Environ Monit Assess (2010) 161:161–176
DOI 10.1007/s10661-008-0735-2

Geochemical characterisation of major and trace elements in the coastal sediments of India

R. Alagarsamy · J. Zhang

Received: 17 July 2008 / Accepted: 23 December 2008 / Published online: 18 March 2009

Abstract Thirty-five surface sediment samples from the Indian continental shelf were recovered offshore from the mouths of the major rivers (Brahmaputra, Ganges, Narmada, Tapti, Godavari, Krishna and Cauvery) discharging into the coastal region of both east and west coasts were analysed using inductively coupled plasma atomic emission spectroscopy for selected major (i.e. Al, Ca, Fe, K, Ti, Mg and Na) and trace elements (e.g. Ba, Co, Cr, Cu, Ga, Ni, P and V), after total dissolution. The main objectives are to understand the processes controlling major and trace elements in the surface sediments and to identify natural and anthropogenic sources in the coastal environment using statistically regressed elemental concentrations to establish regional baseline levels. Metal enrichments observed close to the major urban areas in the east and west coasts are associated with the industrialised activities areas rich in Cu and Co in both the east and west coast sediments. Normalisation of metals to Al indicated that high enrichment factors are in the order of Ca>Ti≥Fe>Na>Mg>Co>Cu>Ga>V>Ba except K and P depletion. This indicated that the characteristic of estuarine sediment showed higher level along the west coast of India, which was reflected in the coastal sediments as similar to the source of its origin from the riverine composition and its abundances.

Keywords Major and trace elements · Sediment · Continental shelf · India · Enrichment factors

Introduction

The long-term environmental monitoring requires an evaluation of the degree of contamination in marine and estuarine areas with particular emphasis upon understanding the environmental processes controlling sediment distribution in the assessment of trace elemental studies. Land-derived polluted materials have been documented in both estuaries and, to a less degree, in shelf sediments (Mil-Homens et al. 2006). However, differences in the environmental settings and the resulting sediment characteristics of different

---

R. Alagarsamy
National Institute of Oceanography,
Council of Scientific and Industrial Research (CSIR),
Donapaula, Goa-403004, India

J. Zhang
State Key Laboratory of Estuarine and Coastal
Research, East China Normal University,
3663 Zhongshan Road North, Shanghai 200062,
People's Republic of China

R. Alagarsamy (✉)
Earth Dynamic System Research Center,
National Cheng Kung University, Tainan,
Taiwan 70101, Republic of China
e-mail: alagar@nio.org

shelf areas have not been emphasised, which is necessary in order to clarify the influences upon the land-to-sea transfer of pollution. Assuming a certain amount of transfer from the estuary to the Indian Ocean, an evaluation of the Indian shelf sediment quality is needed to understand the overall fate of contaminants. In order to meet the objective of this study, the distributions of major and trace elements have been investigated for both east and west continental shelfs of India, located in the vicinities of major river mouths (Brahmaputra, Ganges, Narmada, Tapti, Godavari, Krishna and Cauvery). The studies on the shelf region of India are scarce compared to other world region. The studies related to the east and west coasts of India is dealt with certain part of the region (Paropkari et al. 1978; Jonathan et al. 2004). The geochemistry of Arabian Sea sediments have been studied by Kolla and Biscaye (1973, 1977), Kolla et al. (1976a, b, 1981a, b), Shankar et al. (1987), Paropkari (1990), Pedersen et al. (1992). These studies are mainly focused on the clay mineralogy and elemental distribution in the sediment samples in Arabian Sea, the west coast of India. The present study aims to investigate on the geochemistry of the surficial sediment along the east and west coasts of India influenced by the riverine input. The main objectives are (1) to characterise the behaviour of major (Al, Ca, Fe, Ti, K, Mg and Na) and trace elements (Ba, Co, Cr, Cu, Ga, Ni, P and V) in the surface sediments; (2) to establish baseline models by means of a normalisation method and assess the contribution from natural and anthropogenic sources in the coastal environment; and (3) to evaluate the spatial distribution of major and trace elements in the east and west coasts of India.

Materials and methods

Study area

East coast of India

The outer limit of the eastern continental shelf of India lies at ∼200 m (Fig. 1), and the inner shelf and the continental slope are covered by clastic sediments (Rao 1985). The outer shelf is covered by calcareous relict sediments, and off the river mouths, the shelf is covered by fine-grained terrigenous sediments. The shelf at the mouths of the rivers receives a large part of its sediment from the rivers Ganges, Brahmaputra and Mahanadi in the north, Godavari and Krishna in the central region, all forming fertile and heavily populated deltas. Sediment from the rivers has made the bay a shallow sea, and the waters have reduced the salinity of surface waters along the shore. Sediment input and annual discharge is less from the smaller rivers such as Pennar and Cauvery in the south (Rao 1979, 1985).

West coast of India

The Indus river is the largest source of sediments in the Arabian Sea, which extend outward to a distance of ∼1,000–1500 km (Rao and Rao 1995). It predominantly drains the Precambrian metamorphic rocks of Himalayas and to a lesser extent the semi-arid and arid soils of West Pakistan and NW India (Krishnan 1968). Deccan Trap basalts (Fig. 1) are the predominant rock types cropping out in the Saurashtra and the drainage basins of the Narmada and Tapti rivers, which annually discharge ∼60 × 10^6 tonnes sediment through the Gulf of Cambay (Rao 1975) where a semi-arid climate prevails. The Western Ghats are composed of basalts between Bombay and Goa, and Precambrian granites, gneisses, schists and charnockites between Goa and Cochin (Krishnan 1968). The Ghats are located on the coast between Goa and Bhatkal but are 50–80 km from the coast south of Bhatkal. The source of sediments in rivers originating in the western part of India is derived as the black “cotton soils”, covering the Deccan Traps, a large percentage of which is mainly composed of montmorillonite. The drainage area in the upper reaches of these rivers is a montmorillonite-rich zone, but in the lower reaches, they drain through Precambrian formations that contain kaolinite rich soils that are of secondary significance in the shelf sediments derived from the Godavari and Krishna rivers (Rao 1991). Relic carbonate deposits occurred on the western margin of India (Rao et al. 2003). It is well established that source rock compositions and weathering mechanisms basically control the

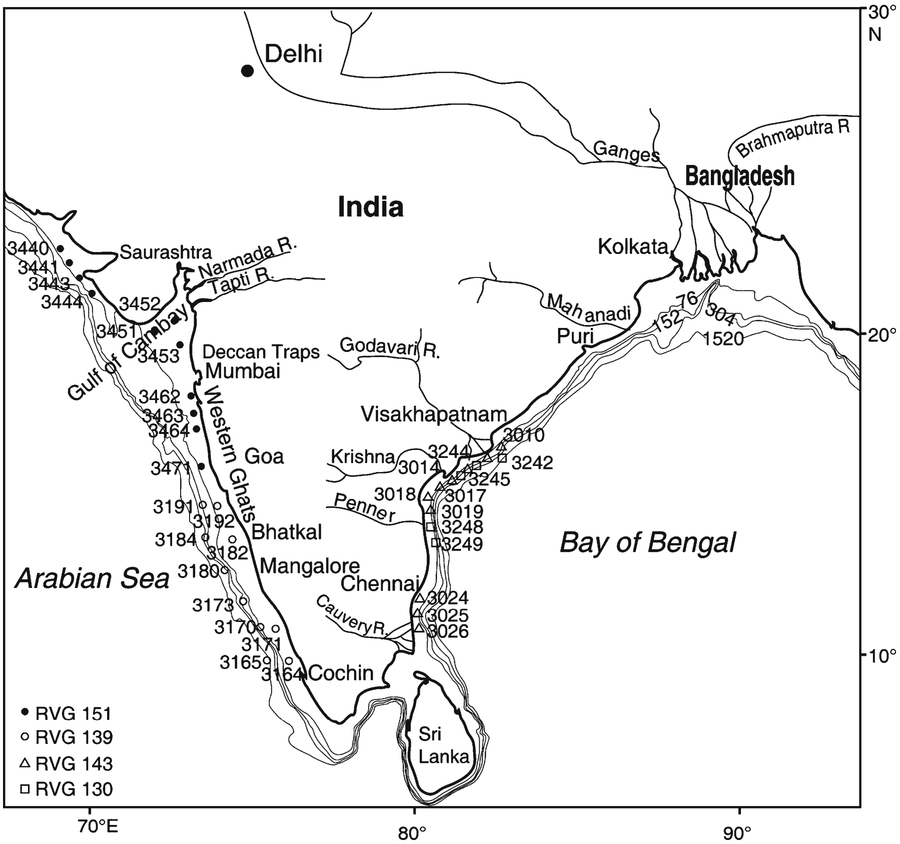


Fig. 1 Location of sediment sampling stations in the coastal region of India. *Empty square* RVG 130; *empty triangle* RVG 143; *empty circle* RVG 139; *filled circle* RVG 151 represent the sampling sites of different cruises

distinct geochemical compositions of sediments in the east and west coasts of India (Alagarsamy and Zhang 2005).

Surface sediments from the east and west coasts of India were collected using a Van Veen Grab/Snapper during several cruises of R.V. Gaveshani (130, 139, 143 and 151; Fig. 1; Table 1). Subsamples were taken from the uppermost layer of the sediment taking care to minimise the contamination. The samples were frozen after collection and later thawed, dried at 50–60°C in an oven and disaggregated in an agate mortar before chemical treatment for total metal analysis. For element analysis, the known quantity (~0.2 g) of the powdered samples were digested with a mixture of concentrated $HF–HNO_3–HClO_4$ for the total metal content (Zhang and Liu 2002). The solutions were analysed for Al, Mg, Ba, Ca, Na, K, Ti, Fe, Cr, Cu, Ni, Co, P, Ga and V using inductively coupled plasma atomic emission spectroscopy (model PE-2000).

Accuracy of the analytical methods was monitored by repeated analysis of standard reference materials (i.e. GSD-9 and NIM-G) together with batch of sediment samples. These data gave satisfactory results with analytical values within ±1–10% for different elements using the certified ones (GSD-9) except K and P and within ±4% for K and P of the certified ones (NIM-G).

Results and discussion

Average concentrations and ranges of all the measured metals in the coastal surface sediments, crustal average (Taylor 1964) and average shale (Turekian and Wedepohl 1961) are depicted in Table 2. The highest values were recorded for Ca, Al and Fe, which originate in a large extent from the earth crust via weathering except Ca. Other metals that are measured in the shelf sediments, originate both from natural and anthropogenic

Table 1 Sample details and locations

Sr. no	Station no.	Latitude (E)	Longitude (N)	Depth (m)
RVG 130				
1	3012	16°26′	81°31.0′	40
2	3013	16°11′	81°47.5′	55
3	3014	15°54.5′	81°14.6′	50
4	3017	15°39.5′	81°00′	48
5	3018	15°22.8′	81°33.1′	52
6	3019	15°0.3′	80°16.′7′	52
7	3024	12°00′	80°05.6′	49
8	3025	12°00′	80°04.2′	50
9	3026	11°00′	80°02.5′	52
RVG 143				
10	3242	16°31′	82°30.7′	700
11	3244	15°39.1′	81°06.4′	660
12	3245	14°54.1′	80°20.5′	80
13	3248	13°30.5′	80°31.7′	120
14	3249	13°7.8′	80°32.6′	120
RVG 139				
15	3164	10°02.5′	76°00.0′	35
16	3165	10°01.0′	75°0.1′	90
17	3170	10°58.2′	75°8.7′	73
18	3171	10°58.2′	75°39.0′	33
19	3173	12°00′	74°40.0′	75
20	3180	12°59′	74°20.9′	60
21	3182	14°00′	74°19.0′	40
22	3184	14°00′	73°40.0′	78
23	3191	14°59.7′	73°20.0′	75
24	3192	14°59.6′	73°40.0′	49
RVG 151				
25	3440	22°53.7′	68°22′	23
26	3441	22°24′	68°38′	22
27	3443	21°54.1′	68°56′	45
28	3444	21°30′	69°10′	57
29	3451	20°41′	70°44.6′	20
30	3452	20°14.1′	72°11.9′	30
31	3453	19°30′	72°16′	30
32	3462	18°20.4′	72°41.6′	25
33	3463	17°50′	72°46′	32
34	3464	17°19′	72°50.5′	60
35	3471	16°06′	73°00′	70

sources. The relative abundances of these metals in the shelf sediments were as follows: Ca > Al > Fe > Na > Mg > Ti > K > Ba > P > V > Cu > Cr > Co > Ni > Ga.

Variation of elements in the east and west coasts of India

When compared with shale value (Fig. 2a–b), Al, Na and V is slightly enriched in the east coast and higher in the west. This could be a dilution with lithic components that are low in Al content, such as dolomite or palygorskite, and affects all other elements that are not enriched in dolomite or palygorskite. Hence, the distribution patterns of all refractory elements, except Mg, reveal minimum concentrations. Mg is enriched in the west coast of India than in the east; The variations of Mg in rocks can largely be attributed to three processes that enrich Mg^{2+} ions in rock-forming minerals: (1) a substitution of Mg^{2+} for Fe^{2+} in crystal structures of Fe-rich minerals, preferentially in ultramafic olivines, pyroxenes, biotite and chlorite and (2) a substitution for Ca^{2+} in carbonates. The magnitude of the Mg incorporation into the carbonates depends on the Mg concentration of the solution, where the carbonates precipitate, culminating in the formation of dolomite. Lastly is the (3) adsorption onto clay particles (the Mg^{2+} ions have a large cation exchange capacity). Ca, Ti, Fe, Cu, Co and Ga are enriched both east and west; among the various carbonates, non-carbonate Ca is primarily found in plagioclase and in marine sediments in the form of apatite—a Ca-phosphate formed from fish bones and other biogenic debris (Sirocko et al. 2000). This high Ti content only occurs in shallower waters near the coast, an observation that might be explained by two processes: (1) winnowing of the sediment surface by the current activity that concentrates Ti-rich heavy minerals (Shimmield et al. 1990) and (2) rapid settling of heavy mineral particles from the area adjacent to basaltic source rocks (Deccan), which are rich in Ti (Turekian and Wedepohl 1961). Fe is leached from the Fe-rich basalts of the Deccan Traps, which could enrich the Fe content in the samples. Organic matter is known to contain up to 100 ppm Co and has high flux rates of organic carbon, which apparently transfers high amounts of Co to the deep-sea where C$_{org}$ is then remineralised—substantial proportions of Co and Ni can, however, be retained by the sediments. K, P and Ba is depleted in both the east and west coasts of India with the exception of Ba enrichment observed in one station in the west. The low value of P could be due to lithic minerals, like quartz, feldspar and biotite, which always exhibit values of <0.03% P. The Ba enrichment can be a result of sequestration of Ba from solution and

Table 2 Chemical composition of major and trace elements abundances in sediment, SPM, soil on a world basis and measured concentrations of metals in the coastal sediments

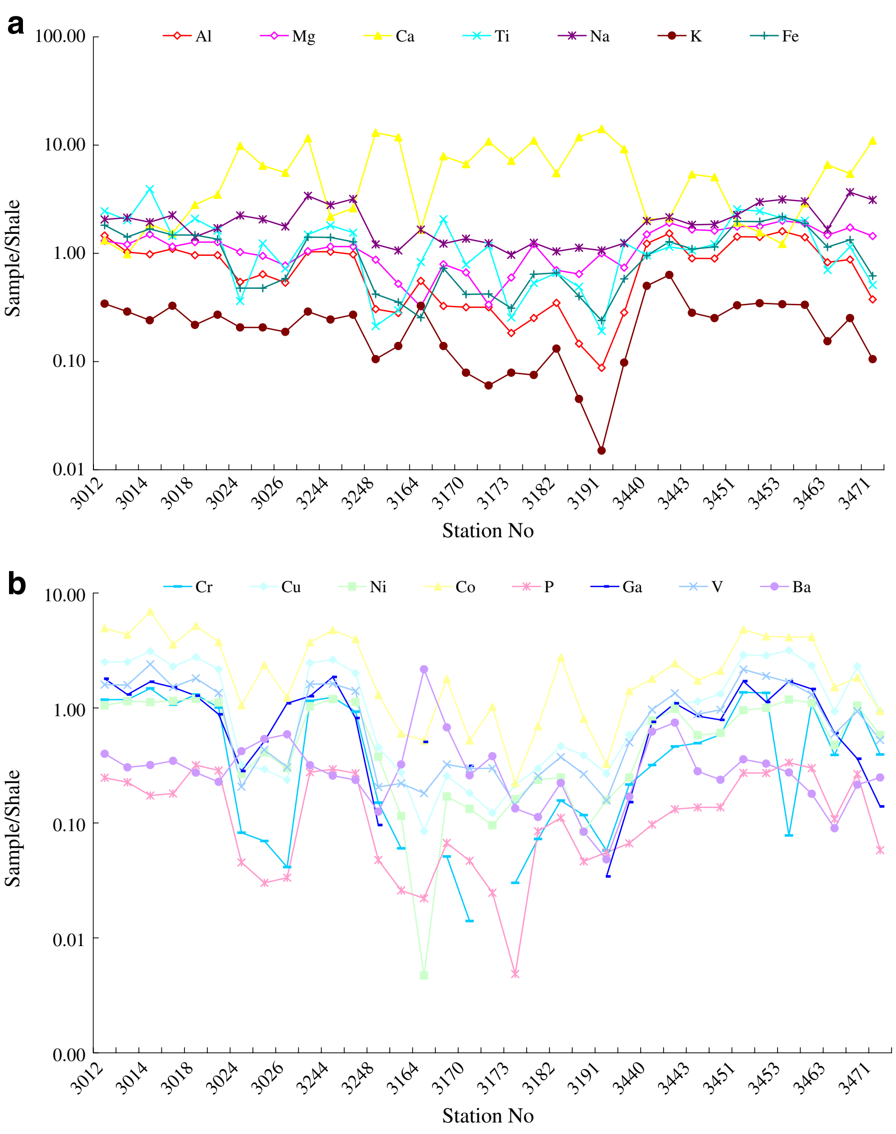
Metals	WA	WSR	WAS	Average shale	Crustal average	East coast			West coast		
						Min	Median	Max	Min	Median	Max
Al (%)	9.4	6.93	7.10	8.00	8.23	2.25	6.77	11.68	0.7	5.82	12.79
Fe (%)	4.8	3.59	4.00	4.72	5.63	1.67	5.27	8.58	1.13	4.54	10.27
Mg (%)	1.18	1.64	0.50	1.49	2.33	0.78	1.62	2.23	0.48	1.83	2.98
Ca (%)	2.15	4.50	1.50	2.21	4.15	2.17	11.85	28.77	2.7	13.80	26.18
Na (%)	0.71	1.42	0.50	0.96	2.36	1.02	2.00	3.26	1.0	1.82	3.52
K (%)	1.42	2.44	1.40	2.66	2.09	0.28	0.63	0.91	0.12	0.58	1.68
Ti* ($\mu g\ g^{-1}$)	4,160	3,800	5,000	4,700	5,700	0.1	0.71	1.84	0.09	0.54	1.2
P ($\mu g\ g^{-1}$)	1150	610	800	698.24	1050	18.07	122.31	221.89	3.38	87.77	233.64
V ($\mu g\ g^{-1}$)	170	97	100	90	135	18.48	104.55	144.86	14.18	68.86	194.82
Cr ($\mu g\ g^{-1}$)	100	97	70	90	100	3.71	70.4	133.22	N.D	45.94	135.86
Co ($\mu g\ g^{-1}$)	20	13	8	19	25	11.39	64.74	98.46	4.22	35.91	91.28
Ni ($\mu g\ g^{-1}$)	90	49	50	68	75	7.8	56.39	81.76	< 1	35.05	80.47
Cu ($\mu g\ g^{-1}$)	100	32	30	45	55	10.63	78.27	140.14	3.82	48.49	142.78
Ba ($\mu g\ g^{-1}$)	600	445	500	580	425	72.68	193.72	341.71	27.93	216.36	1258.10
Ga ($\mu g\ g^{-1}$)				19	15	N.D	21.04	35.57	N.D	14.70	32.46

WA World's average suspended sediments and *WSR* world's surface rock is taken from Martin and Meybeck (1979); *WAS* world's average soils from Bowen (1979). The average shale is taken from Turekian and Wedepohl (1961) and crustal average is taken from Taylor (1964). Ti* in % for east and west coast sediment samples

by selected sediment components such as $CaCO_3$. The highest Ba contents are found in sediments rich in biogenic opal as diatom frustules can contain up to 30,000 ppm Ba (Collier and Edmond 1984). This Ba is removed from the water column by adsorption or by the formation of $BaSO_4$ crystals in reducing micro-environments of sinking organic particles (Bishop et al. 1977). The crystals are stable in the sediments and dissolve only under extreme reducing conditions. The enrichment of Ga observed in the samples is related to weathering of basaltic rocks, and high Ga values are related to alkaline igneous rocks. Cr and Ni is slightly enriched in the east coast than the west except some low values (Cr and Ga) in samples, which is not shown in Fig. 2a–b. High Cr contents in clay minerals (illite) that are derived from soils and trapping of Cr in strongly reducing sediments could increase the Cr content in the sediment. Like Cr and Co, Ni concentrations are highest in ultramafic rocks (Turekian and Wedepohl 1961). In ocean water, the dissolved Ni content reveals higher values well below the surface rather than at the surface, and the depth profile is similar to the dissolved Zn content, which in turn is related to the nutrient H_4SiO_4 content (Broecker and Peng 1982; Bruland 1980). The connection between Ni and the nutrient cycle is also reflected by high Ni contents found in marine organic matter (Collier and Edmond 1984). A third factor affecting Ni concentrations in sediments is its tendency to bind to metals, especially sulfides to Fe (pyrite). Copper concentrations in rocks reveal average values between 5 and 100 ppm—basalts have the highest values and feldspar-rich rocks have the lowest (Turekian and Wedepohl 1961). Bruland (1980) and Broecker and Peng (1982) demonstrated that Cu concentrations in ocean waters increase with water depth—a pattern dependent on the nutrient content of the water and reflected in the chemical composition of plankton (Collier and Edmond 1984) and also by Saager et al. (1992) in the Arabian Sea. Cu is found to be highly enriched in the clay fraction and associated with high organic matter content. Thus, the Cu enrichment appears to be caused by the fine-grained texture of sediments solely in this region.

Cu and Co enrichment is observed in the region close to Visakhapatnam and Mumbai coast, where industrial and harbour activities are intense. Visakhapatnam hosts several major industries viz. steel, refinery, petroleum products, petrochemicals, zinc, polymers, etc. Transportation to and from the port and industrial activities

Fig. 2 **a-b** Plot showing the variation of shale normalised metals in the east and west coasts of India



also play a major role in increasing the metal level in this region. Similarly, Mumbai coast is also affected due to shipping and harbour activities, industrial and urban waste discharges, and dredging, etc. could contribute to the enrichment of metals in the coastal environment. The sediment metal concentrations found in this study (Table 3) were of the same order of magnitude as metal concentrations found by diverse authors in sediments of Indian estuaries (Biksham and Subramanian 1988; Subramanian et al. 1988; Ramesh et al. 1990; Ramanathan et al. 1993; Alagarsamy 2006) except for Fe and Mn observed in the Mandovi estuary, west coast of India (Table 4). The normalised values of Mg, Ca, K, Ti and Fe with Al indicated that the estuarine sediment showed higher level along the west coast of India, which was reflected in the coastal sediments as similar to the source of its origin from the riverine composition.

Geochemical normalisation and EF

In an attempt to compensate for the natural variability of major and total trace elements in sediments, normalisation was done so that any

Table 3 Comparison of the major and trace elements abundances in the estuarine and coastal sediments from different areas of India

Metals	Ganges[a]	Brahmaputra[a]	Krishna[a]	Narmada[a]	Tapti[a]	Cauvery[a]	Godavari[a]	Hugli[b]	Coastal Bay of Bengal[c]
Al (%)	4.66	5.6	3.38	2.89	4.44	4.87	4.78	1.93–3.12	2.07
Fe (%)	2.16	2.9	4.23	3.14	1.09	1.76	6.03	2.53–4.01	1.50
Mg (%)	1.32	1.66	1.30	1.02	2.40	1.10	1.15	0.68–1	1.72
Ca (%)	2.34	1.93	5.34	2.01	8.16	1.50	3.81	0.49–0.96	0.91
Na (%)	–	–	–	–	–	–	–	0.029–0.97	1.18
K (%)	1.33	1.24	1.07	0.93	0.42	1.10	1.02	0.28–0.47	0.49
Ti (μg g^{-1})	0.30	0.31	0.55	0.40	2.11	0.30	0.80	0.3–0.39	–
V (μg g^{-1})	86	137	203	249	456	88	310	29–47	–
Cr (μg g^{-1})	52	100	–	–	–	–	140	28.8–49.3	57
Co (μg g^{-1})	22	31	47	29	36	64	50	10.4–15.9	9
Ni (μg g^{-1})	20	47	–	–	–	–	52	26.5–44.5	30
Cu (μg g^{-1})	21	17	49	46	126	12	73	21.5–64.1	20
Ba (μg g^{-1})	348	347	425	330	280	444	537	75.8	58.6
Ga (μg g^{-1})	–	–	–	–	–	–	–	5.26–9.28	–

[a] Biksham and Subramanian (1988)
[b] Sarkar et al. (2004)
[c] Selvaraj et al. (2004)

anthropogenic metal contributions could be detected and quantified. Loring (1991) indicated that the natural mineralogical and granular variability is best compensated by the geochemical normalisation of major and trace metal data.

The following equation was used to estimate the enrichment factor (EF) of metals (Fig. 3a–b) from each sediment station using Al as a normaliser to correct for differences in sediments grain size and mineralogy:

$$EF=(Me/Al)_{sample}\Big/(Me/Al)_{crustal\ average}$$

where (Me/Al)$_{sample}$ and (Me/Al) $_{crustal\ average\ value}$ are, respectively, the metal concentration (μg/g dw) except Mg, Ca, Ti, Na, K and Fe in relation to Al levels (% dw) in sediment samples; crustal average values were taken from Taylor (1964). EFs are close to unity point to crustal origin, while those greater than 10 are considered to be non-crustal source (Nolting et al. 1999). EF values lower than 0.5 can reflect mobilisation and loss of these elements relative to Al or indicate an overestimation of the reference metal contents (Zhang 1995). The higher EF values are observed in the order of Ca>Ti≥Fe>Na>Mg>Co>Cu>Ga>V>Ba except K and P depletion. The minimum EFs were less than the unity observed in the samples and the depletion of K and P, implying that these elements are depleted in some of the phases relative to crustal abundances in the study area.

Gradient method

The major and trace elements variation showed significant correlation against aluminium in the sediments (Tables 5 and 6). As discussed above, it was assumed priori that aluminosilicate minerals (i.e. kaolinite and smectite) are the major natural metal bearing phases in these sediments. The results appear to support this assumption, since aluminium accounts for most of the variability of other metals with the exception of calcium and barium, confirming that these elements are assocciated with aluminosilicate minerals (Rubio et al. 2000). Clearly, other phases such as iron oxides and organic matter could be important contributors to total natural metal concentrations in these sediments. The relatively close relationship between iron and aluminium, however, suggests that iron oxides are not important (i.e., iron is associated with aluminium in aluminosilicate phases).

For the metals that do correlate with aluminium, the relationship provides a useful method to normalise the relatively large range of observed

Table 4 Comparison of the major and trace elements abundances in the sediments from the other region

Metals	Coastal sediments–Brazilian Antarctic station[a]	Peru margin[b]	Namibian mud lens[b]	Gulf of California[b]
Al (%)	3.16	4.71	1.26	4.72
Fe (%)	6.47	2.17	1.00	2.15
Mg (%)	0.14	1.19	0.46	0.95
Ca (%)	0.58	4.75	2.21	1.48
Na (%)	–	3.74	0.98	1.06
K (%)	–	1.27	0.48	1.38
Ti (%)	0.58	0.25	0.10	0.23
P (%)	–	0.36	0.21	0.10
V (μg g^{-1})	204	152	138	101
Cr (μg g^{-1})	31	98	83	44
Co (μg g^{-1})	–	6.1	3.5	6.6
Ni (μg g^{-1})	101	74	46	38
Cu (μg g^{-1})	92	49	37	27
Ba (μg g^{-1})	41	314	324	566
Ga (μg g^{-1})	–	–	–	–

[a] Santos et al. (2005)
[b] Brumsack (2006)

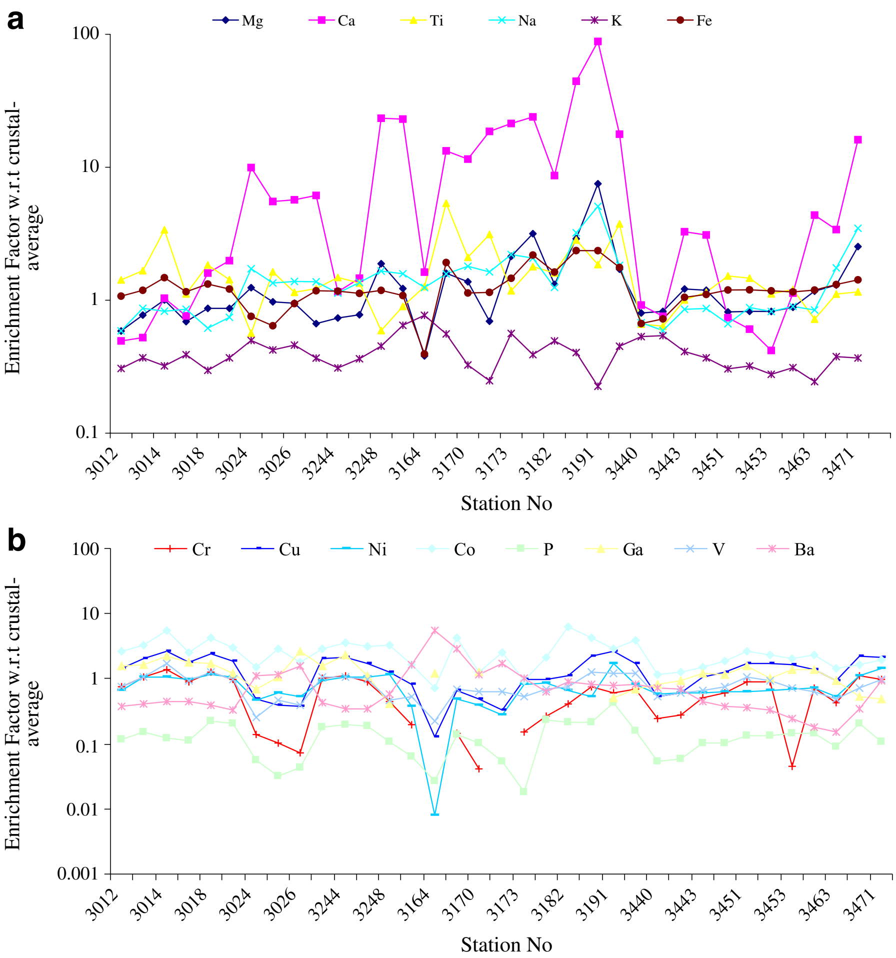


Fig. 3 **a**–**b** Plot showing the variation of enrichment factor in the east and west coasts of India

Table 5 Coefficient of determination (R^2) for metals in surface sediments of east coast of India ($R^2 > 0.24$, $p < 0.05$, $n = 14$, bold numbers are significant)

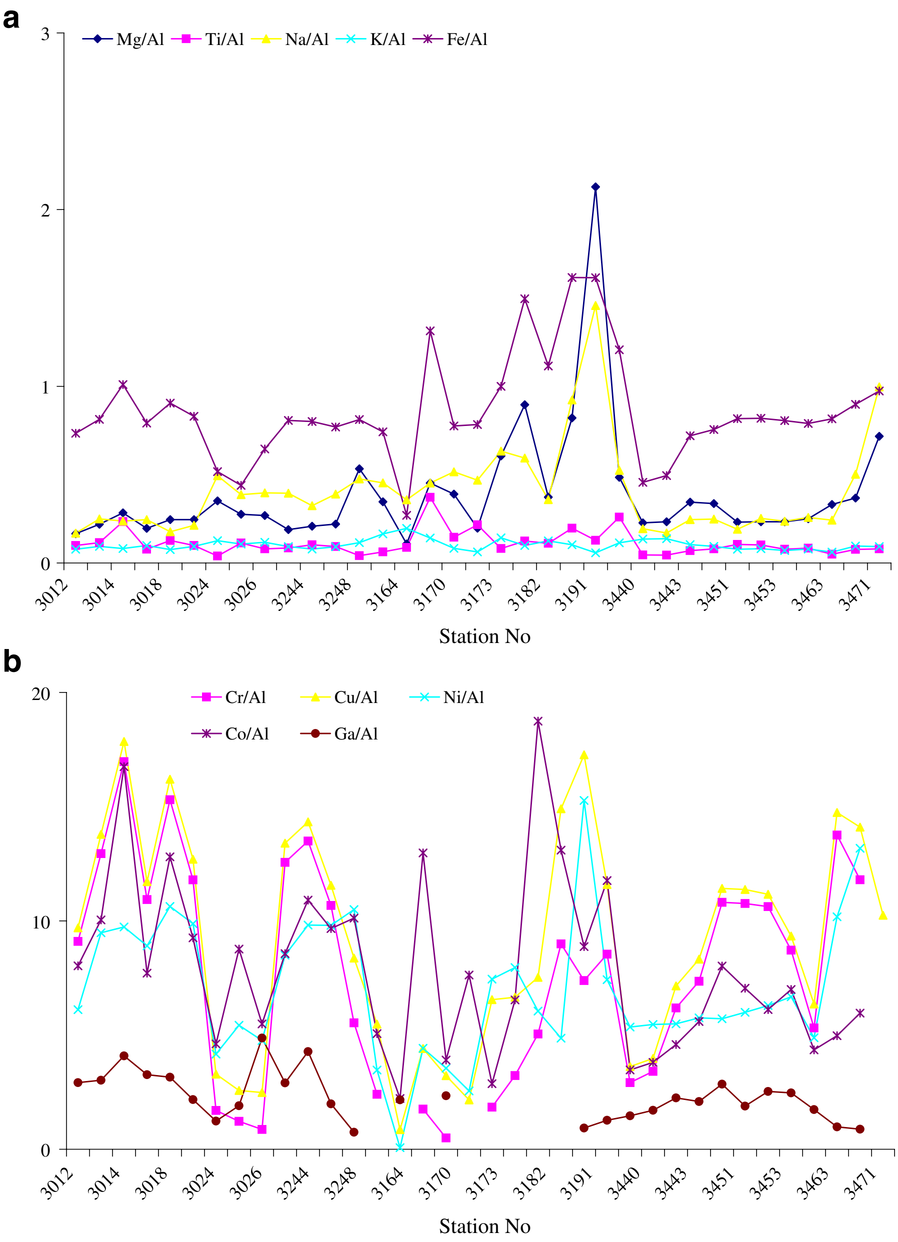
	Al	Mg	Ca	Ti	Na	K	Fe	Cr	Cu	Ni	Co	P	Ga	V	Ba
Al	**1.00**														
Mg	**0.64**	**1.00**													
Ca	**0.58**	**0.53**	**1.00**												
Ti	**0.55**	**0.74**	**0.52**	**1.00**											
Na	**0.27**	0.10	0.04	0.05	**1.00**										
K	**0.87**	**0.45**	**0.47**	**0.33**	**0.35**	**1.00**									
Fe	**0.89**	**0.73**	**0.56**	**0.70**	0.16	**0.69**	**1.00**								
Cr	**0.66**	**0.51**	**0.34**	**0.35**	0.22	**0.46**	**0.75**	**1.00**							
Cu	**0.74**	**0.72**	**0.47**	**0.70**	0.15	**0.52**	**0.94**	**0.80**	**1.00**						
Ni	**0.74**	**0.72**	**0.47**	**0.70**	0.15	**0.52**	**0.94**	**0.80**	**1.00**	**1.00**					
Co	**0.77**	**0.71**	**0.55**	**0.57**	0.22	**0.58**	**0.89**	**0.86**	**0.93**	**0.93**	**1.00**				
P	**0.67**	**0.82**	**0.55**	**0.92**	0.10	**0.40**	**0.84**	**0.60**	**0.89**	**0.89**	**0.80**	**1.00**			
Ga	**0.70**	**0.74**	**0.50**	**0.82**	0.15	**0.49**	**0.91**	**0.69**	**0.97**	**0.97**	**0.87**	**0.94**	**1.00**		
V	**0.67**	**0.37**	**0.51**	**0.56**	0.07	**0.46**	**0.72**	**0.38**	**0.64**	**0.64**	**0.54**	**0.61**	**0.65**	**1.00**	
Ba	0.01	0.06	0.00	0.01	0.00	0.00	0.07	0.22	0.16	0.16	0.17	0.07	0.10	0.00	**1.00**

natural metal levels in these sediments. In the case of the coastal sediments of India, aluminium clearly accounts for most of the grain size effect. As Al is mostly land-derived, the element/Al ratios of the clay fraction give information about changes in the terrigenous fraction (Fig. 4a–c). The abundances of major elements and their ratios relative to Al are found to be higher in the west coast than in the east except K, Mg/Al, Ca/Al and Na/Al ratio, which follow the similar trend and showed a higher enrichment of Mg/Al (2.13), Ca/Al (44.6) and Na/Al (1.46) at station 3191 that exceeded the crustal average at several stations. The higher concentration of Mg is attributed to Mg^{2+} by the ion exchange process with Ca^{2+} and the skeletal fragments, and organisms from the skeletal debris are made up of high Mg-calcite, contributing Mg to the present sediments and the dissolution of Mg in the shelf sediments available for reprecipitation (Rao 1978). There was no significant change in the K/Al ratio within the sediments of east coast, suggesting that no changes in the relative illite content of the terrigenous fraction have occurred at this site. K/Al ratio is

Table 6 Coefficient of determination (R^2) for the metals in surface sediments of west coast of India ($R^2 > 0.18$, $p < 0.05$, $n = 21$, bold numbers are significant)

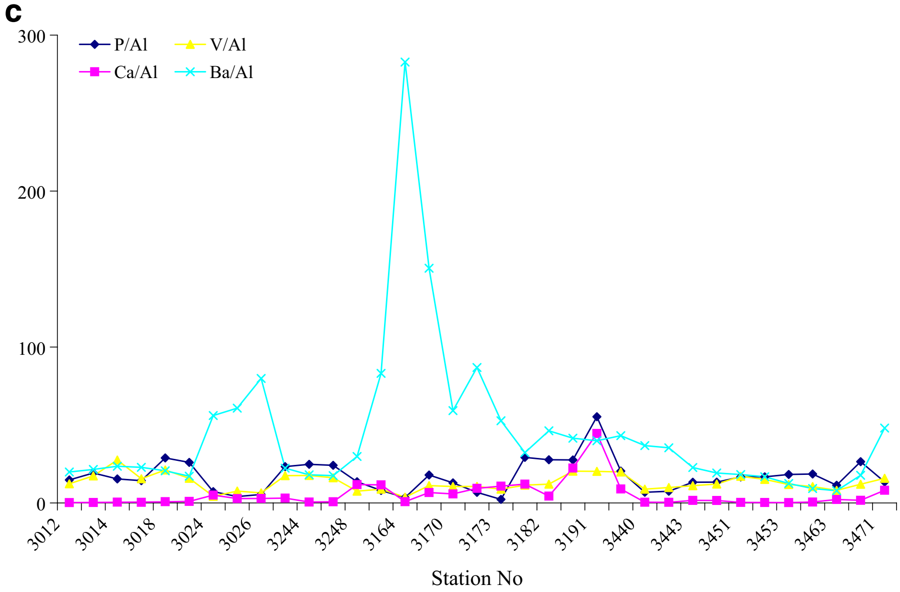
	Al	Mg	Ca	Ti	Na	K	Fe	Cr	Cu	Ni	Co	P	Ga	V	Ba
Al	**1.00**														
Mg	**0.70**	**1.00**													
Ca	**0.71**	**0.27**	**1.00**												
Ti	**0.49**	**0.25**	**0.37**	**1.00**											
Na	**0.50**	**0.55**	**0.26**	**0.26**	**1.00**										
K	**0.76**	**0.42**	**0.71**	**0.22**	**0.27**	**1.00**									
Fe	**0.83**	**0.74**	**0.48**	**0.65**	**0.55**	**0.51**	**1.00**								
Cr	**0.67**	**0.66**	**0.38**	**0.56**	**0.62**	**0.29**	**0.91**	**1.00**							
Cu	**0.69**	**0.67**	**0.38**	**0.57**	**0.67**	**0.37**	**0.91**	**0.93**	**1.00**						
Ni	**0.69**	**0.67**	**0.38**	**0.57**	**0.67**	**0.37**	**0.91**	**0.93**	**1.00**	**1.00**					
Co	**0.83**	**0.87**	**0.43**	**0.40**	**0.75**	**0.70**	**0.85**	**0.81**	**0.83**	**0.75**	**1.00**				
P	**0.69**	**0.48**	**0.47**	**0.74**	**0.35**	**0.30**	**0.86**	**0.79**	**0.77**	**0.47**	**0.64**	**1.00**			
Ga	**0.85**	**0.67**	**0.51**	**0.65**	**0.77**	**0.70**	**0.89**	**0.76**	**0.85**	**0.82**	**0.80**	**0.52**	**1.00**		
V	**0.84**	**0.47**	**0.61**	**0.72**	0.18	**0.77**	**0.79**	**0.63**	**0.62**	**0.56**	**0.56**	**0.67**	**0.78**	**1.00**	
Ba	0.01	0.07	**0.19**	0.01	0.00	**0.24**	0.02	0.04	0.03	0.03	0.00	0.01	0.00	0.00	**1.00**

Fig. 4 **a–c** Plot showing the variation of Al normalised metal in the east and west coasts of India



depleted compared to crustal average. One of the end products of chemical weathering of Deccan Traps is smectites, which may be trapping K and thereby contributing to its limited mobility (Das and Krishnaswami 2006). A correlation of K and Al ($R^2 = 0.87$ in the east coast; 0.76 in the west coast) suggests that in the sediments, detrital minerals exclusively control K. K is mainly held in illite and feldspar; therefore, the variation in the K/Al ratio may reflect the variations in illite and feldspar present in the sediments. A higher potassium content relative to Al in sediments implies greater feldspar contribution. A low montmorillonite, high illite and kaolinite plus chlorite concentrations were observed in the sediment trap samples, which are derived from the Indus (Ramaswamy and Nair 1989). The higher Fe/Al reveals that Fe is enriched over Al in few stations in the west coast of India than in the east coast along with Ti/Al. Part of Fe and/or Ti

Fig. 4 (continued)



in sediments is known to be associated with the coarser size fractions, whereas Al is more concentrated in the finer fraction, the clay minerals. As a result, Al and Fe (Ti) can be fractionated in solid phases of rivers draining in to the sea. This co-variation is attributable to the presence of weathering resistant Fe–Ti minerals. In general, Ti shows a tight correlation with Fe (R^2 =~0.70), indicating a strong association between them in sediments of both east and west coasts of India. Ti/Al records appears to be controlled by two mechanisms, i.e. local precipitation that is determined by changes in rainfall and laterite production and eolian transportation, which supplies Ti-rich dust from the Arabian Peninsula during dry periods. Ti/Al occurs in the coastal sediments, indicating the major transition to dominance of carbonate dilution over insoluble residue. P/Al ratio indicates that the higher concentration of P was fixed in association with iron and supply of detrital phosphate or newly formed phosphatised limestone from neighbouring land (Jonathan et al. 2004). The abundances of trace elements (Ba, Co, Ni, Cu, Cr, Ga and V) and their ratios relative to Al in the sediments are highly variable in both east (abundances are higher for Cu, Ni, Ga and V) and west coast sediments. All elements except Ca, Na and Ba showed good relationship with Al and Ti, probably resulting from its incorporation in Fe-rich minerals and adsorption on oxides/hydroxides for Fe.

Factors controlling the distribution of trace metals in the coastal sediments

In order to determine the factor controlling the spatial distribution of both major and trace elements, as well as the relationships between them, statistical analysis were used. Correlation analyses performed on the metal data in the shelf sediments indicate strong correlations between Al and Mg, Ti, K, Fe, P, Cr, Cu, Ni, Co, V and Ga (Tables 5 and 6), which indicate a similarity in their geochemical source, i.e. weathering of crustal rocks in the drainage area of the shelf region. Chromium, copper, nickel, cobalt, phosphorus, vanadium and gallium are significantly correlated with iron ($R^2 = 0.72 - 0.94$) in the shelf sediments. The relationship observed between Fe with P, Cr, Cu, Ni, Co, V and Ga may result from their similar behaviour in the redox condition, which influences the processes of their accumulation and remobilisation from the sediment. The positive correlation between trace elements and Al is related to the abundance of clays (Horowitz et al. 1988). Thus, most of the variability of those element concentrations in the sediment can be explained by the Al concentration,

Fig. 5 **a**–**d** Plot showing the variation of non-normalised and gallium normalised metal in the east and west coasts of India

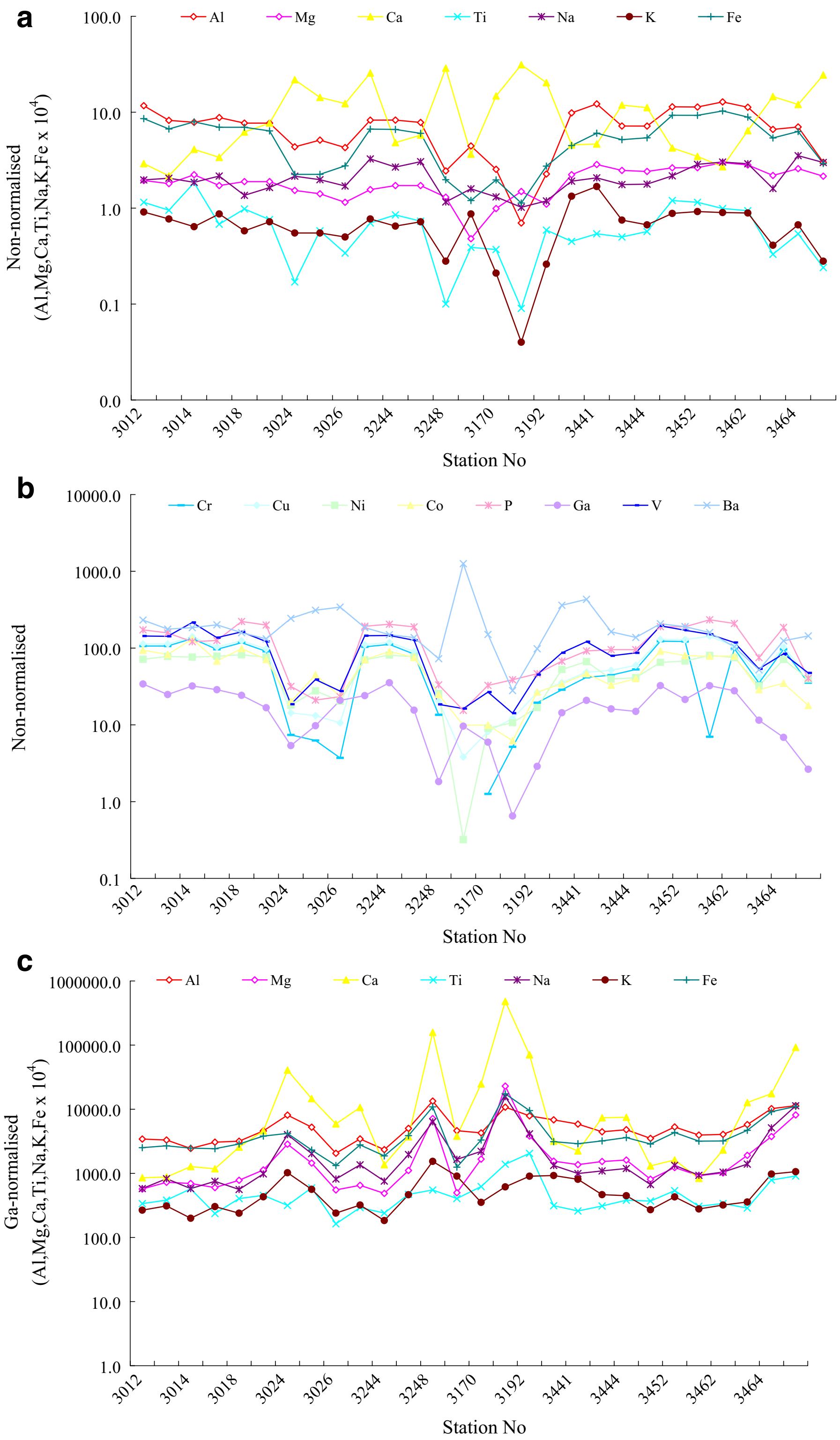
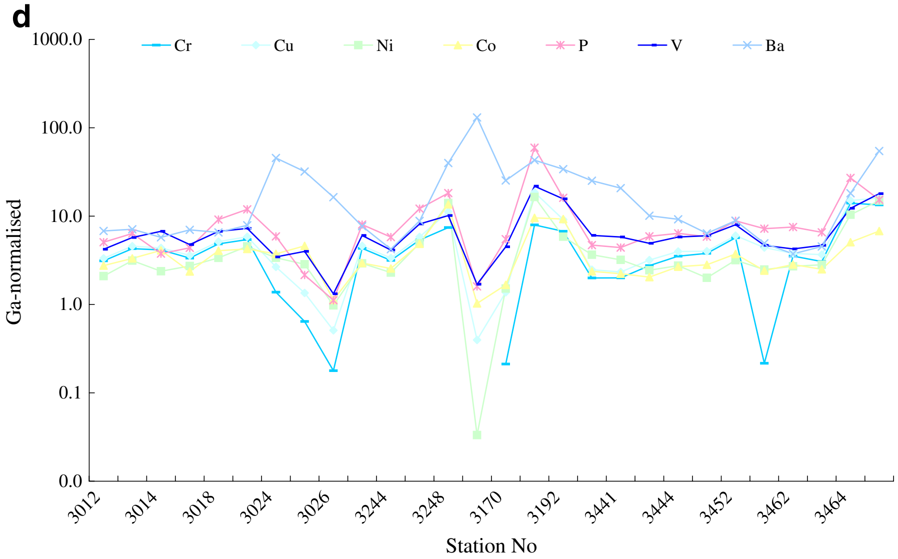


Fig. 5 (continued)



which reflects its texture and mineralogy. Therefore, the variation of these metal concentrations shows the same trend from one sampling point to another. Sodium and barium did not correlate with any metals, and calcium is inversely correlated with all metals except sodium, potassium and barium.

The statistical analysis of intermetallic relationship revealed that the high degree of correlation and significant regression relation among the metals indicate the identical behaviour of metals during its transport in the coastal environment (Tables 5 and 6). The positive correlations between Mg and transition trace elements, such as Fe, P, Cr, Cu, Ni Co, V and Ga indicate that these elements are usually associated in sediments containing chlorite and serpentine, in turn derived from weathering of mother rocks rich in olivine, pyroxenes and spinel. A negative correlation between Ca and Al in both east ($R^2 = 0.58$) and west coasts ($R^2 = 0.71$) of India indicates that CaO is mainly hosted within carbonates, thus precluding a significant presence of CaO-bearing silicates (Bianchini et al. 2002). The relic carbonate deposits occurred on the western margin of India (Rao et al. 2003). Carbonates have a diluting effect on this group of elements, which are of terrigenous origin (Rubio et al. 2000). In the present study, the poor association of Na and Ba with other metals (Al, Mg, Ca, Ti, K, Fe, Cr, Cu, Ni, Co, V and Ga) suggests that Na oxide and barite may be only a minor host phase for these elements in the coastal environment.

Anthropogenic inputs to the coastal sea along the east and west coasts of India

Using the general principles applied in the examples discussed above, an attempt can be made to estimate anthropogenic inputs of metals to the coastal sea. Natural background levels and anthropogenic inputs of selected metals to the coastal sea can be estimated for each of the stations studied along the east and west coasts. Ga values for station nos. 3249, 3165, 3171, 3173, 3180, 3182, 3184 are not detectable and these are not shown in the Fig. 5a–d. Using the upper crustal average and the grain size proxy Ga normalised data on which the spidergrams (Fig. 5a–d) are based, the method involves the establishment of a background value for each element for east and west coasts of India, determination of the average input of each element to the shelf region, calculation of the difference expressed as a percentage and the application of this percentage difference to calculate the percentage of the original (non-normalised) metal concentration in the shelf sediment that can be attributed to anthropogenic activity. It is necessary to use normalised data in the initial calculation of the percentage input in order to minimise the effects of different grain size distributions in the shelf sediment samples. Elements that are associated with clays or oxide coatings on clay minerals (Al, Mg, Na, K and Fe) are abundant in the sediments compared to other trace metals, which showed the similar variation pattern as EF.

Conclusions

The first data presented for the concentration, distribution and possible sources of selected major (i.e. Al, Ca, Fe, K, Ti, Mg and Na) and trace elements (e.g. Ba, Co, Cr, Cu, Ga, Ni, P and V) in the coastal sediments revealed the importance of geochemical processes and possible environmental consequences of potential pollution due to the nearby industrial activities. Metal enrichments observed close to the major urban areas in the east and west coasts are associated with the industrialised activity areas rich in Cu and Co in both the east and west coast sediments. Sediment metal concentrations found in both east and west coasts were comparable to aquatic systems classified as contaminated from other regions of the world.

This study first aimed to evaluate a reference element for normalising sediment major and trace metal concentrations along the east and west coasts of India. Application of the reference element technique identified the areas contaminated by examining bulk sediment concentrations alone. The normalisation technique enabled to assess the magnitude of enrichment relative to naturally occurring concentrations rather than relying on a limited number of measurements from the selected areas. The baseline reference element relationship will provide a tool for other scientists and managers involved in environmental monitoring and assessment programs or other research projects for assessing natural background levels of potentially important sediment contaminants in the east and west coasts of India.

Acknowledgements The authors wish to express their sincere gratitude to the Chinese Ministry of Education and SKLEC/ECNU, Shanghai for financial support. RA thanks Drs. S.W.A. Naqvi, E. Desa, former Director, NIO, S. R. Shetye, Director, NIO and CSIR, New Delhi for their kind permission during the period of work. We thank Nathalie Fagel, Andrew Hursthouse and an anonymous reviewer for their helpful comments. Pawaskar Pramod drafted Figure1. This is NIO contribution No. 4485.

References

Alagarsamy, R., & Zhang, J. (2005). Comparative studies on trace metal geochemistry in Indian and Chinese rivers. *Current Science, 89,* 299–309.

Alagarsamy, R. (2006). Distribution and seasonal variation of trace metals in surface sediments of Mandovi estuary, Goa in the west coast of India. *Estuarine, Coastal and Shelf Science, 67*(1–2), 333–339. doi:10.1016/j.ecss.2005.11.023.

Bianchini, G., Laviano, R., Lovo, S., & Vaccaro, C. (2002). Chemical–mineralogical characterisation of clay sediments around Ferrara (Italy): A tool for an environmental analysis. *Applied Clay Science, 21*(3–4), 165–176. doi:10.1016/S0169-1317(01)00086-2.

Biksham, G., & Subramanian, V. (1988). Elemental composition of Godavari sediments (Central and Southern Indian Subcontinent). *Chemical Geology, 70,* 275–286. doi:10.1016/0009-2541(88)90098-8.

Bishop, J. K., Edmond, J. M., Ketten, D. R., Bacon, M. P., & Silker, W. B. (1977). The chemistry, biology, and vertical flux of particulate matter from the upper 400 m of the equatorial Atlantic Ocean. *Deep-Sea Research, 24,* 511–548. doi:10.1016/0146-6291(77)90526-4.

Bowen, H. J. M. (1979). *Environmental chemistry of the elements* (pp. 1–320). New York: Academic.

Broecker, W. S., & Peng, T.-H. (1982). *Tracers in the sea.* New York: Eldigio.

Bruland, K. W. (1980). Oceanographic distributions of cadmium, zinc, nickel and copper in the North Pacific. *Earth and Planetary Science Letters, 47,* 176–198. doi:10.1016/0012-821X(80)90035-7.

Brumsack, H. J. (2006). The trace metal content of recent organic carbon-rich sediments: Implications for Cretaceous black shale formation. *Palaeogeography, Palaeoclimatology, Palaeoecology, 232*, 344–361.

Collier, R., & Edmond, J. (1984). The trace element geochemistry of marine biogenic particulate matter. *Progress in Oceanography, 13,* 113–199. doi:10.1016/0079-6611(84)90008-9.

Das, A., & Krishnaswami, S. (2006). Barium in Deccan Basalt Rivers: Its abundance, relative mobility and flux. *Aquatic Geochemistry, 12,* 221–238. doi:10.1007/s10498-005-5856-4.

Horowitz, A. J., Elrick, K., & Callender, E. (1988). The effect of mining on the sediment-trace element geochemistry of cores from the Cheyenne River arms of Lake OaheSouth Dakota, USA. *Chemical Geology, 67,* 17–33. doi:10.1016/0009-2541(88)90003-4.

Jonathan, M. P., Ram-Mohan, V., & Srinivaslu, S. (2004). Geochemical variations of major and trace elements in recent sediments, off the Gulf of Mannar, the southeast coast of India. *Environmental Geology, 45*, 466–480. doi:10.1007/s00254-003-0898-7

Kolla, V., Bà, A. W. H., & Biscaye, P. E. (1976a). Calcium carbonate distribution in the surface sediments of the Indian Ocean. *Journal of Geophysical Research, 81,* 2605–2616. doi:10.1029/JC081i015p02605.

Kolla, V., & Biscaye, P. E. (1973). Clay mineralogy and sedimentation in the eastern Indian Ocean. *Deep-Sea Research, 20,* 727–738.

Kolla, V., & Biscaye, P. E. (1977). Distribution and origin of quartz in the sediments of the Indian Ocean. *Journal of Sedimentary Petrology, 47,* 642–649.

Kolla, V., Henderson, L., & Biscaye, P. E. (1976b). Clay mineralogy and sedimentation in the western Indian Ocean. *Deep-Sea Research, 23,* 949–961.

Kolla, V., Kostecki, J. A., Robinson, F., Biscaye, P. E., & Ray, P. K. (1981a). Distribution and origin of clay minerals and quartz in surface sediments of the Arabian Sea. *Journal of Sedimentary Petrology, 51,* 563–569.

Kolla, V., Ray, P. K., & Kostecki, J. A. (1981b). Surficial sediments of the Arabian Sea. *Marine Geology, 41,* 183–204. doi:10.1016/0025-3227(81)90080-3.

Krishnan, M. S. (1968). *Geology of India and Burma* (p. 536). Madras: Higginbothoms Ltd.

Loring, D. H. (1991). Normalization of heavy-metal data from estuarine and coastal sediments. *ICES Journal of Marine Sciences, 48,* 101–115.

Martin, J. M., & Meybeck, M. (1979). Elemental mass-balance of material carried by major world rivers. *Marine Chemistry, 7,* 173–206. doi:10.1016/0304-4203(79)90039-2.

Mil-Homens, M., Stevens, R. L., Abrantes, F., & Cato, I. (2006). Heavy metal assessment for surface sediments from three areas of the Portuguese continental shelf. *Continental Shelf Research, 26,* 1184–1205. doi:10.1016/j.csr.2006.04.002.

Nolting, R. F., Ramkema, A., & Everaarts, J. M. (1999). The geochemistry of Cu, Cd, Zn, Ni and Pb in sediment cores from the continental slope of the Banc d'Arguin (Mauritania). *Continental Shelf Research, 19,* 665–691.

Paropkari, A. L. (1990). Geochemistry of sediments from the Mangalore-Cochin shelf and upper slope off southwest India: Geological and environmental factors controlling dispersal of elements. *Chemical Geology, 81,* 99–119. doi:10.1016/0009-2541(90)90041-5.

Paropkari, A. L., Rao, Ch. M., & Murty, P. S. N. (1978). Geochemical studies on the shelf sediments off Bombay. *Indian Journal of Marine Sciences, 7,* 8–11.

Pedersen, T., Shimmield, G. B., & Price, N. B. (1992). Lack of enhanced preservation of organic matter in sediments under the oxygen minimum on the Oman margin. *Geochimica et Cosmochimica Acta, 56,* 545–551. doi:10.1016/0016-7037(92)90152-9.

Ramanathan, A. L., Vaithiyanathan, P., Subramanian, V., & Das, B. K. (1993). Geochemistry of the Cauvery estuary, East Coast of India. *Estuaries, 16,* 459–474. doi:10.2307/1352594.

Ramaswamy, V., & Nair, R. R. (1989). Lack of cross shelf transport of sediments on the western margin of India: Evidence of clay mineralogy. *Journal of Coastal Research, 5,* 541–546.

Ramesh, R., Subramanian, V., & Van Grieken, R. (1990). Heavy metal distribution in sediments of Krishna river basin, India. *Environmental Geology and Water Sciences, 15,* 207–216. doi:10.1007/BF01706412.

Rao, Ch. M. (1978). Distribution of $CaCO_3$, Cu^{2+} and Mg^{2+} in sediments of the northern half of western continental shelf of India. *Indian Journal of Marine Sciences, 7,* 151–154.

Rao, Ch. M. (1985). Distribution of suspended particulate matter in the waters of eastern continental margin of India. *Indian Journal of Marine Sciences, 14,* 15–19.

Rao, K. L. (1975). *India's water wealth* (p. 255) New Delhi: Orient Longman.

Rao, K. L. (1979). *India's water wealth: Its assessment, uses and projections* (p. 267). New Delhi: Orient Longman.

Rao, V. P. (1991). Clay mineral distribution in the continental shelf and slope off Saurashtra, west coast of India. *Indian Journal of Marine Sciences, 20,* 1–6.

Rao, V. P., Rajagopalan, G., Vora, K. H., & Almeida, F. (2003). Late Quaternary sea level and environmental changes from relic carbonate deposits of the western margin of India. *Journal of Earth System Science, 112,* 1–25. doi:10.1007/BF02710040.

Rao, V. P., & Rao, B. R. (1995). Provenance and distribution of clay minerals in the sediments of the western continental shelf and slope of India. *Continental Shelf Research, 15,* 1757–1771. doi:10.1016/0278-4343(94)00092-2.

Rubio, B., Nombela, M. A., & Vilas, F. (2000). Geochemistry of major and trace elements in sediments of the Ria de Vigo (NW Spain): An assessment of metal pollution. *Marine Pollution Bulletin, 40,* 968–980. doi:10.1016/S0025-326X(00)00039-4.

Saager, P. M., DeBaar, H. J. W., & Howland, R. J. (1992). Cd, Zn, Ni and Cu in the Indian Ocean. *Deep-Sea Research, 39,* 9–35. doi:10.1016/0198-0149(92)90017-N.

Santos, I. R., Silva Filho, E. V., Schaefer, C. E., Albuquerque-Filho, M. R., & Campos, L. S. (2005). Heavy metal contamination in coastal sediments and soils near the Brazilian Antarctic Station, King George Island. *Marine Pollution Bulletin, 50,* 185–194. doi:10.1016/j.marpolbul.2004.10.009.

Sarkar, S. K., Bilinski, S. F., Bhattacharya, A., Saha, M., & Bilinski, H. (2004). Levels of elements in the surficial estuarine sediments of the Hugli River, northeast India and their environmental implications. *Environment International, 30*, 1089–1098. doi:10.1016/j.envint.2003.10.009.

Selvaraj, K., Ram Mohan, V., & Szefer, P. (2004). Evaluation of metal contamination in coastal sediments of the Bay of Bengal, India: Geochemical and statistical approaches. *Marine Pollution Bulletin, 49,* 174–185. doi:10.1016/j.marpolbul.2004.02.006.

Shankar, R., Subbarao, K. V., & Kolla, V. (1987). Geochemistry of surface sediments from the Arabian Sea. *Marine Geology, 76,* 253–279. doi:10.1016/0025-3227(87)90033-8.

Shimmield, G. B., Price, N. B., & Pedersen, T. F. (1990). The influence of hydrography, bathymetry and productivity on sediment type and composition of the Oman Margin and in the northwest Arabian Sea. In A. H. F. Robertson, M. P. Searle, & A. C. Ries (Eds.), *The geology and tectonics of the Oman Region* (pp. 759–769). Geological Society Special Publication.

Sirocko, F., Garbe-Schönberg, D., & Devey, C. (2000). Processes controlling trace element geochemistry of Arabian Sea sediments during the last 25,000 years. *Global and Planetary Change, 26,* 217–303. doi:10.1016/S0921-8181(00)00046-1.

Subramanian, V., Jha, P. K., & Van Grieken, R. (1988). Heavy metals in the Ganges estuary. *Marine Pollution Bulletin, 19,* 290–293. doi:10.1016/0025-326X(88)90602-9.

Taylor, S. R. (1964). The abundance of chemical elements in the continental crust–a new table. *Geochimica et Cosmochimica Acta, 28,* 1373–1285.

Turekian, K. K., & Wedepohl, K. H. (1961). Distribution of the elements in some major units of the earth's crust. *Geological Society of America Bulletin, 72,* 175–192. doi:10.1130/0016-7606(1961)72[175:DOTEIS]2.0.CO;2.

Zhang, J. (1995). Geochemistry of trace metals from Chinese river/estuary systems: An overview. *Estuarine, Coastal and Shelf Science, 41,* 631–658. doi:10.1006/ecss.1995.0082.

Zhang, J., & Liu, C. L. (2002). Riverine composition and estuarine chemistry of particulate metals in China—Weathering features, anthropogenic impact and chemical fluxes. *Estuarine, Coastal and Shelf Science, 54,* 1051–1070. doi:10.1006/ecss.2001.0879.