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Distribution of rare earth elements and heavy metals in the surficial sediments of the Himalayan river system

R. RAMESH,[1] AL. RAMANATHAN,[2] S. RAMESH,[1] R. PURVAJA[1] and V. SUBRAMANIAN[3]

[1]Institute for Ocean Management, Anna University, Chennai 600 025, India
[2]Department of Geology, Annamalai University, Annamalai Nagar 608 002, India
[3]School of Environmental Sciences, Jawaharlal Nehru University, New Delhi 110 067, India

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Rare earth elements (REEs) are considered as useful tracers of various surface geological processes in the river system. REEs and heavy metals (V, Pb, Cr, Co, Ag, Zn, Cd, Ni) were analyzed from the suspended sediments of Ganges and surficial sediments of Yamuna, Brahmaputra, Jamuna, Padma and Meghna, using VG Thermal Ionization Mass Spectrometer. Physical weathering process seems to be a major controlling factor for the distribution of REE and trace metals in the sediments of the Himalayan rivers. Weathering of the surface crustal area in the drainage basin shows significant variations due to changes in lithology and influence of tributaries. The distribution of REE shows an almost uniform pattern due to factors such as river transportation processes and high level of terrigenous mixing in the bed sediments. The results show that finer grain size and high content of clay mineral (illite) in these sediments are possible traps for the accumulation of metals. Anthropogenic activities seem to have very little influence in controlling the elemental distribution in the Himalayan rivers.

INTRODUCTION

Rare Earth Elements (REEs) and heavy metals possess some unique but, identical physical and chemical properties, which make them useful probes of low temperature geochemical reactions. REE in terrigenous grains are largely unreactive (Sholkovitz *et al.*, 1994) and contribute an inherited signature. The role of sediments as carriers and potential sources of REEs and metals is well established and a number of studies on river basin and estuaries have yielded fundamental features of the aquatic geochemistry of the REEs (Martin *et al.*, 1976; Goldstein and Jacobsen, 1987; Sholkovitz and Elderfield, 1988; Elderfield *et al.*, 1990; Sholkovitz, 1992, 1993, 1995; Sholkovitz *et al.*, 1992; Ramesh *et al.*, 1999). These studies indicate that chemical-weathering reactions on the continent leads to extensive fractionation between the dissolved REEs and that of the river suspended particles and continental rocks. Fractionation of REEs and metals occur predominantly in the solid phase during transport in the river systems.

The Ganges-Brahmaputra (Himalayan river system) one of the world's largest river ranks first in terms of sediment transport and fourth in terms of water discharge (Fig. 1). Despite its global significance, the distribution of REE in surficial sediments of these Himalayan rivers is still poorly known (Martin and Meybeck, 1979). However, studies have been carried out by various researchers on the heavy metal distribution and geochemical characteristics of the Himalayan rivers (Galy and France-Lanord, 1999; Subramanian, 1993; Subramanian and Jha, 1988; Subramanian *et al.*, 1985, 1987a, 1987b, 1988; Krishnaswami *et al.*, 1992; Modak *et al.*, 1992; Sarin *et al.*, 1989, 1990).

All the above research work on the Himalayan rivers, have been carried out within the territorial boundary of the Indian subcontinent. Nearly 80% of the lower reaches of Himalayan rivers draining in the Bengal Basin falls under the political bound-

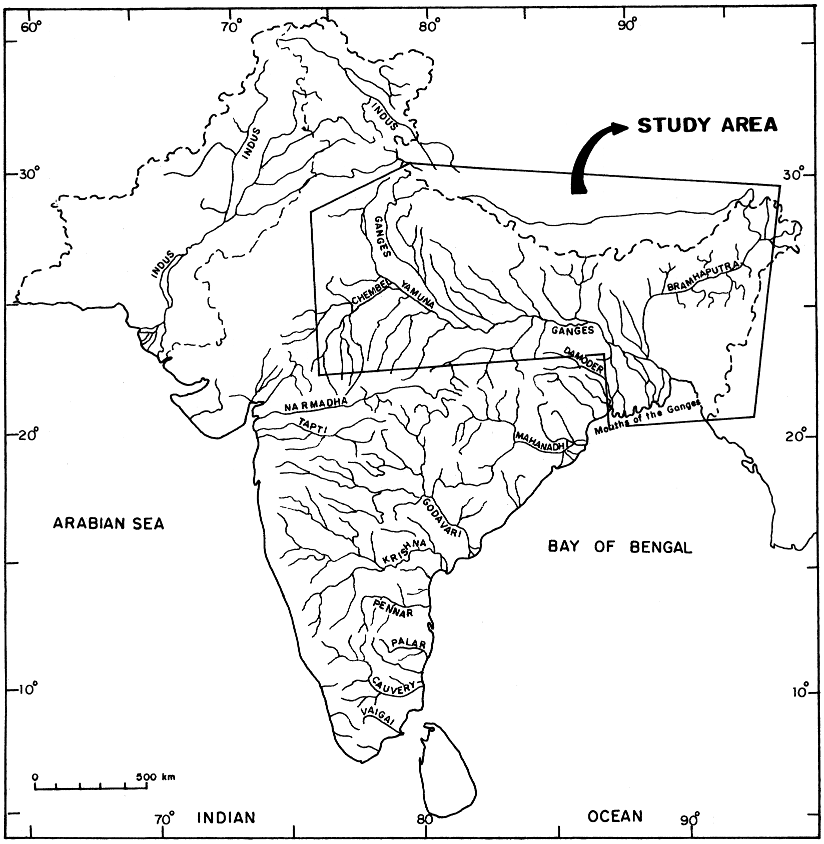

Fig. 1. Location map of the Ganges, Brahmaputra and the Bengal Basin.

ary of Bangladesh, but only scant information is available on the distribution and fractionation of heavy metals in this region (Datta and Subramanian, 1997, 1998). Furthermore, to the authors' knowledge, there has been no study on the REE composition of river sediments in India, in particular the Himalayan rivers. Thus, this paper attempts to provide a comprehensive database for one of the highest sediment dispersal systems of the world and also to understand the behavior of REEs during weathering and transport in a secondary sedimentary environment.

STUDY AREA

Ganges

The drainage basin of the Ganges River, occupies an area of about 10^6 km^2 of the Indian subcontinent (Rao, 1975), covering virtually the entire Northern India (Fig. 2(a)). The Ganges originates from the Gangothri and drains in the Himachal-Kumaon region of Himalayas, where the dominant lithology is fine-grained sericite chlorite schist. The outer Kumaun Himalayas are composed of Miocene to Pleistocene age sediments. In the central and lower Himalayas, there are three main zones: a) the outer Krol belt of upper carboniferous age consisting of dolomitic limestone, calcareous shale and sandstones; b) the inner sedimentary belt consisting of thick limestone, over-lined by a sequence of shales and quartzites and c) the zone of metamorphic and igneous crystalline rocks separating the two units above. These rocks are dominated by biotite-chlorite schist, augen gneisses and granites (Valdiya, 1980; Wadia, 1981). The tributaries joining from the northern side drains mostly in outer Himalayas of Siwalik system. The main channel of the Ganges predominantly drains alluvial sediments of recent origin (Valdiya, 1979).

The tributaries of Yamuna (Fig. 2(b)) drain into two different lithological domains. The tributaries joining from the southern side of the river drains into the Bundlekhand plateau, which is a stable block made up of Bundlekhand gneiss and schist of the Precambrian age. The headwaters of the tributaries Chambal, Betwa and Ken draining into the Deccan basalts, contribute to most of the mafic-rich elements into the river system (Valdiya, 1979).

Brahmaputra

The Brahmaputra River originates from the Chamyungdung glacier at an elevation of 5200 m in the Tibetan Himalayas (Fig. 2(c)). The lithology of the southern part of Tibetan plateau mostly comprises the Tethyan sedimentary series, composed primarily of the palaeozoic-mesozoic carbonates and clastic sediments. Himalayan crystalline rocks are the main formations in the higher ranges and consist of ortho- and para-gneisses, migmatites and marbles (Burg *et al.*, 1984). Gansser (1983) described leucogranite sheets, tens of hundreds of meters thick within the high Himalayan crystallines in the southern wall of the Khula Khangri massif and reported that this rock type occurs in the total Khula Khangri range of Nepal. The headwaters of the river drain mostly into the Nepal-Sikkim Himalayas and Bhutan-Arunachal Himalayas. The Nepal-Sikkim region is dominated by the quartzopelitic series, quartzite, gray schist, biotite gneiss and calcareous bluish black shale (Remy, 1979). Apart from metamorphics, high Himalayan crystallines are also exposed in central Bhutan (Edwards *et al.*, 1999). The Bhutan-Arunachal Himalayas is dominated by the high-grade metamorphic rocks (migmatites), ortho gneiss, mica schist, marble, cal-silicates, apart from the Tethyan sediments like limestones, phyllites and schists (Janpangi, 1979). The samples for the present study has been collected from the main channel of the Brahmaputra which is draining into the recent alluvium of Assam apart from the Siwalik sediments, which is dominated by the gritty slate, feldspathic quartzite, cherty quartzite and phyllite and Darjeeling gneiss in the south (Acharya, 1979).

Bengal Basin

The Ganges and Brahmaputra river merge in Bangladesh and subsequently break up into a number of distributaries called the Bengal Basin before they drain into the Bay of Bengal (Fig. 2(d)). Most of the drainage area consists of the deltaic recent alluvium and estuarine sediments. They are estimated to cover an area of approximately 200,000 km^2 within the political boundaries of India and Bangladesh. The Bengal basin is one of the largest deltas of the world (Coleman, 1981), which is mainly drained by the rivers Jamuna, Padma and Meghna. The river system supplies sediments to the Bay of Bengal and then to the biggest submarine-fan (Bengal Fan) in the world (Kuehl *et al.*, 1989). This region has a low level of industrialization, but extensive areas are under irrigation. This region also has a high population density that is one of the highest in the world, ranging from 400 to 1200 people per km^2 (Milliman *et al.*, 1989).

The Bengal Basin is underlain by Pre-Cambrian basement rocks, bordered on the west by the Indian Shield, north by the Shillong Shield, east by the Naga-Lusai orogenic belt and is open to the Bay of Bengal in the south (Sengupta, 1966). Nearly 85% of the basin is covered by alluvium of Pleistocene and recent age (Alam *et al.*, 1990). The bedrock that is exposed in the Bengal Basin can be broadly grouped into the Neogene (mainly clastic sediments with intercalated sandstone and shale) and Palaeogene (alternative sandstone, siltstone, shale and limestone).

Materials and methods

The Ganges-Brahmaputra river system, the Bengal Basin along with the sampling stations is shown in Figs. 1 and 2(a) to 2(d) respectively. For this study, freshly deposited bed sediments were collected from 43 locations and suspended

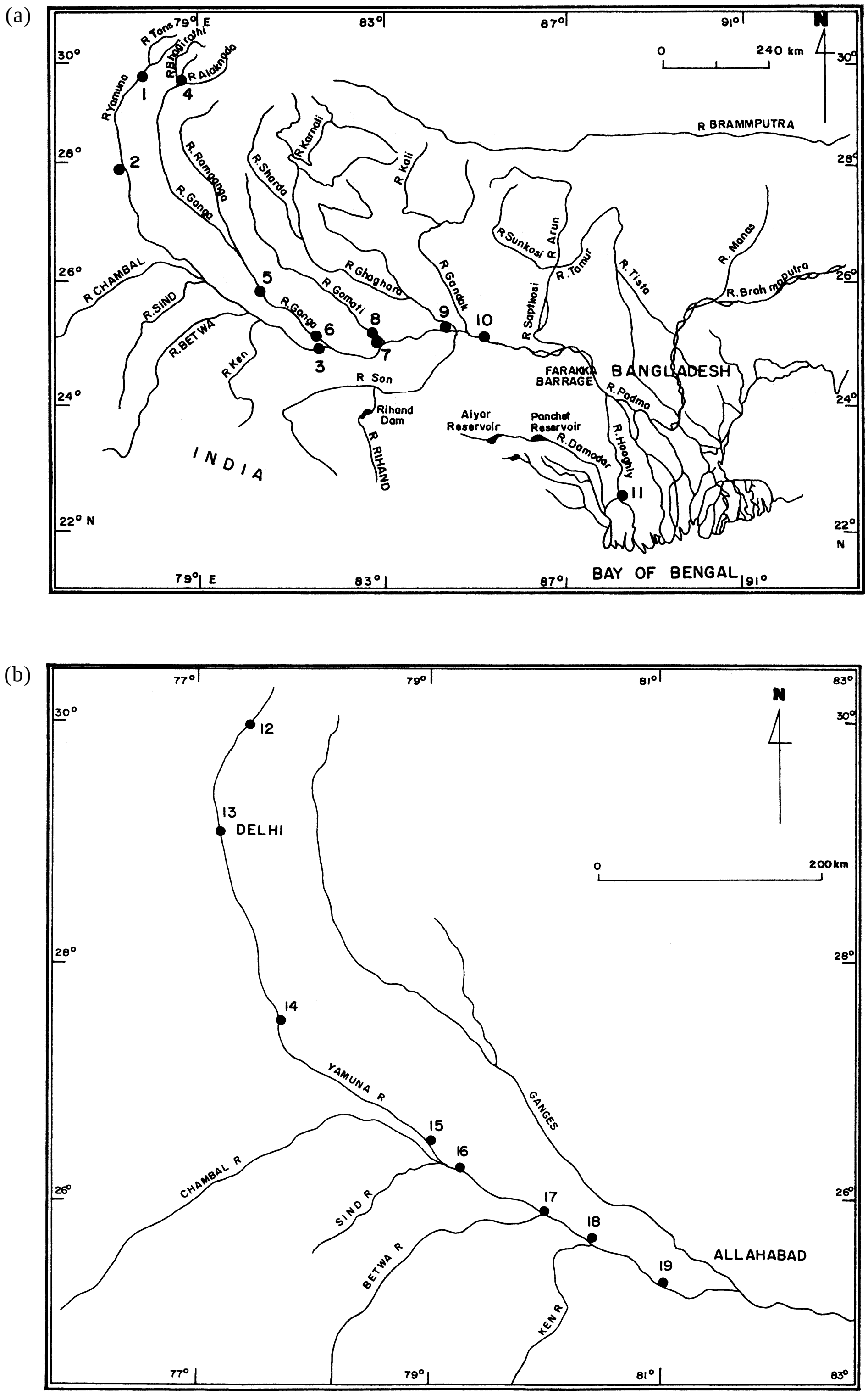

Fig. 2. Location map of the rivers a) Ganges, b) Yamuna, c) Brahmaputra and d) Jamuna-Meghna-Padma showing locations of sediment sampling.

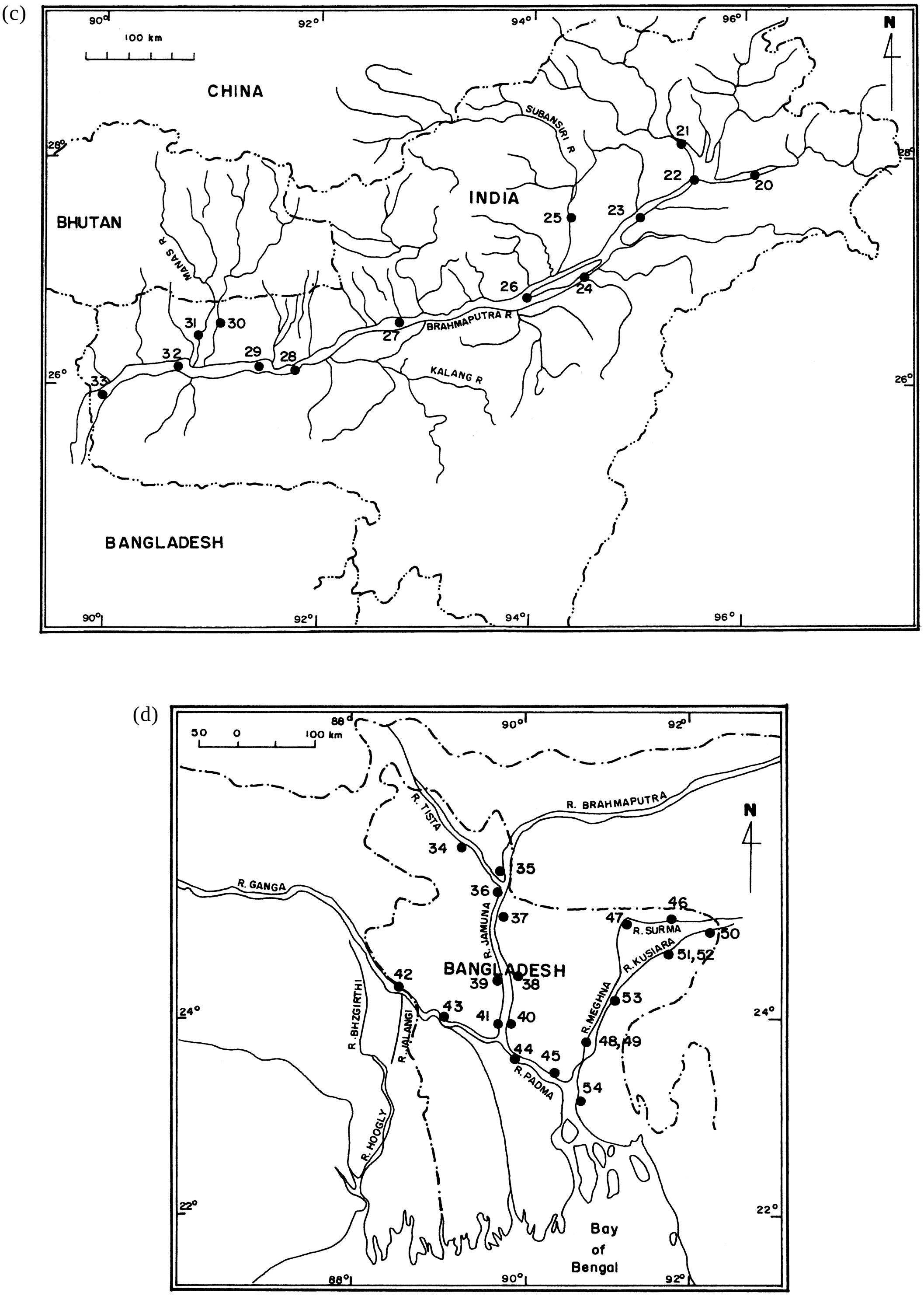

Fig. 2. (continued).

sediments from 12 locations in the Himalayan river system. Allegre *et al.* (1996) demonstrated that the composition of river suspended sediments would be highly useful in tracing the chemical composition of the continental crust. Suspended sediment samples were collected from a large volume of water sample at 12 locations along the main stream of the Ganges river. Bed sediments include 14 samples from Brahmaputra, 8 from Yamuna, 4 from Padma, 8 from Jamuna and 9 from Meghna. Bed sediments were scooped with a plastic spade, care being taken not to lose the fines, transferred to pre-cleaned plastic bags, sealed and brought to the laboratory. The sediment samples were kept at 4°C until prepared for further analysis. Prior to sample preparation for VG Thermal Ionization Mass Spectrometer analysis, the sediment samples were air-dried in the laboratory.

The dehydrated samples were then crushed to a homogeneous powder using a mortar and pestle. All samples were prepared in a flux mixture consisting of 100 mg sample, 100–150 mg lithium metaborate ($LiBO_2$) (melting point: 845°C), 100–150-lithium tetra borate (LiB_4O_7) (melting point: 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 then 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 Plasma Quad analysis by taking 1.5 ml of this dilution, adding 0.1 ml internal standard of 9.997 $\mu g\ l^{-1}$ Indium and 8.4 ml deionized water. This preparation yielded an aqueous solution with a whole sediment sample dilution of ~3300× and In concentration of 99.97 $\mu g\ l^{-1}$. These extracted samples were then analyzed for REE and metal concentration, using a VG Thermal Ionization Mass Spectrometer at Harvard University. 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 ±3% for the trace metals and REE analyzed. The low value of Er observed in sample number 17 in the Yamuna river appears to be an analytical error.

RESULTS AND DISCUSSION

The average concentrations of major elements in surficial sediments and the distribution of clay minerals in the Himalayan rivers from the earlier studies are given in Tables 1(a) and 1(b). It can be observed that Si in the Ganges-Brahmaputra (GB) basin and the average for the Indian rivers, is much more than average concentration for the rivers and surficial rocks of the world, whereas Al and other major elements are less than or equal to world average and surficial rocks (Table 1(a)). In G-B system illite is the most abundant clay mineral (Table 1(b)) followed by kaolinite, smectite and chlorite (Sarin *et al.*, 1989). Illite and kaolinite constitute 80% of the total clay mineral distribution in the rivers of the Bengal basin (Meghna, Padma and Jamuna) and has an almost negligible montmorillonite content (Datta and Subramanian, 1997). The richness of illite is related to the dominance of its precursor, the muscovite type mica in the source rock (Segall and Kuehl, 1992) and due to the neotectonic activity of the basin (Irion, 1991; Pant and Sharma, 1993). The ratio of physical/chemical erosion rate is very high in Gandhak and Son followed by Ganges, Brahmaputra and Yamuna (Galy and France-Lanord, 1999). The abundance of Si, Al, kaolinite and illite also confirm the higher physical erosion rate in G-B system.

Generally, bulk of the REE reside in the silt and clay size fraction however, a direct correlation does not exist between the REE and clay minerals. Nevertheless, the clay structure is important for the accumulation for trivalent REE (McLennan, 1989). Rare earth elements in the sedimentary rocks are mostly terrigenous and reveal the source rock composition reflecting the

Table 1(a). Average concentration of major elements (in wt. %) in the Himalayan river sediments in comparison to the Indian, World river sediment averages and surficial rocks

	Ganges[1]	Brahmaputra[1]	Indian average[1]	World average[2]	Surficial rocks[2]
Si	31.2	28.4	24.5	28.5	27.5
Al	4.66	5.6	5.0	9.4	6.93
Fe	2.2	2.9	2.9	4.8	3.59
Mg	1.32	1.66	1.47	1.18	1.64
Ca	2.34	1.93	2.46	2.15	4.5
Na	—	—	—	0.71	1.42
K	1.33	1.24	1.21	1.42	2.44

[1] *After Subramanian et al. (1987a).*
[2] *Martin and Meybeck (1979).*

Table 1(b). Clay mineral distribution in the Himalayan River sediments (in wt. %) (after Sarin et al., 1989)

Locations	Clay mineral			
	Smectite	Illite	Kaolinite	Chlorite
Devprayag	—	78.0	11.0	8.0
Kanpur	35.4	53.2	6.3	5.2
Varanasi	78.2	15.1	3.4	3.3
Aricha	56.2	31.9	5.4	7.0
Agra	25.0	58.4	9.2	7.4
Hamirpur	71.1	22.4	3.2	3.2
Ghagara (Ayodhya)	19.2	59.2	11.7	10.0
Brahmaputra (Gauhati)	—	62.5	18.8	18.8
Gaolpara	—	57.1	22.7	20.2
Arichaghat	15.2	61.7	12.3	10.9

REE distribution in the exposed continental crust (McLennan, 1989). By comparing the concentration of REE in samples of relative origin, it is possible to trace some of the processes responsible in the geochemcial evolution of the sample by following changes in REE distribution (Coryell *et al*., 1963). The geochemistry of large rivers will provide insights to the erosional processes of the study region on a global scale due to the differential mobility-taking place between the metals by denudation (Stallard and Edmond, 1987; Negrel *et al*., 1993). Water-rock interaction, especially at low temperature is unlikely to cause substantial change in REE distribution in all sediments. Hence the REEs are insoluble with extremely low concentrations in dissolved form in river and are mainly transported and deposited as detrital materials in the river basins (Henderson, 1984; Sholkovitz, 1995). The REE has chemical properties, which make them excellent natural probes of particle/solution interaction and redox reactions at the earth's surfaces. To check the accuracy and precision of the measurements, reference materials (MESS-1; BCSS-1) were also analyzed (Table 2). Repeated measurements for elemental abundances are in good agreement (±3%) with the reported values. The concentration of REEs measured in various surficial sediments of the Himalayan rivers are given in Table 3. REE distribution in the Himalayan rivers shows a fairly distinct variation among these rivers. Table 3 also shows that the LREEs are enriched by a factor of about 16 to 27 when compared to HREEs in all the rivers of the Himalayan system. Cerium (Ce)

Table 2. Concentration of the reference materials (NRC, 1990) and the recommended values ($\mu g\ g^{-1}$)

Elements	MESS-1 Recom. value	MESS-1 Average value*	BCSS-1 Recom. value	BCSS-1 Average value*
Y	35	36 ± 7	50	52 ± 11
V	100 ± 17	103 ± 21	110 ± 4.9	112 ± 16
Cr	60 ± 11	62 ± 13	90 ± 14	92 ± 13
Co	14 ± 1.9	14 ± 3	18 ± 2.1	18 ± 3
Ni	50 ± 2.7	52 ± 11	70 ± 3.6	71 ± 10
Zn	200 ± 17	206 ± 42	140 ± 12	143 ± 20
Ag	ND	0.01	ND	0.02
Cd	0.5 ± 0.10	0.52 ± 0.1	ND	0.41
Pb	40 ± 6.1	41 ± 8	28 ± 3.4	29 ± 6
La	30	31 ± 8	33	34 ± 7
Ce	60	59 ± 8	70	72 ± 15
Pr	10	10 ± 1	7	6.8 ± 1
Nd	40	39 ± 6	30	29.1 ± 6
Sm	8	7.8 ± 1	9	8.7 ± 2
Eu	1	1.0 ± 1	2	1.9 ± 1
Gd	8	8.2 ± 2	11	10.7 ± 2
Tb	1	1.0 ± 2	2	1.9 ± 1
Dy	8	8.2 ± 2	14	13.6 ± 3
Ho	2	2.1 ± 1	3	2.9 ± 1
Er	4	4.1 ± 1	8	8.2 ± 2
Tm	0.6	0.6 ± 1	1	1.0 ± 1
Yb	6	6.2 ± 1	7	7.2 ± 1
Lu	ND	0.3	ND	0.4

**Average of three measurements MESS-1: Miramichi River Estuary; BCSS-1: Baie des Chalerus (NRC, 1990). ND: Not Detected.*

is the most abundant element among the LREEs in all these river sediments, due to the substantial fractionation that takes place within the weathering profile. This results in Ce anomalies associated with the formation of Ce^{4+} and stable Ce-hydroxides.

The North American Shale Composite (NASC) normalized REE distribution patterns of the Himalayan river sediments are given in Figs. 3 and 4. The major rivers such as the Ganges and Brahmaputra have REE distribution patterns that are moderately enriched in LREE (Fig. 3). The rivers such as Jamuna, Padma and Meghna have a REE distribution patterns that are strongly enriched in LREE (Fig. 4). These observations show that the REEs are dominantly derived from intermediate and felsic rocks (McLennan, 1989).

The smaller rivers/tributaries show wide variations in the LREE pattern, while the major rivers appear to have a relatively uniform distribution, attributable to the variations in sedimentological processes and mineralogy (Goldstein and Jacobsen, 1988). An almost uniform REE pattern is observed for the Himalayan rivers of the present study. This is because of the fact that the Himalayan source rivers have a high-suspended load of particles enriched in REE, making fractionation insignificant during deposition. This may be due to a greater extent of mixing of the REE and also the limited time available for preferential adsorption (Murray *et al.*, 1992). Higher rate of transportation leads to a lesser degree of fractionation between LREE and HREE, resulting in a uniform distribution pattern (Turner *et al.*, 1981). According to Sholkovitz (1993) flat REE distribution is commonly observed from the river sediments due to the average upper crustal surface composition and source rocks. Sholkovitz (1995) also suggested that the mixing and homogenizing effects of sedimentary processes will

Table 3. *Rare earth element concentration (in $\mu g\ g^{-1}$) in the Himalayan river sediments*

S. No*	Location	La	Ce	Pr	Nd	Sm	ΣLREE	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	ΣHREE
Ganges River Suspended sediments																	
1	Dhakpathar	21	39	5	15	3	83	0.6	4	0.5	3	0.7	1.5	0.2	1.5	0.3	11
2	Okhla	20	37	4	14	3	78	0.6	3	0.4	3	0.6	1.6	0.2	1.4	0.3	11
3	Allahabad Sangam	22	41	5	16	3	87	0.7	4	0.5	3	0.7	1.6	0.2	1.5	0.2	12
4	Devapryag	14	27	3	10	2	56	0.4	3	0.4	2	0.5	1.2	0.2	1.1	0.2	9
5	Kanpur	21	42	5	16	3	87	0.7	4	0.5	3	0.7	1.5	0.2	1.4	0.3	11
6	Allahabad Ganges	17	33	4	13	3	69	0.5	3	0.4	3	0.5	1.3	0.2	1.2	0.2	10
7	Varanasi Ganges	18	35	4	13	3	73	0.6	4	0.4	2	0.6	1.3	0.2	1.2	0.2	10
8	Varanasi Gomti	21	42	5	15	4	86	0.6	4	0.5	3	0.7	1.7	0.3	1.6	0.3	12
9	Arrah	23	44	5	16	3	92	0.7	4	0.4	3	0.7	1.5	0.2	1.4	0.2	11
10	Gandhak	26	52	6	19	4	108	0.9	4	0.5	3	0.7	1.8	0.3	1.6	0.2	12
11	Calcutta	25	47	5	17	3	97	0.7	4	0.5	3	0.7	1.7	0.3	1.5	0.2	12
Average		21	40	5	15	3	83	0.6	4	0.5	3	0.6	1.5	0.2	1.4	0.2	11
Yamuna River																	
12	Dhakpathar	21	41	5	16	3	86	0.5	4	0.4	3	0.7	1.4	0.2	1.4	0.2	11
13	Wazirabad	23	44	5	17	4	93	0.7	4	0.5	3	0.7	1.6	0.2	1.4	0.2	12
14	Agra	27	54	7	21	4	113	0.7	3	0.5	3	0.8	1.7	0.3	1.6	0.3	12
15	Etawa	22	43	5	17	3	91	0.7	4	0.5	3	0.6	1.6	0.3	1.5	0.2	12
16	Jagmanpur	19	37	5	15	3	79	0.6	3	0.4	3	0.7	1.5	0.2	1.4	0.2	11
17	Hamirpur	18	36	4	14	3	75	0.6	3	0.4	2	0.6	0.3	0.2	1.2	0.2	8
18	Lalouli	25	48	6	18	4	100	0.6	4	0.5	4	0.9	2.0	0.3	1.9	0.3	13
19	Rajapur	20	39	5	15	3	82	0.6	4	0.4	3	0.6	1.5	0.2	1.4	0.2	11
Average		22	43	5	17	3	90	0.6	4	0.5	3	0.7	1.5	0.2	1.5	0.2	11

**Refer to Figs. 2(a) and 2(b) for sampling locations.*

Table 3. (continued)

S. No*	Location	La	Ce	Pr	Nd	Sm	ΣLREE	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	ΣHREE
Brahmaputra River																	
20	Tezu	16	30	4	12	2	65	0.7	3	0.4	3	0.6	1.3	0.2	1.3	0.2	10
21	Pasighat	31	64	7	22	4	128	0.6	4	0.5	3	0.8	1.7	0.3	1.5	0.3	12
22	Saikhowa	24	47	6	18	4	99	0.7	4	0.5	3	0.7	1.5	0.2	1.3	0.2	11
23	Dibrugarh	25	49	6	18	3	101	0.7	3	0.4	2	0.5	1.1	0.2	1.0	0.2	9
24	Nimatighat	16	31	4	11	3	64	0.5	3	0.3	2	0.5	1.1	0.2	0.9	0.2	8
25	Subansiri	7	13	2	6	1	28	0.3	1	0.2	1	0.3	0.6	0.1	0.5	0.1	4
26	Badatighat	7	14	2	5	1	30	0.3	1	0.2	1	0.3	0.6	0.1	0.5	0.1	4
27	Bhomioraguri	23	43	5	17	4	92	0.7	4	0.5	3	0.6	1.4	0.2	1.2	0.2	11
28	Guwahati	22	42	5	16	3	88	0.6	3	0.4	2	0.6	1.3	0.2	1.2	0.2	10
29	Pandu	20	39	5	15	3	81	0.6	3	0.4	3	0.6	1.4	0.2	1.2	0.2	10
30	Beki	19	37	5	15	3	78	0.6	3	0.4	3	0.6	1.3	0.2	1.2	0.2	9
31	Manas	24	46	5	17	4	97	0.6	4	0.4	2	0.5	1.1	0.2	1.1	0.2	10
32	Goalpara	19	37	4	15	3	77	0.6	3	0.4	2	0.5	1.2	0.2	1.0	0.2	9
33	Dhobri	49	88	10	28	5	179	0.8	5	0.7	4	0.9	1.9	0.3	1.9	0.3	15
Average		21	41	5	15	3	86	0.6	3	0.4	2	0.6	1.2	0.2	1.1	0.2	9
Jamuna																	
34	Tista Bridge	19	38	5	15	3	80	0.5	3	0.3	2	0.4	1.0	0.1	0.8	0.1	7
35	Chilmari	35	69	8	26	5	144	0.9	5	0.6	4	0.9	1.9	0.3	1.6	0.3	15
36	Phoolcheri	16	31	4	11	2	64	0.4	2	0.3	2	0.5	1.1	0.2	1.0	0.2	8
37	Bahadurabad	94	168	21	67	13	364	1.6	13	1.5	10	2.0	4.8	0.7	4.3	0.7	36
38	Jagannathganj Ghat	67	121	15	47	9	259	1.2	9	1.1	7	1.5	3.6	0.5	3.3	0.6	26
39	Sirajganj	48	93	11	35	7	194	1.0	7	0.9	6	1.4	3.3	0.5	3.1	0.5	23
40	Aricha	22	44	5	17	4	92	0.7	4	0.4	3	0.6	1.3	0.2	1.2	0.2	11
41	Nagarbari	31	62	8	24	5	130	0.8	5	0.7	4	0.9	2.2	0.3	1.9	0.3	15
Average		42	78	10	30	6	166	0.9	6	0.7	5	1.0	2	0.3	2	0.4	18

**Refer to Figs. 2(c) and 2(d) for sampling locations.*

Table 3. (continued)

S. No*	Location	La	Ce	Pr	Nd	Sm	ΣLREE	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	ΣHREE
Padma																	
42	Rajshahi	34	72	9	27	5	147	0.6	4	0.6	4	1.0	2.5	0.4	2.5	0.4	16
43	Pakshi	44	84	10	31	6	175	0.8	6	0.7	5	1.1	2.6	0.4	2.4	0.4	18
44	Daulatdia	22	42	5	16	3	87	0.5	3	0.4	3	0.6	1.5	0.2	1.3	0.2	10
45	Maoa	17	34	4	13	3	71	0.6	3	0.4	2	0.6	1.3	0.2	1.2	0.2	9
Average		29	58	7	22	4	120	0.6	4	0.5	3	0.8	2	0.3	1.8	0.3	13
Meghna																	
46	Sylhet	16	31	4	12	2	64	0.4	2	0.3	2	0.5	1.3	0.2	1.3	0.2	9
47	Sunamganj	19	38	4	15	3	78	0.5	3	0.4	2	0.5	1.2	0.2	1.1	0.2	9
48	Meghna Ghat	25	50	6	19	4	104	0.6	4	0.5	3	0.7	1.6	0.2	1.5	0.3	12
49	Meghna Ghat	29	58	7	23	4	122	0.7	5	0.6	4	0.8	2.0	0.3	1.8	0.3	14
50	Sheola	9	17	2	7	1	37	0.3	1	0.2	1	0.3	0.5	0.1	0.5	0.1	4
51	Sherpur	23	46	6	17	3	95	0.5	3	0.4	3	0.7	1.8	0.3	1.8	0.3	12
52	Sherpur	16	31	4	12	2	65	0.5	3	0.3	2	0.6	1.3	0.2	1.2	0.2	9
53	Ashuganj	61	116	14	42	9	241	1.0	9	1.3	9	2.0	5.2	0.8	4.7	0.8	32
54	Chandpur	44	86	10	32	6	178	1.0	7	0.8	5	1.3	2.8	0.5	2.7	0.5	21
Average		27	52	6	20	4	109	0.6	4	0.5	4	0.8	2	0.3	2	0.3	13

*Refer to Fig. 2(d) for sampling locations.

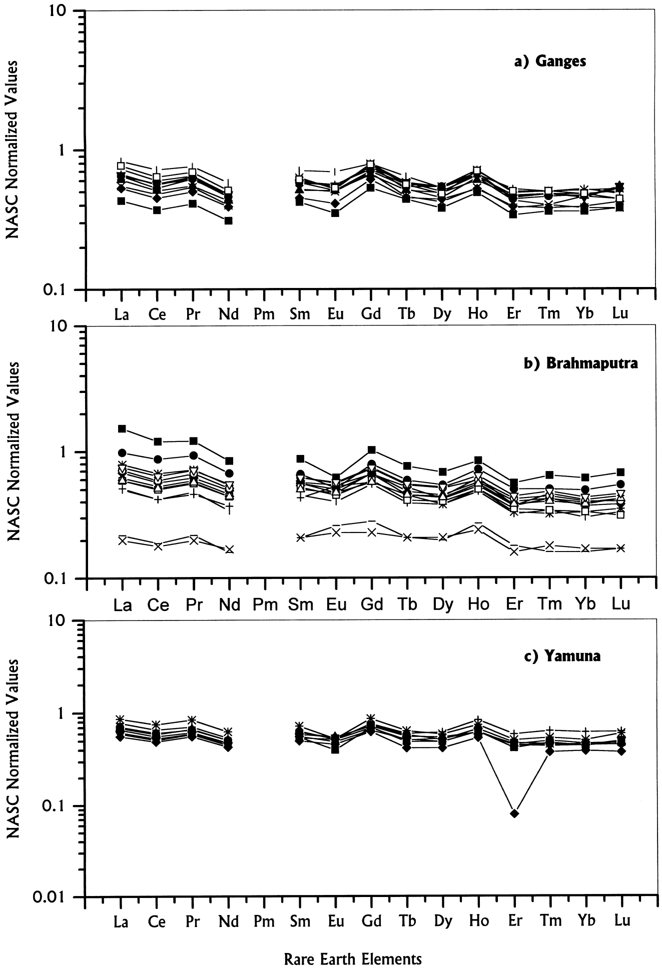

Fig. 3. The North American Shale (NASC) normalised REE distribution pattern at various locations in the suspended sediments of the a) Ganges river, bed sediments of the rivers, b) Brahmaputra and c) Yamuna. The element Pm has been included in the figure to show the ionic radius however, its quantification has not been made.

produce uniform REE pattern and they will reflect the abundance in the upper continental crust.

As observed by us, the following is the dominance of LREE and HREE in the Himalayan river system:

LREE - Jamuna > Padma > Meghna
> Ganges > Yamuna > Brahmaputra
HREE - Jamuna > Padma > Meghna
> Yamuna > Ganges > Brahmaputra

The enrichment of LREE reflects the intense silicate weathering of crustal materials and a resultant increase in LREEs in the detritals. The LREE/HREE ratios vary from 6.82 to 11.77 in these river sediments (Table 4), which is much lesser than the upper crustal ratio and is equal to shale ratio, except at a few locations. Similarly the La/Yb ratio also varies from 1.27 to 2.49. This ratio is high in the Brahmaputra river, which is dominated by medium-fine grained sediments with higher physical erosion rate. The increase in the La/Yb ratio by a factor of 1 to 1.12 in the Brahmaputra river, reflects high erosion rates in the river system. This suggests that the removal of La from the drainage basin, results in a high

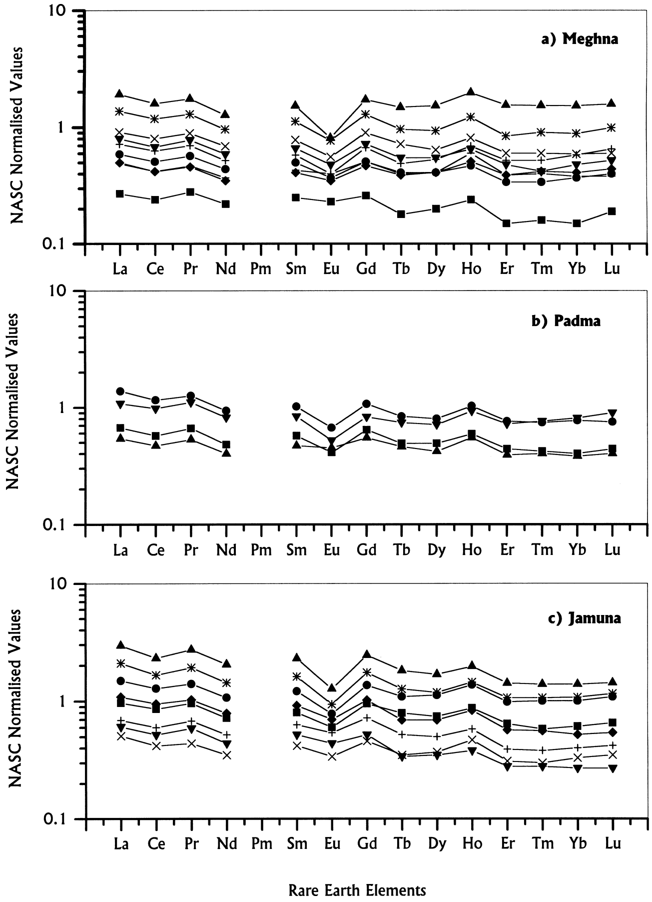

Fig. 4. The North American Shale (NASC) normalised REE distribution pattern at various locations in the bed sediments of the rivers a) Meghna, b) Padma and c) Jamuna. The element Pm has been included in the figure to show the ionic radius however, its quantification has not been made.

deposition rate in the main channel.

Further, since the physical weathering process is predominant in the fine-grained sediments in all these terrains, it is unlikely that the intense fractionation of REE might have taken place in these rivers. This is primarily because of the fact that the extent of fractionation is inversely related to the residence time and size of the particle. The La/Yb ratio shows large fluctuations in the Brahmaputra, Yamuna, Jamuna, Padma and Meghna rivers, indicating the differential erosion rate and lithological control (Fig. 5(a)). In general, the La/Yb ratio is found to be very low in sediments rich in coarse size fractions and felsic minerals (McLennan, 1988). The Jamuna river, which drains through the oldest crystalline terrain covered partially by shales, has a higher concentration of HREE and a La/Yb ratio. The concentration of REEs particularly HREEs is depleted in Ganges and Brahmaputra rivers in comparison to the Jamuna, Padma and Meghna rivers. On the other hand, the LREEs are enriched in the G-B basin, which in turn reflects the intense silicate weathering in the upper surface of the Himalayan crust. Y displays a close similarity with the REEs and exhibits a high positive correlation with the LREEs (0.90), suggesting its association with detritals.

In general LREEs are more dominant in Himalayan rivers in comparison to the HREEs

Table 4. Distribution of ∑LREE, ∑HREE, ∑REE, ∑LREE/∑HREE, and ratios of Ce/Ce, Eu^A, $(\mathrm{La/Yb})_n$, $(\mathrm{Sm/Nd})_n$ in the Himalayan river sediments*

S. No*	Location	∑LREE	∑HREE	∑REE	∑LREE/∑HREE	Ce/Ce*	Eu/Eu*	$(\mathrm{La/Yb})_n$
Ganges River Suspended Sediments								
1	Dhakpathar	83	11	95	7.31	0.84	0.70	1.38
2	Okhla	78	11	90	7.25	0.88	0.77	1.31
3	Allahabad Sangam	87	12	99	7.48	0.86	0.75	1.39
4	Devapryag	56	9	65	6.65	0.87	0.64	1.18
5	Kanpur	87	11	99	7.62	0.90	0.73	1.46
6	Allahabad Ganges	69	10	79	7.25	0.88	0.69	1.37
7	Varanasi Ganges	73	10	83	7.48	0.87	0.74	1.46
8	Varanasi Gomti	86	12	99	7.08	0.89	0.64	1.27
9	Arrah	92	11	103	8.38	0.88	0.72	1.57
10	Gandhak	108	12	121	8.77	0.90	0.82	1.59
11	Calcutta	97	12	109	8.28	0.87	0.68	1.59
Average		83	11	95	8.00	0.90	0.70	1.40
Yamuna River								
12	Dhakpathar	86	11	97	7.97	0.88	0.56	1.51
13	Wazirabad	93	12	105	8.03	0.89	0.71	1.58
14	Agra	113	12	126	9.36	0.88	0.60	1.67
15	Etawa	91	12	103	7.83	0.87	0.74	1.45
16	Jagmanpur	79	11	90	7.38	0.86	0.72	1.34
17	Hamirpur	75	8	84	8.91	0.88	0.72	1.44
18	Lalouli	100	13	114	7.46	0.88	0.65	1.27
19	Rajapur	82	11	94	7.37	0.87	0.74	1.34
Average		90	11	102	8.00	0.90	0.70	1.50
Brahmaputra River								
20	Tezu	65	10	75	6.82	0.87	1.07	1.23
21	Pasighat	128	12	141	10.49	0.91	0.70	1.99
22	Saikhowa	99	11	111	8.74	0.88	0.84	1.76
23	Dibrugarh	101	9	110	11.22	0.88	0.88	2.42
24	Nimatighat	64	8	73	7.80	0.87	0.81	1.67
25	Subansiri	28	4	32	6.74	0.87	1.02	1.18
26	Badatighat	30	4	34	6.80	0.88	1.05	1.34
27	Bhomioraguri	92	11	103	8.43	0.86	0.84	1.78
28	Guwahati	88	10	98	9.06	0.88	0.82	1.82
29	Pandu	81	10	92	8.10	0.88	0.76	1.59
30	Beki	78	9	88	8.35	0.87	0.87	1.54
31	Manas	97	10	107	10.16	0.89	0.72	2.12
32	Goalpara	77	9	87	8.78	0.87	0.81	1.76
33	Dhobri	179	15	195	11.77	0.88	0.66	2.49
Average		86	9	96	9.00	0.90	0.80	1.80

**Refer to Figs. 2(a)–(c) for sampling locations.*

(Table 3). The midstream and downstream regions of the Himalayan rivers show an enrichment of LREE in comparison to its tributaries in the upstream area. The HREE concentrations are relatively uniform in all the rivers, with the exceptions of Jamuna, Padma and Meghna. On the other hand, the concentration of LREE is lower than the upper crust and NASC with the exception of a few locations in the Jamuna, Padma and Meghna rivers. The total REE concentration of the Himalayan rivers is significantly lower than the values for shale, the Amazon river, Loess and upper crust (Table 5). The REE concentration reflects the amount of terrigenous material present in these

Table 4. (continued)

S. No*	Location	∑LREE	∑HREE	∑REE	∑LREE/∑HREE	Ce/Ce*	Eu/Eu*	$(La/Yb)_n$
Jamuna								
34	Tista Bridge	80	7	88	10.70	0.87	0.84	2.27
35	Chilmari	144	15	159	9.71	0.90	0.73	2.11
36	Phoolcheri	64	8	73	8.35	0.89	0.77	1.55
37	Bahadurabad	364	36	402	9.98	0.81	0.54	2.14
38	Jagannathganj Ghat	259	26	287	9.80	0.83	0.56	1.95
39	Sirajganj	194	23	219	8.31	0.88	0.61	1.49
40	Aricha	92	11	103	8.62	0.88	0.80	1.73
41	Nagarbari	130	15	146	8.40	0.89	0.69	1.61
Average		166	18	185	9.00	0.90	0.70	1.90
Padma								
42	Rajshahi	147	16	163	9.30	0.90	0.62	1.33
43	Pakshi	175	18	194	9.92	0.88	0.64	1.79
44	Daulatdia	87	10	98	8.43	0.86	0.68	1.67
45	Maoa	71	9	81	7.82	0.88	0.89	1.42
Average								
Meghna		120	13	134	9.00	0.90	0.70	1.60
46	Sylhet	64	9	73	7.42	0.89	0.79	1.22
47	Sunamganj	78	9	87	9.21	0.89	0.73	1.60
48	Meghna Ghat	104	12	117	8.97	0.87	0.70	1.65
49	Meghna Ghat	122	14	137	8.51	0.89	0.67	1.54
50	Sheola	37	4	41	9.17	0.86	0.89	1.77
51	Sherpur	95	12	107	8.08	0.89	0.65	1.24
52	Sherpur	65	9	74	7.29	0.88	0.86	1.27
53	Ashuganj	241	32	275	7.45	0.87	0.50	1.26
54	Chandpur	178	21	200	8.62	0.88	0.64	1.55
Average		109	13	123	8.00	0.90	0.70	1.50

**Refer to Fig. 2(d) for sampling locations.*

river sediments, suggesting the high intensity of physical and the low intensity of chemical weathering processes in these river systems.

The results of the ratios of (Ce/Ce*) and (Eu/Eu*) and their anomalies are given in Table 4. The elements Cerium (Ce) and Europium (Eu) exist in two-oxidation states and behave differently when compared to their strictly trivalent neighbors under different oxygenated conditions (Piper, 1974). Variation in Ce anomalies is influenced by a number of factors, including terrigenous input, the depositional environment and diagenetic conditions. Ce anomaly (Ce/Ce*) is quantified by the ratio of the observed value of Ce to an expected value (Ce*) obtained by the interpolation from the shale normalized value of trivalent neighbors such as La and Pr (Murray *et al.*, 1992). The values of Ce/Ce* > 1 and <1 indicate the positive and negative anomalies respectively (Toyoda *et al.*, 1990).

The negative Ce/Ce* observed in the sediments is due to the presence of oxic environments in the river basin. This also implies the mixing of a two-component system with terrigenous clay (detrital) and marine limestones of the Himalayas. Changes in the depositional setting in the riverbanks may also have caused this anomaly. This is an evidence of an active weathering process of the carbonate-silicate system in the study areas. However, significant variations of Ce/Ce* were not observed from the upstream to the downstream areas in these river systems (Fig. 5(b)).

The Eu/Eu* ratios in this study was predominantly <1, except at few locations where it was >1 (Table 4), suggesting that the origin of this element (Eu) is rich in feldspar source, contribut-

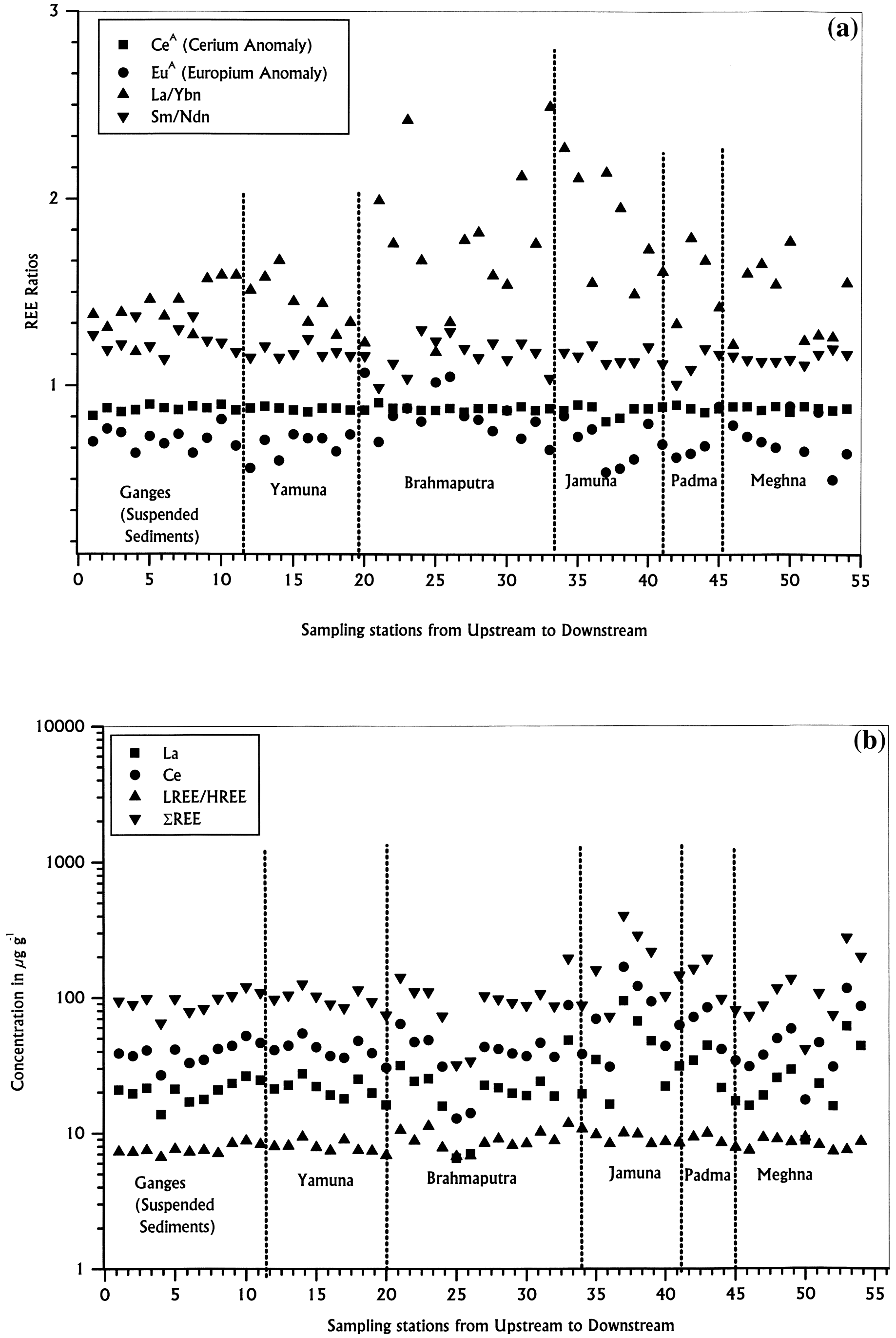

Fig. 5. (a) Downstream variation of Cerium and Europium anomalies, $(La/Yb)_n$ and $(Sm/Nd)_n$ ratios in the suspended sediments of the Ganges river, bed sediments of the rivers Yamuna, Brahmaputra, Jamuna, Padma and Meghna. The X-axis contains the total number of samples analysed while the cross bars in the figure represent the downstream variations within individual river basins. (b) Downstream variation of La, Ce, LREE/HREE ratio and ∑REE in the suspended sediments of the Ganges river, bed sediments of the rivers Yamuna, Brahmaputra, Jamuna, Padma and Meghna. The X-axis contains the total number of samples analysed while the cross bars in the figure represent the downstream variations within individual river basins.

Table 5. Average concentrations ($\mu g\ g^{-1}$) of rare earth and trace elements in the Himalayan river sediments in comparison with various cosmochemical and geochemical reservoirs. The values are means ±SD of: Brahmaputra: 14, Ganges: 11, Meghna: 9, Padma: 4, Jamuna: 8 and Yamuna: 8 replicates.

Element	Brahmaputra[1]	Ganges[1]	Meghna[1]	Padma[1]	Jamuna[1]	Yamuna[1]	Amazon[2]	NASC[3]	PASS[4]	Loess[5]	Crustal[4]	
											Upper	Total
La	20.66 ± 10.26	20.86 ± 3.57	22.99 ± 16.28	27.99 ± 12.35	32.99 ± 27.06	21.66 ± 3.15	51	32	38.2	35.4	30	16
Ce	40.23 ± 18.84	40.93 ± 6.90	46.09 ± 30.91	56.67 ± 24.01	65.97 ± 46.97	42.09 ± 6.10	103	73	79.6	78.6	64	33
Pr	4.80 ± 2.03	4.90 ± 0.75	5.53 ± 3.64	6.97 ± 2.78	7.87 ± 6.09	5.04 ± 0.72	ND	7.9	8.83	8.46	7.1	3.9
Nd	15.62 ± 5.85	15.19 ± 2.34	17.17 ± 10.90	21.46 ± 8.59	24.91 ± 18.98	16.24 ± 2.08	47.4	33	33.9	33.9	26	16
Sm	3.21 ± 0.99	3.33 ± 0.47	3.28 ± 2.27	4.01 ± 1.43	4.90 ± 3.61	3.28 ± 0.40	9.1	5.7	5.55	6.38	4.5	3.5
Eu	0.61 ± 0.14	0.64 ± 0.11	0.50 ± 0.24	0.60 ± 0.14	0.81 ± 0.37	0.64 ± 0.07	1.9	1.24	1.08	1.18	0.88	1.1
Gd	3.43 ± 1.02	3.73 ± 0.43	3.46 ± 2.37	3.83 ± 1.20	5.11 ± 3.51	3.59 ± 0.23	ND	5.2	4.66	4.61	3.8	3.3
Tb	0.40 ± 0.12	0.46 ± 0.05	0.42 ± 0.33	0.53 ± 0.16	0.63 ± 0.43	0.46 ± 0.06	0.98	0.85	0.77	0.81	0.64	0.6
Dy	2.49 ± 0.72	2.82 ± 0.31	3.05 ± 2.28	3.46 ± 1.04	4.14 ± 2.70	3.06 ± 0.36	ND	5.8	4.68	4.82	3.5	3.7
Ho	0.56 ± 0.16	0.67 ± 0.08	0.68 ± 0.53	0.79 ± 0.25	0.88 ± 0.57	0.66 ± 0.09	ND	1.04	0.99	1.01	0.8	0.78
Er	1.27 ± 0.36	1.54 ± 0.18	1.63 ± 1.36	1.99 ± 0.64	2.05 ± 1.38	1.54 ± 0.51	ND	3.4	2.85	2.85	2.3	2.2
Tm	0.21 ± 0.06	0.24 ± 0.03	0.21 ± 0.20	0.29 ± 0.10	0.29 ± 0.10	0.24 ± 0.03	ND	0.5	0.4	ND	0.33	0.32
Yb	1.17 ± 0.35	1.44 ± 0.16	1.49 ± 1.23	1.83 ± 0.72	1.74 ± 1.26	1.41 ± 0.21	3.7	3.1	2.82	2.71	2.2	2.2
Lu	0.19 ± 0.06	0.23 ± 0.03	0.25 ± 0.04	0.29 ± 0.12	0.29 ± 0.20	0.24 ± 0.04	ND	0.48	0.43	ND	0.32	0.3
ΣREE	94.81 ± 38.01	96.96 ± 32.21	106 ± 48.58	130 ± 45.50	152 ± 40.25	100 ± 13.58	217.08	173	184.8	181	146	87
Y	15.53 ± 4.38	18.58 ± 2.00	20.09 ± 12.04	19.03 ± 5.28	23.93 ± 13.46	19.77 ± 2.83	ND	35	27	ND	22	20
V	112 ± 8.99	156 ± 24.56	62.9 ± 22.19	54.81 ± 6.35	79.99 ± 23.94	104 ± 27.41	ND	130	150	90	60	230
Cr	100 ± 66.13	134 ± 31.05	61.5 ± 23.55	41.2 ± 29.39	69.25 ± 21.62	84.95 ± 27.43	100	125	110	50	35	185
Co	14.47 ± 5.77	23.89 ± 7.43	19.29 ± 35.30	7.06 ± 5.16	9.36 ± 2.72	13.64 ± 4.49	17	26	23	15	10	29
Ni	80.39 ± 59.97	133.16 ± 54.00	36.79 ± 15.88	24.54 ± 20.14	33.68 ± 8.89	49.6 ± 18.71	38	58	55	45	20	105
Zn	78.26 ± 37.42	203.84 ± 58.05	45.62 ± 12.86	55.84 ± 26.55	56.94 ± 16.64	76.8 ± 27.75	ND	ND	104.24	92	71	80
Ag	0.07 ± 0.03	0.21 ± 0.10	0.06 ± 0.03	0.05 ± 0.03	0.06 ± 0.04	0.08 ± 0.02	ND	ND	ND	ND	0.05	0.08
Cd	0.47 ± 0.20	0.36 ± 0.13	0.45 ± 0.26	0.24 ± 0.01	0.54 ± 0.39	0.45 ± 13.05	ND	ND	ND	ND	0.1	0.1
Pb	9.61 ± 7.62	22.84 ± 8.22	15.14 ± 19.36	8.88 ± 1.58	9.91 ± 1.89	9.56 ± 2.15	23.5	20	20	20	20	8

ND = Not Detected.

[1] Present study (the REE and trace metal concentrations presented for the Ganges are based on the analysis of suspended sediments while the averages for all the other Himalayan rivers are based on the analysis of bed sediments).

[2] Gaillardet et al. (1997).

[3] Haskin et al. (1968).

[4] Taylor and McLennan (1985).

[5] Taylor et al. (1983).

Table 6. Trace metal concentration (in $\mu g\ g^{-1}$) in the Himalayan River sediments

S. No*	Location	Y	V	Cr	Co	Ni	Zn	Ag	Cd	Pb
Ganges River Suspended Sediments										
1	Dhakpathar	20	176	164	23	275	160	0.13	0.21	14
2	Okhla	20	163	176	22	141	261	0.16	0.44	29
3	Allahabad Sangam	19	155	117	21	96	198	0.19	0.30	21
4	Devapryag	15	190	141	41	169	307	0.22	0.24	24
5	Kanpur	20	168	135	28	113	204	0.23	0.31	32
6	Allahabad Ganges	17	105	79	16	69	124	0.21	0.50	12
7	Varanasi Ganges	16	152	121	22	115	154	0.18	0.38	12
8	Varanasi Gomti	20	177	185	30	140	237	0.12	0.24	28
9	Arrah	18	152	125	23	121	258	0.16	0.33	31
10	Gandhak	20	163	124	25	130	207	0.49	0.38	32
11	Calcutta	20	123	108	12	97	133	0.17	0.63	15
Average		19	157	134	24	133	204	0.21	0.36	23
Yamuna River										
12	Dhakpathar	19	66	33	9	27	53	0.09	0.19	9
13	Wazirabad	20	127	101	18	64	117	0.08	0.39	13
14	Agra	22	79	86	8	33	53	0.06	0.69	9
15	Etawa	20	126	100	17	62	117	0.10	0.36	13
16	Jagmanpur	19	130	112	17	68	79	0.07	0.60	8
17	Hamirpur	16	122	99	17	63	77	0.11	0.49	8
18	Lalouli	25	71	52	7	23	45	0.07	0.38	8
19	Rajapur	18	113	95	16	58	74	0.09	0.48	8
Average		20	104	85	14	50	77	0.08	0.45	10
Brahmaputra River										
20	Tezu	18	164	124	20	138	77	0.04	0.30	6
21	Pasighat	21	94	55	13	36	63	0.07	0.78	18
22	Saikhowa	18	146	180	20	172	79	0.06	0.66	8
23	Dibrugarh	15	158	94	15	64	68	0.09	0.41	5
24	Nimatighat	14	156	284	27	224	100	0.11	0.27	7
25	Subansiri	8	45	27	6	21	30	0.04	0.10	4
26	Badatighat	7	57	38	7	32	38	0.06	0.16	6
27	Bhomioraguri	16	149	121	19	101	93	0.08	0.57	9
28	Guwahati	16	96	77	13	45	76	0.09	0.58	8
29	Pandu	17	129	109	17	70	88	0.05	0.61	7
30	Beki	15	99	97	12	82	70	0.05	0.46	34
31	Manas	15	68	51	10	32	64	0.05	0.59	8
32	Goalpara	14	111	92	15	77	190	0.11	0.50	7
33	Dhobri	24	109	62	9	32	58	0.10	0.54	8
Average		16	113	101	14	80	78	0.07	0.47	10

**Refer to Figs. 2(a)–(c) for sampling locations.*

ing to a positive anomaly in the river system. This may also be due to the weathering of granite and the granitic gneiss in the source region (Burg *et al.*, 1984; Gansser *et al.*, 1983). There is a consistent decline in the Eu/Eu* ratio from the upstream to downstream regions, with minor fluctuations in the midstream regions of the rivers Brahmaputra and Jamuna (Fig. 5(a)). This highlights the contribution of the tributaries joining the main stream and also due to changes in the lithology during the erosional process (Allegre *et al.*, 1996).

In the Ganges, the suspended particles were analyzed for REE from upstream to down stream region, to understand the chemical evolution of REE from the Himalayas to the Bay of Bengal. In

Table 6. (continued)

S. No*	Location	Y	V	Cr	Co	Ni	Zn	Ag	Cd	Pb
Jamuna										
34	Tista Bridge	8	48	38	6	23	36	0.01	0.21	11
35	Chilmari	16	74	61	11	39	62	0.08	0.39	11
36	Phoolcheri	14	62	49	8	33	65	0.03	0.14	8
37	Bahadurabad	42	93	94	8	24	46	0.06	1.35	8
38	Jagannathganj Ghat	45	127	102	13	40	85	0.06	0.82	9
39	Sirajganj	30	71	69	7	25	37	0.13	0.52	8
40	Aricha	17	91	67	11	44	68	0.05	0.48	11
41	Nagarbari	19	74	57	11	41	56	0.08	0.40	13
Average		24	80	67	9	34	57	0.06	0.54	10
Padma										
42	Rajshahi	24	49	27	4	13	33	0.08	0.24	7
43	Pakshi	23	41	34	4	15	33	0.03	0.26	8
44	Daulatdia	13	35	21	5	15	77	0.01	0.23	10
45	Maoa	16	93	83	15	55	81	0.07	0.23	10
Average		23	79	65	10	36	55	0.08	0.48	10
Meghna										
46	Sylhet	15	50	70	10	46	59	0.03	0.35	10
47	Sunamganj	12	43	57	8	39	40	0.09	0.22	9
48	Meghna Ghat	15	57	44	7	22	33	0.04	0.35	9
49	Meghna Ghat	22	73	49	6	24	40	0.04	0.46	10
50	Sheola	6	34	36	8	36	34	0.08	0.06	7
51	Sherpur	20	47	49	7	39	43	0.03	0.50	7
52	Sherpur	15	87	115	113	73	72	0.08	0.46	8
53	Ashuganj	46	77	57	7	26	39	0.03	0.68	10
54	Chandpur	31	99	77	8	26	51	0.09	0.95	7
Average		20	63	62	19	37	46	0.06	0.45	8

**Refer to Fig. 2(d) for sampling locations.*

the upstream reaches of the Ganges and its tributaries, we did not observe any significant variation in LREE, HREE, Ce, Eu, La/Yb content in the river particulates excepting at Devaprayag and Allahabad where the LREE concentrations reduced by a factor of 0.3 and 0.5 respectively (Fig. 5). However, in the downstream region of the Gandhak and Calcutta, LREE and La/Yb ratio was high, indicating that the flat topography might have enhanced the physical erosion rate to a large extent in the Ganges resulting in an excess removal of the upper crust material in the drainage basin.

In addition to the physical processes mentioned above, chemical factors such as pH, the carbonate ion concentration etc., play a vital role in mobilizing the REE in the river sediments (Dupre *et al*., 1996). In this study, characteristic changes in pH were observed in the mainstream of the Ganges river with a consequent change in the concentration of REEs, especially at regions where the tributaries joined the main stream (Fig. 5(b)). It has been demonstrated that rivers with high pH values and high carbonate content enhance the dissolved REE concentration by remobilizing them from the bed sediments (Sarin *et al*., 1989; Galy and France-Lanord, 1999).

In the surficial sediments of the Himalayan rivers, we can observe a wider fluctuation in REE distribution from the upstream to downstream region, mainly due to a variation in lithology and partly to the input from the tributaries. For example, in the Brahmaputra and Jamuna rivers, the REE concentration decreases considerably after their tributaries Subansiri (sample numbers 25 and 26) and Padma, join the main river. But, it has been observed that in the sediments draining from

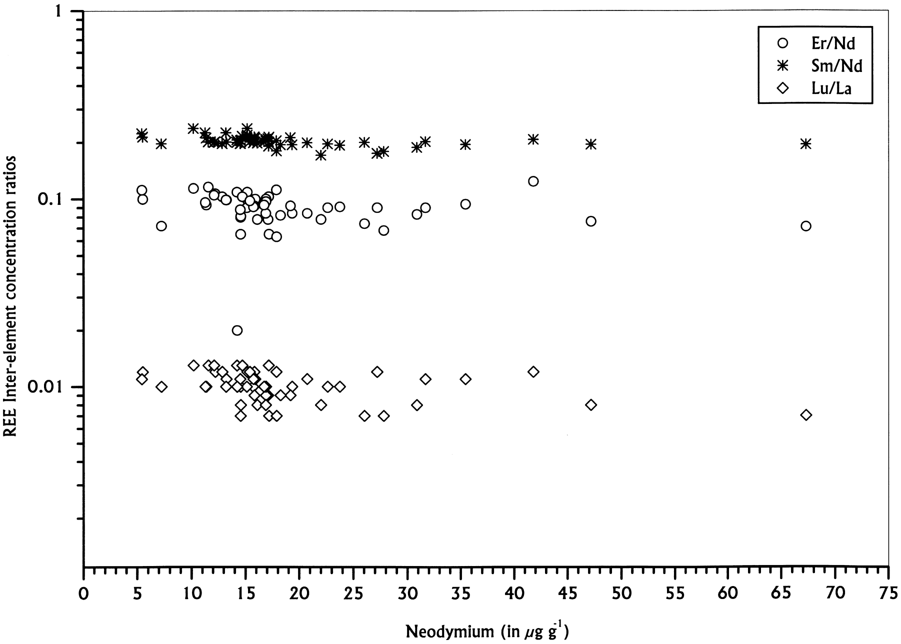

Fig. 6. REE inter-element concentration ratios of a) Sm/Nd, b) Er/Nd and c) Lu/La versus Nd concentration in the Himalayan river sediments.

the Deccan trap region of the Ganges (sample number 3), the REE and the other trace metal concentrations remained relatively constant.

Table 5 shows the average REE and heavy metal concentration of the Himalayan rivers and a comparison has been made with the Amazon river and other geochemical reservoirs such as PAAS, NASC, LOESS and the continental crust. The Brahmaputra, Ganges and the Yamuna rivers, have a similar lithology, rich in felsic minerals and hence the REE concentration is similar to that of the total crustal abundances. The rivers Meghna and Padma, have HREE pattern similar to that of the upper crust. The Jamuna river displays a close similarity with PAAS and NASC composition. These three smaller rivers have HREE concentration close to shale reflecting its drainage lithology. The Ganges and the Amazon river data presented in Table 5, represent the particulate fraction (<45 µm) of the REE distribution. Our results highlight the fact that the REEs are enriched by a factor of two in the Amazon when compared to their concentration in the Ganges.

The REE fractionation associated with each of these rivers may be recognized from the plots of REE—inter elemental ratios versus the REE concentration using Neodymium. Figure 6 shows the bi-variate plots of Nd vs. Lu/La, Er/Nd and Sm/Nd. The results exhibit that the ratios are reasonably constant over most of the REE concentration, which is similar to the observations made by Elderfield *et al.* (1990), for the other major river basins of the world.

The concentration of heavy metals in the Himalayan river system is given in Table 6 and its distribution towards the downstream is depicted in Figs. 7(a) and 7(b) respectively. The concentration of metals in the suspended sediments of the Ganges is higher followed by the bed sediments of the rivers Yamuna, Brahmaputra, Meghna, Padma and Jamuna. Most of the heavy metals studied show significant variation within the Himalayan rivers. The concentration of metals in the Ganges is comparable to NASC and is higher than the upper continental crust (Table 5). Similar trends were also observed for the surficial

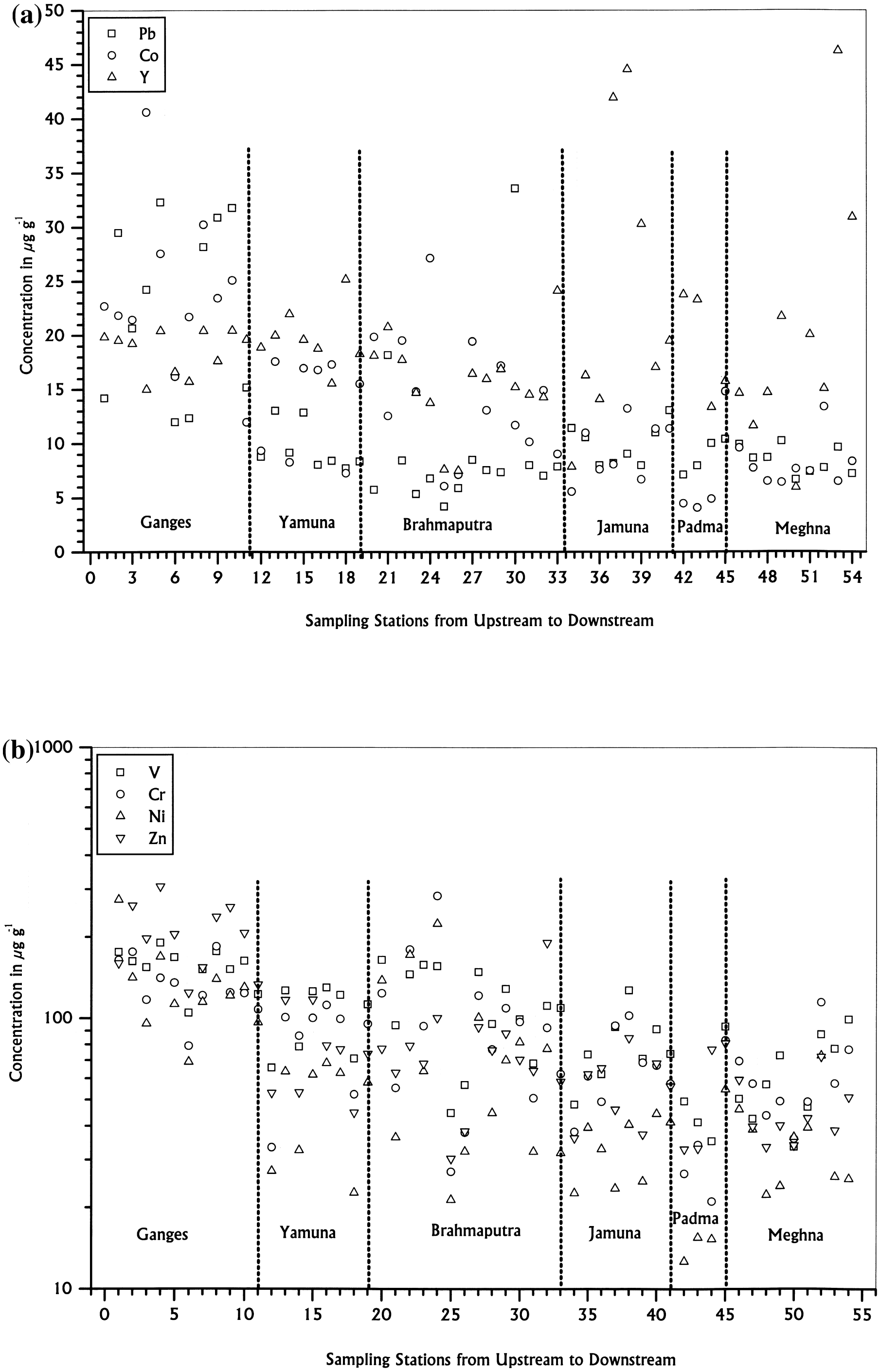

Fig. 7. (a) Spatial and downstream variation of heavy metals (Pb, Co and Y) in the Himalayan river sediments. The X-axis contains the total number of samples analysed while the cross bars in the figure represent the downstream variations within individual river basins. (b) Spatial and downstream variation of heavy metals (V, Cr, Ni and Zn) in the Himalayan river sediments. The X-axis contains the total number of samples analysed while the cross bars in the figure represent the downstream variations within individual river basins.

sediments of the other Himalayan rivers. We have observed that in particular, metals such as V, Cr, Zn, Ni and Cd are enriched in these sediments than their concentration in the upper continental crust. The concentration of trace metals shows wide fluctuations in their downstream distribution in the Ganges river. In the rivers Brahmaputra, Yamuna, Jamuna, Meghna and Padma, there is a systematic variation in metal concentration before and after the confluence of tributaries suggesting not only the lithological control but also the considerable influence of the tributaries.

Forstner and Wittmann (1986) have reported that the suspensions are fine grained possessing a larger surface area, rich in organic and multiple hydroxide coatings in the alkaline pH range during the weathering process in the river basin. This phenomenon makes it possible for the sediments to act as a sink for heavy metals discharged into the river system. For example, in several large rivers such as the Mississippi, the heavy metal distribution in suspended sediments is markedly different from that of the bed sediments (Trefry and Presley, 1976). Similar observations have been made by us for the Ganges river, where the trace metals such as Cd, Zn, Ni, Cr and V seem to be enriched in the suspended sediments by several folds, in comparison to the NASC and upper crustal rocks.

It has been emphasized by several researchers (Sarin *et al*., 1989; Galy and France-Lanord, 1999) that the physical erosion rate is dominant in the Himalayan source region than the chemical erosion rate, due to the less active role played by chemical weathering processes. The Pb concentration in the suspended sediments of the Ganges river and in the surficial sediments of a few locations in Yamuna (sample numbers 13 and 15) and Brahmaputra (sample numbers 21, 22 and 30) are enriched when compared to the surficial crustal rocks. These results show, besides the natural weathering process, anthropogenic inputs might have also contributed significantly to the enhanced metal concentration in these river basins.

The metal concentration generally decreases from upstream to downstream barring a few locations, which are dictated by the impact from diverse localized, natural and anthropogenic factors (Fig. 7). Trace metals such as V, Cr, Co and Zn were enriched in the river Yamuna in comparison to other Himalayan rivers. This implies that the river receives sediments from the southern side draining from the bundlekhand gneiss and basaltic landmass that are the natural sources for these elements. Apart from this, the river Yamuna passes through the metropolitan city of Delhi, where anthropogenic inputs from industrial and domestic sources reach the river. In general, there is an enrichment of metals such as V, Cr, Co, and Ni in the Ganges-Brahmaputra-Yamuna river system in comparison to the average continental soil (V 90 μg g^{-1}; Cr 70 μg g^{-1}; Co 8 μg g^{-1}; Ni 50 μg g^{-1}; Martin and Whitfield, 1983) due to the immense human activities occurring in these river systems.

Nearly 40 to 60% of the sediment load of the Ganges-Brahmaputra river system acts as a sink for trace metals in the Bengal Basin, which is a zone of subsidence (Milliman and Syvitski, 1992). The concentration of trace elements such as Cr, Ag, Zn, Cd and Pb also exhibit a large variation in the Himalayan river sediments. The distribution patterns of these metals mainly reflect the lithological control of the drainage basin (Fig. 7). This is also supported by the abundance of Al, Si in these river sediments (Table 1(a)).

The LREE and HREE in all the sediments show a good positive correlation (0.99). Y and Cd also show a good correlation (0.92) with the REEs. The metals have a negative to poor positive correlation with the REEs (–0.21 to 0.14). Among the metals V, Cr, Co, Ni, Zn shows good correlation (V-Cr (0.84); Cr-Co (0.58); Co-Ni (0.52); Ni-Zn (0.67); V-Co (0.45); V-Ni (0.81); V-Zn (0.77); Cr-Ni (0.88); Cr-Zn (0.62); Co-Zn (0.43)). Negative to a weak positive correlation is observed between Cd and Pb (–0.38) and between Ag and REE (–0.21) in the sediments of the rivers Padma, Meghna and Jamuna.

Factor analysis was carried out for 54 samples to group and identify the parameters influencing the REE and heavy metal distribution. Factor 1 represents Ag, Cr, Ni, Zn and V and the factor 2 shows the association among LREE, HREE and Y. These two statistical analyses show that there are three different processes operating in these basins, which helps us to understand their behavior and distribution. Based on these results, we suggest that LREE, HREE, Y, Cd are derived by the dominance of weathering processes. Enrichment of metals such as Cr, Co, Ni and Zn in the sediment is due to the adsorption with clay minerals in the sediments. The trace metals such as Cd, Pb and Ag are derived from diverse sources including natural and anthropogenic inputs. Further, in order to understand the nature of heavy metals in sediments, the geochemical index (I_{geo}) was made. Observations made for the I_{geo} of Cd from the earlier studies by Datta and Subramanian (1997) in the Bengal basin rivers show a marginal enrichment factor, while other heavy metals have a negative I_{geo} value. This suggests that the influence of anthropogenic contaminants in the deposited sediments is minimal. Based on this estimate, we can conclude that the basin geology and weathering characteristics in the source region played a vital role in the accumulation of REE and heavy metals in the Himalayan river sediments. However, in the downstream reaches, the influence of human additions contributed to an enhancement in the trace metal concentration in the river sediments.

From the above discussion it is concluded that the REE and metal distribution in the Himalayan river reflects the excessive crustal erosion activated by physical weathering process and contribute more material to the Bay of Bengal. The basin lithology and inputs from the tributaries largely control their distribution and the chemical evolution from the origin to the Bay of Bengal. We can argue from this that the anthropogenic impact to their distribution is seems to be insignificant in these locations. As silica values are higher in these terrains, there may be a possibility of partial biogeochemical coupling, besides a physiochemical process for REE distribution. It is hence suggested that the various forms of Si and its relationship to REE have to be investigated in detail in the future.

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REFERENCES

Acharya, S. K. (1979) Eastern Himalayas. *Tectonic Geology of the Himalayas* (Saklani, P. S., ed.), 243–248, Today and Tomorrow Printers, New Delhi.

Alam, M. K., Hasan, A. K. M. S., Khan, M. R. and Whitney, J. W. (1990) Geological map of Bangladesh. Geological Survey of Bangladesh, Dhaka, 102 pp.

Allegre, C. J., Dupre, B., Negrel, P. and Gaillardet, J. (1996) Sr-Nd-Pb isotope systematic in Amazon and Congo river systems: Constraints about erosion processes. *Chem. Geol.* **131**, 93–112.

Burg, J. P., Brunel, M., Gapais, D., Chen, G. M. and Liu, G. H. (1984) Deformation of the crystalline main central sheet in southern Tibet (China). *J. Struc. Geol.* **6**, 535–542.

Coleman, J. M. (1981) *Deltas: Processes of Deposition and Models for Exploration*. 2nd ed., Burgess, Minneapolis, 208 pp.

Coryell, C. D., Chase, J. W. and Hinchester, J. W. (1963) A Procedure for geochemical interpretation of terrestrial rare earth abundance patterns. *J. Geophys. Res.* **68**, 559–575.

Datta, D. K. and Subramanian, V. (1997) Texture and mineralogy of sediments from the Ganges-Brahmaputra-Meghna river system in the Bengal basin, Bangladesh and their environmental implications. *Environ. Geol.* **30**, 181–188.

Datta, D. K. and Subramanian, V. (1998) Distribution and fractionation of heavy metals in the surface sediments of the Ganges-Brahmaputra-Meghna river system in the Bengal basin. *Environ. Geol.* **36**, 93–101.

Dupre, B., Gaillardet, J., Rousseau, D. and Allegre, C. J. (1996) Major and trace elements of river-borne material: The Congo basin. *Geochim. Cosmochim. Acta* **60**, 1301–1321.

Edwards, M. A., Pecher, A., Kidd, W. S. F., Burchfiel, B. C. and Royden, L. H. (1999) Southern Tibet detachment system at Khula Kangri, Eastern Himalaya: A large-area, shallow detachment stretching into Bhutan? *J. Geology* **107**, 623–631.

Elderfield, H., Upstill-Goodard, R. and Sholkovitz, E. R. (1990) The rare earth elements in rivers, estuaries and coastal sea waters: processes affecting crustal input of elements to the ocean and their significance to the composition of seawater. *Geochim. Cosmochim. Acta* **55**, 1807–1813.

Forstner, U. and Wittmann, G. T. W. (1986) *Metal Pollution in the Aquatic Environment*. Springer-Verlag, Berlin, 486 pp.

Gaillardet, J., Dupre, B., Allegre, C. J. and Negrel, P. (1997) Chemical and physical denudation in the Amazon river basin. *Chem. Geol.* **142**, 141–173.

Galy, A. and France-Lanord, C. (1999) Weathering processes in the Ganges-Brahmaputra basin and the riverine alkalinity budget. *Chem. Geol.* **159**, 31–60.

Gansser, A. (1983) Geology of Bhutan Himalayas: Denkenschrift der Schweizerischen Naturforschenden Gesellschaft. Band. 96, Basel, Birkhäuser, 181 pp.

Goldstein, S. J. and Jacobsen, S. B. (1987) The Nd and Sr in isotopic systematics of river water dissolved material, implications for sources of Nd and Sr in seawater. *Chem. Geol.* **66**, 245–272.

Goldstein, S. J. and Jacobsen, S. B. (1988) Rare earth elements in river waters. *Earth Planet. Sci. Lett.* **89**, 35–47.

Haskin, L. A., Haskin, M. A., Frey, F. A. and Wildman, T. R. (1968) Relative and absolute terrestrial abundance's of the rare earths. *Origin and Distribution of the Elements* (Ahrens, L. H., ed.), 889–912, Pergamon, New York.

Henderson, P. (1984) General geochemical properties and abundance of the rare earth elements. *Rare Earth Element Geochemsitry* (Henderson, P., ed.), 510 pp., Elsevier, Oxford.

Irion, G. (1991) Minerals in rivers. *Biogeochemistry of Major World Rivers* (Degens, E. T., Kempe, S. and Richey, J. F., eds.), 265–281, SCOPE 42, New York.

Janpangi, B. S. (1979) Four transverse subdivisions of Himalayas. *Tectonic Geology of the Himalayas* (Saklani, P. S., ed.), 221–242, Today and Tomorrow Printers, New Delhi.

Krishnaswami, S., Trivedi, J. R., Sarin, M. M., Ramesh, R. and Sharma, K. K. (1992) Strontium isotopes and rubidium in the Ganga-Brahmaputra river system: Weathering in the Himalaya, fluxes to the Bay of Bengal and contributions to the evolution of oceanic ^{87}Sr/^{86}Sr. *Earth Planet. Sci. Lett.* **109**, 243–253.

Kuehl, S. A., Hariu, T. M. and Moore, W. S. (1989) Shelf sedimentation of the Ganges-Brahmaputra river system: Evidence for sediment by-passing to the Bengal Fan. *J. Geology* **17**, 1132–1135.

Martin, J. M. and Meybeck, M. (1979) Elemental mass-balance of material carried by major world rivers. *Mar. Chem.* **7**, 173–206.

Martin, J. M. and Whitfield, M. (1983) The significance of river input of chemical elements to the ocean. *Trace Metals in Seawater* (Wong, C. S., Boyle, E., Bruland, K. W., Burton, J. D. and Goldberg, E. D., eds.), 265–296, Plenum, New York.

Martin, J. M., Hogdahl, O. and Phillipots, J. C. (1976) Rare earth elements supply to the oceans. *J. Geophys. Res.* **81**, 3119–3124.

McLennan, S. M. (1988) Recycling of the continental crust. *Pure Appl. Geophys. (PAGEOPH)* **128**, 683–724.

McLennan, S. M. (1989) Rare earth elements in sedimentary rocks: Influence of provenance and sedimentary processes. *Rev. Mineral.* **21**, 116–200.

Milliman, J. D. and Syvitski, J. P. M. (1992) Geomorphic/tectonic control of the sediment discharge to the ocean: The importance of small mountainous rivers. *J. Geol.* **100**, 525–544.

Milliman, J. D., Broadus, J. M. and Gable, F. (1989) Environmental and economic implications of rising sea level and subsiding deltas—the Nile and Bengal example. *Ambio* **18**, 340–345.

Modak, D. P., Singh, K. P., Chandra, H. and Ray, P. K. (1992) Mobile and bound form of trace metals in sediments of the lower Ganges. *Water Research* **26**, 1541–1548.

Murray, R. W., Bucholtz Ten Brink, M. R., Gerlach, D. C., Ruess, G. P., III and Jones, D. L. (1992) Interoceanic variation in rare earth, major and trace element depositional chemistry of Chert: Perspectives gained from DSDP and ODP record. *Geochim. Cosmochim. Acta* **56**, 1897–1913.

National Research Council (NRC) (1990) Marine Analytical chemistry standards program, Division of Chemistry, NRC, Canada. BCSS-1, MESS-1, PACS-1, BEST-1, Marine sediment reference materials for trace elements and other constituents, 1–4.

Negrel, P., Allegre, C. J., Dupre, B. and Lewin, E. (1993) Erosion sources determined by inversion of major and trace element ratios in river water: the Congo basin case. *Earth Planet. Sci. Lett.* **120**, 59–76.

Pant, C. C. and Sharma, K. K. (1993) Quaternary sedimentation in the Indo-Gangetic basin. A review. *Curr. Sci.* **64**, 855–862.

Piper, D. Z. (1974) Rare earth elements in the sedimentary cycle: a summary. *Chem.Geol*. **14**, 285–304.

Ramesh, R., Ramanathan, A. L., Arthur James, R., Subramanian, V., Jacobsen, S. B. and Holland, H. D. (1999) Rare earth elements and heavy metal distribution in estuarine sediments of east coast of India. *Hydrobiologia* **57**, 1–11.

Rao, K. L. (1975) *India's Water Wealth*. Orient Longman Ltd., New Delhi, 255 pp.

Remy, J. M. (1979) Nepal Himalayas. *Tectonic Geology of the Himalayas* (Saklani, P. S., ed.), 129–150, Today and Tomorroe Printers, New Delhi.

Sarin, M. M., Krishnaswami, S., Dilli, K., Somayajulu, B. L. K. and Moore, W. S. (1989) Major ion chemistry of the Ganga-Brahmaputra river system: Weathering processes and fluxes to the Bay of Bengal. *Geochim. Cosmochim. Acta* **53**, 997–1009.

Sarin, M. M., Krishnaswami, K., Somayajulu, B. L. K. and Moore, W. S. (1990) Chemistry of uranium-thorium and radium isotopes in the Ganga-Brahmaputra river system: Weathering processes and fluxes to the Bay of Bengal. *Geochim. Cosmochim. Acta* **54**, 1387–1396.

Segall, M. P. and Kuehl, S. A. (1992) Sedimentary processes on the Bengal continetal shelf as revealed by clay size mineralogy. *Cont. Shelf Res*. **12**, 517–541.

Sengupta, S. (1966) Geological and geophysical studies in the western part of the Bengal basin, India. *Amer. Assoc. Pet. Geol. Bull* **50**, 1001–1017.

Sholkovitz, E. R. (1992) Chemical evolution of the rare earth elements: Fractionation between colloidal and solution phases of filtered river water. *Earth Planet. Sci. Lett*. **114**, 77–84.

Sholkovitz, E. R. (1993) The geochemistry rare earth elements in the amazon river Estuary. *Geochim. Cosmochim. Acta* **57**, 2181–2190.

Sholkovitz, E. R. (1995) The aquatic chemistry of rare earth elements in rivers and estuaries. *Aquatic Geochemistry* **1**, 1–34.

Sholkovitz, E. R. and Elderfield, H. (1988) The cycling of dissolved rare earth elements in Chesapeake Bay. *Global Biogeochem. Cycles* **2**, 157–176.

Sholkovitz, E. R., Shaw, T. J. and Schinder, D. L. (1992) The geochemistry of rare earth elements in the seasonally anoxic water column and pore waters of Chesapeake Bay. *Geochim. Cosmochim. Acta* **56**, 3389–3402.

Sholkovitz, E. R., Landing, W. M. and Lewis, B. L. (1994) Ocean particle chemistry: The fractionation of rare earth elements between suspended particles and seawater. *Geochim. Cosmochim. Acta* **58**, 1567–1579.

Stallard, R. F. and Edmond, J. M. (1987) Geochemistry of the Amazon, 3. Weathering chemistry and limits to dissolved inputs. *J. Geophys. Res*. **92**, 8293–8302.

Subramanian, V. (1993) Phosphorus, silicon and some trace contaminates in the Ganges estuary. *Estuaries* **16**, 453–458.

Subramanian, V. and Jha, P. K. (1988) Geochemical studies on the Hoogly (Ganges) estuary. *Mitt. Geol. Palaontol. Inst. Univ. Hamburg, SCOPE/UNEP Sonderb* **66**, 267–288.

Subramanian, V., Van't Dack, L. and Van Grieken, R. (1985) Chemical composition of river sediments from the Indian subcontinent. *Chem. Geol*. **48**, 271–279.

Subramanian, V., Van't Dack, L. and Van Grieken, R. (1987a) Heavy metal distribution in the sediments of Ganges and Brahmaputra river. *Environ. Geol. and Water Sci*. **9**, 93–103.

Subramanian, V., Van't Dack, L. and Van Grieken, R. (1987b) Transport and fractionation of Pb in river sediments from the Indian subcontinent. *J. Geol. Soc. India* **30**, 217–226.

Subramanian, V., Jha, P. K. and Van Grieken, R. (1988) Heavy metals in the Ganges estuary. *Mar. Poll. Bull*. **19**, 290–293.

Taylor, S. R. and McLennan, S. M. (1985) *The Continental Crust: Its Composition and Evolution*. Blackwell Publ., Oxford, 312 pp.

Taylor, S. R., McLennan, S. M. and McCulloch, M. T. (1983) Geochemistry of LOESS, continental crustal composition and crustal model ages. *Geochim. Cosmochim. Acta* **47**, 1897–1905.

Toyoda, K., Nakumara, Y. and Masuda, A. (1990) Rare earth elements of Pacific pelagic sediments. *Geochim. Cosmochim. Acta* **54**, 1053–1103.

Trefry, J. H. and Presley, B. J. (1976) Heavy metal transport from the Mississippi River to the Gulf of Mexico. *Marine Pollutant Transfer* (Windom, H. L. and Duce, R. A., eds.), 39–76, Lexington Books, Lexington, Mass.

Turner, D. R., Whitefield, M. and Dickson, A. K. (1981) The equilibrium speciation of dissolved components in freshwater and seawater at 25°C and 1 atm. Pressure. *Geochim. Cosmochim. Acta* **54**, 1093–1103.

Valdia, K. S. (1979) Kumaon Himalayas. *Tectonic Geology of the Himalayas* (Saklani, P. S., ed.), 1–14, Today and Tomorrow Printers, New Delhi.

Valdiya, K. S. (1980) *Geology of Kumaon Lesser Himalayas*. Wadia Inst. of Himalayan Geology, Dehra Dun, 291 pp.

Wadia, D. N. (1981) *Geology of India*. Tata McGraw-Hill, New Delhi, 508 pp.