94	0.78	0.64	0.92	0.95	1.00	
Pb	0.68	0.63	0.47	0.59	0.50	0.43	0.55	0.67	0.65	1.00

Table 3d. Correlation matrix for the Cauvery estuary

	LREE	HREE	V	Cr	Co	Ni	Zn	Ag	Cd	Pb
LREE	1.00									
HREE	0.59	1.00								
V	0.50	0.11	1.00							
Cr	0.49	0.30	0.73	1.00						
Co	0.69	0.61	0.66	0.56	1.00					
Ni	0.69	0.53	0.77	0.72	0.94	1.00				
Zn	0.50	0.27	0.28	0.23	0.20	0.34	1.00			
Ag	0.44	0.65	−0.04	0.25	0.39	0.29	0.25	1.00		
Cd	0.27	0.59	−0.27	−0.04	0.20	0.04	−0.10	0.71	1.00	
Pb	0.69	0.78	0.02	0.23	0.51	0.44	0.49	0.77	0.58	1.00

Table 4. Overall estimate of varimax rotated factor matrix for major estuaries along the east coast of India (n=48)

	Variance Rotated Matrix			
	Factor 1	Factor 2	Factor 3	Communality
LREE	−0.03	0.97	−0.09	0.95
HREE	−0.10	0.84	0.42	0.88
V	0.94	−0.02	0.02	0.92
Cr	0.92	0.05	0.22	0.89
Co	0.94	−0.18	0.18	0.96
Ni	0.94	−0.08	0.18	0.90
Zn	0.85	−0.37	0.37	0.85
Ag	−0.04	0.45	0.85	0.93
Cd	0.53	0.89	0.89	0.79
Pb	−0.42	0.72	0.44	0.89
Eigen Value	5.10	3.17	0.67	
Variance (%)	51.00	31.70	6.70	
Cum. Var*.	82.80	82.80	89.50	

*Cumulative variance.

Factor and correlation analysis was used to delineate the sources of heavy metal and REEs and their interrelationships (Tables 2 to 5). Overall correlation of all estuarine sediment samples reveals a good correlation between LREEs, HREEs, Pb and partially Ag (Table 2). Correlation matrix of the REEs, and metal data for individual estuaries are shown in Tables 3a, b, c and d. They show moderate to good correlations, except certain metals like Ag–V; Ag–Co; Pb–Cr; Pb–Ni. This is mainly because the sediments are homogeneous influencing the elemental composition. Among the REEs, metals such as Pb and Ag show good correlation, and Cd shows a moderate correlation with HREEs.

Factor analysis (Table 4) indicates three trends in the data. Using ten variables, nearly 83% of total variability was accounted for by two factors. The number of significant factors was established considering only those with an Eigenvalue > 1.0. Factor 1 represents over 50% of the variance among elements. The metals

Table 5. Varimax Rotated Factor Matrix for the Major Estuaries along the East Coast of India

Variance	Rotated Factor Matrix											
	Hoogly			Godavari			Krishna			Cauvery		
Element	Factor 1	Factor 2	Com*.	Factor 1	Factor 2	Com.	Factor 1	Factor 2	Com.	Factor 1	Factor 2	Com.
LREE	0.13	0.96	0.95	0.35	0.92	0.98	0.74	0.57	0.89	0.56	0.64	0.77
HREE	0.12	0.93	0.88	0.60	0.78	0.96	0.77	0.47	0.94	0.36	0.36	0.78
V	0.26	0.28	0.92	0.93	0.37	0.97	−0.02	0.19	0.96	0.54	0.22	0.89
Cr	0.97	0.12	0.89	0.66	0.70	0.99	0.90	0.39	0.98	0.81	0.81	0.69
Co	0.33	0.17	0.96	0.80	0.58	0.99	−0.22	0.24	0.98	0.65	0.54	0.86
Ni	0.96	0.12	0.90	0.87	0.45	0.97	0.78	0.19	0.96	0.91	0.91	0.93
Zn	0.25	0.26	0.85	0.51	0.84	1.00	−0.29	0.38	0.98	0.36	0.32	0.96
Ag	0.38	0.22	0.93	0.13	0.81	0.92	0.21	0.96	0.98	0.13	0.13	0.78
Cd	−0.22	0.77	0.79	0.18	0.31	0.96	0.21	0.73	0.97	0.13	0.46	0.86
Pb	0.83	0.28	0.89	0.21	0.722	0.98	0.18	0.33	0.98	0.18	0.18	0.92
Eigen Value	6.68	1.80		6.27	0.36		6.66	0.75		4.97	2.42	
Variance (%)	66.80	18.00		89.60	5.20		83.10	9.30		49.80	24.20	
Cum. Var§.	66.80	84.80		89.60	94.80		83.10	92.40		49.80	74.00	

*Communality., §Cumulative variance.

involved namely, V, Cr, Co, Ni and Zn, suggest that these are derived partly from anthropogenic inputs and partly due to complex estuarine processes. Factor 2 accounts for over 30% of the variance and represents LREEs, HREEs, Cd, Pb, and Ag, revealing their geochemical association with detritals brought by the rivers. This trend is more or less similar in the Hoogly and Cauvery estuaries (Table 5). In the Krishna and Godavari estuaries the situation is entirely different, mainly because all elements are confined to one factor, indicating that geochemical weathering plays a major role in their distribution, with estuarine processes and anthropogenic input relatively insignificant.

Individual correlation and factor analysis show that geochemical weathering brought by the rivers has undergone complex estuarine alteration before entering the sea along with additional anthropogenic inputs. This elemental behaviour clearly reveals a role of salinity and other physical-chemical processes in the geochemical behaviour of REEs major elements in these estuarine zones. The Hoogly and Cauvery have higher estuarine salinity, hence behaviour of elements is similar, even though they possess a diverse geology, geographical positioning and climatic conditions.

Conclusions

Geochemical weathering plays a significant role in REE and elemental distribution in the major estuaries of the east coast of India. Continental weathering processes are the main source for REEs and metal distribution in these estuaries and there is no significant input from coastal/ marine environments. These elements are considerably altered in estuarine zones of different salinities due to complex physical-chemical processes operating here. Anthropogenic input of these elements to the estuaries is also inferred. These river-estuarine systems constitute a LREEs flux (70%)∼ and HREEs flux (∼30%) to the Bay of Bengal in almost similar proportions. Hence, we suggest that REE distribution in these estuaries can be used as an approximation of continental weathering processes on the Indian sub-continent.

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