Bulletin of the Geological Survey of Japan, vol. 52 (8), p. 371–382, 2001

Reports

Geochemistry of bottom sediments from a river-estuary-shelf mixing zone on the tropical southwest coast of India

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SHAJAN Kuttickat Paul (2001) Geochemistry of bottom sediments from a river-estuary-shelf mixing zone on the tropical southwest coast of India. *Bull. Geol. Surv. Japan,* vol. 52 (8) p. 371–382, 3 figs, 5 tables

Abstract : Geochemical study of bottom sediments of the Periyar and Muvattupuzha rivers, Cochin estuary and the adjoining nearshore continental shelf was carried out to understand the distribution and enrichment pattern, sources, possible factors responsible for the enrichment and depletion of elements and environmental contamination of the systems. The river sediments are sand to sandy silt, estuarine sediments are sandy silt to clay and inner shelf sediments are mud. The study indicate that the sediment texture is the major controlling factor in the distribution of elements here. The fine grained sediments of the inner shelf and estuary are rich in MgO, CaO, Al_2O_3, TiO_2, Fe_2O_3, Na_2O, P_2O_5, K_2O, MnO, Li, Sc, V, Cr, Co, Ni, Cu, Zn, As, Rb, Ta, Zr, Nb, Pb, LOI and poor in SiO_2. The organic rich sediments exhibit a similarity in the distribution of elements like Fe_2O_3, Al_2O_3, MgO, P_2O_5, Cu, Ni, Co, Cr and V. The other possible factors for the enrichment of certain elements are the presence of metal scavenging phases like Fe/Mn hydoxides and the higher content of heavy minerals in the area. The higher concentration of Fe_2O_3, MgO, P_2O_5, Zn, Ba, Pb, Cd, Bi and Cr in many samples indicates that all the sampling units are anthropologically contaminated, with the Periyar river and it's estuarine area showing maximum heavy metal contamination in the study area.

1. Introduction

Geochemical studies of bottom sediments of water bodies such as rivers, estuaries and marine basins are very helpful in understanding the different sediment sources, element distribution pattern and evaluating the environmental conditions existing in an area. The areas on the south west coast of India which is a part of south Indian Precambrian shield offer an excellent study area in this regard with a number of high gradient perennial rivers, estuaries and lagoons, absence of deltas and a narrow continental shelf. It is one of the heavily populated areas of the world. Many geochemical studies were carried out on the shelf and slope sediments of southwest coast of India (Siddique and Chowdhury, 1968 ; Marchig, 1972 ; Murty *et al.,* 1973 ; Shankar *et al.,* 1987 ; Paropkari, 1990 ; Manjunatha and Shankar, 1997), while only few studies on the riverine and estuarine sediments have been presented mainly dealing with trace metal chemistry (Venugopal *et al.,* 1982 ; Nair *et al.,* 1990 ; Padmalal and Seralathan, 1993 ; 1995 ; Padmalal *et al.,* 1997). An integrated geochemical study incorporating major and trace element composition of riverine, estuarine and nearshore shelf areas has not been carried out so far in this area. This paper reports the major and trace element composition of selected riverine, estuarine and nearshore sediments from Cochin area in India.

2. Study Area

The study area includes parts of the Periyar and Muvattupuzha rivers, Cochin estuary and adjoining nearshore continental shelf in the state of Kerala on the central part of the southwest coast of India (Fig. 1). The area lies between latitude 9°45′ to 10°15′N and longitude 76°05′ to 76°30′E. The area has a tropical humid climate with a temperature variation of 13 to 42℃ and the average annual rainfall is 3000 mm (Soman, 1997).

3. Physiography and geology of the area

The study area is situated in the central part of the

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Keywords : Bottom sediments, Sediment chemistry, Cochin inner shelf, Cochin estuary, Periyar river, Muvattupuzha river

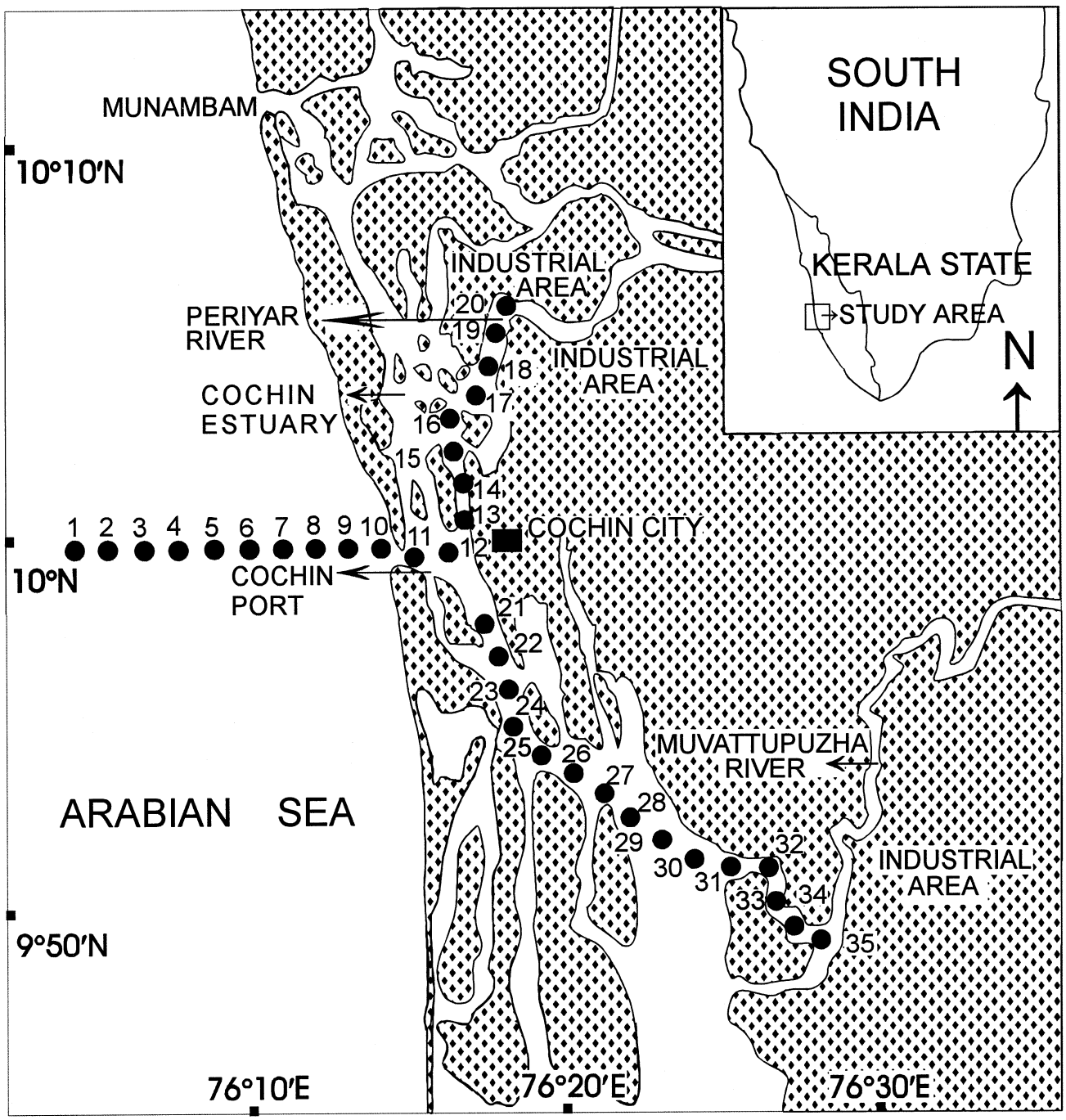

Fig. 1 Location map of sediment samples from Cochin inner shelf, estuary, Periyar and Muvattupuzha rivers on the SW coast of India.

state of Kerala in India. It is a narrow strip of land on the southwestern part of peninsular India with a 560 km long coast and an average width of 80 km, which is lying between Arabian sea on the west and Western Ghats, a continuos mountain chain on the east. Topography of the area covers altitudes ranging from below mean sea level to above 3000 m in Western Ghats area. It is characterised by 41 short and swift flowing mansoon fed perennial rivers, which originate from the Western Ghats and drain into either estuaries or the Arabian sea. The most conspicuous feature of this coast is the wide spread distribution of estuaries and lagoons, thought to be the remnants of the receding sea (Krishnan Nair, 1996). Physiographically, the area can be divided into three well defined natural divisions, viz. low lands or coastal plains, midlands or the lateritic plateaus and gneissic high lands. The coastal tract is a low lying featureless plain country comprising depositional and denudational landforms and the shoreline is characterised by broad sandy beaches. The continental shelf is narrow with an average width of only 50 km. The Cochin

Table 1 Details of Periyar and Muvattupuzha rivers, India (Soman, 1997).

No.	Name of the river	Length (km)	Catchment area (km^2)	Run off (Million m^3/yr)
1	Periyar river	244	5398	5180
2	Muvattupuzha river	121	1554	4780

estuary is the northern portion of Vemband estuary, the largest estuary on the west coast of India with an area of 233 sq.km. The details of the two rivers are given in Table 1.

The Archaean metamorphic units in southern India broadly comprise a granite-green stone terrain in the north and a granulite terrain in the south (Omana and Santhosh, 1996). Study area occupies the southwestern part of this large southern Indian granulite terrain. The watershed areas of the Cochin estuary and the catchment areas of the Muvattupuzha and Periyar rivers are occupied by four major rock units. They are 1) Precambrian crystalline 2) Tertiary sedimentary 3) Pleistocene lateritic, and 4) Recent to sub-Recent sedimentary units (Padmalal *et al.,* 1997). The Precambrian crystalline rocks expose all through the highland western ghat area and a considerable portion of the midlands, and they are mainly comprised of massif charnockites, garnet biotite gneisses and hornblende gneisses. A large part of these rocks has undergone polymetamorphic and polydeformational activities. At many places the Precambrian crystalline rocks are intruded by acidic (granite and pegmatite) and basic (gabro and dolerite) rocks. The country rocks have undergone extensive lateritizaton process and this insitue laterites cover the Precambrian crystalline unit and Tertiary sedimentary unit at many places, mainly in midland and coastal areas. The Tertiary sedimentary rocks, which have very few exposures in the coastal areas, are represented by Vaikkom, Quilon and Warkalli formations, which in turn are composed of sandstones, clays and limestones. The coastal terrain, river mouths, estuary and the nearshore shelf areas are underlined by a thick succession of Quaternary sediments comprised of sand, silt, clay, peat and shell beds and Tertiary sediments and the basement is made up of charnockite (Nair and Rao, 1980).

4. Samples and Method of analysis

A total of 35 bottom sediment samples were collected using a stainless steel Vanveen grab at 1.25 km interval from parts of the Periyar and Muvattupuzha rivers, the Cochin estuary and the adjoining nearshore continental shelf on the south west coast of India (Fig. 1). Representative samples were taken from the top 10 cm of the grab samples and stored in plastic bags. The depth of sampling ranges from 3 to 12 m for riverine and estuarine area and 5 to 16 m for the shelf area. Samples were washed salt free with distilled water, dried in an oven at 50℃ and powdered in an agate mortar to less than 100 mesh size. All the major elements and some of trace elements such as Ag, Ba, Be, Bi, Cd, Co, Cr, Cu, Mn, Mo, Ni, P, Pb, Sr, V, Zn were determined using a SEIKO SPS-1200 inductively — coupled plasma atomic emission spectrometer (ICP-AES) at the Geological Survey of Japan, Tsukuba, Japan. All other trace elements (As, Hf, Li, Nb, Rb, Sc, Th, U, Y and Zr) were determined by a Yokogawa Analytical Systems PMS-200 inductively coupled plasma mass spectrometer (ICP-MS) at the GSJ. More detailed description of the procedures is given in Imai (1990).

5. Results

The major and trace element compositions of Cochin inner shelf sediments (Sample no. 1 to 10), Cochin estuary (northern part) and Periyar river (Sample no. 11 to 20) and Cochin estuary (southern part) and Muvattupuzha river (Sample no. 21 to 35) are given in Table 2, Table 3 and Table 4 respectively. Figure 2 presents the spatial distribution of major and trace elements in the above three sampling units.

5.1 Major elements

Shelf sediments

The shelf sediments show distinctly higher concentration of MgO, CaO and LOI and lower concentration of SiO_2 than the estuarine or riverine samples. Rest of the major elements exhibit a more or less similar distribution to that of the estuarine area. Al_2O_3, TiO_2, Fe_2O_3, Na_2O and P_2O_5 show moderately higher concentration, whereas K_2O and MnO are similar or lower than the estuarine sediments. In the shelf area, the concentration of SiO_2, MnO, CaO and K_2O are higher and MgO and P_2O_5 are lower in the nearshore zone. A slight enrichment of TiO_2, Al_2O_3 and Fe_2O_3 and sharp depletion of Na_2O is observed in the central part while loss on ignition (LOI) is higher in the offshore samples.

Table 2 Major and trace element composition of the bed sediments of Cochin inner shelf on the SW coast of India (sample nos. 1 to 10).

Sample No.	1	2	3	4	5	6	7	8	9	10
Water Depth (m)	16	14	12	11	9	8	6	6	5	5
Sediment Type	Mud	Mud	Mud	Mud	Mud	Mud	Mud	Mud	Mud	Mud
SiO_2 (%)	39.22	41.38	40.00	41.26	42.59	45.06	41.45	43.31	47.96	43.02
TiO_2	0.91	0.90	0.90	0.98	0.97	0.98	0.95	0.97	0.86	0.89
Al_2O_3	16.33	16.05	16.12	17.27	17.53	16.95	17.20	17.43	15.71	15.82
Fe_2O_3	8.88	8.83	8.97	9.55	9.60	9.03	9.47	9.53	7.47	8.46
MnO	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.05	0.06
MgO	3.48	3.42	3.42	3.43	3.47	3.34	3.41	3.33	2.89	3.18
CaO	2.66	3.17	2.64	2.21	2.52	3.12	2.35	2.51	3.65	3.16
Na_2O	2.12	2.81	3.17	0.54	0.64	1.03	0.60	0.86	2.73	3.03
K_2O	1.41	1.56	1.45	1.41	1.48	1.67	1.46	1.56	1.91	1.66
P_2O_5	0.48	0.46	0.47	0.47	0.48	0.45	0.47	0.50	0.36	0.41
LOI	22.45	21.43	22.88	21.17	20.24	18.26	20.50	19.52	16.66	19.81
Li (ppm)	69	100	119	103	34	30	37	123	96	111
Be	1.5	1.5	2.0	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Sc	43	55	59	56	33	33	38	15	12	12
V	96	90	96	109	97	97	99	92	81	84
Cr	203	189	205	220	205	199	206	194	161	169
Co	16	12	15	17	16	18	16	15	14	17
Ni	81	78	80	92	88	80	88	81	67	70
Cu	34	28	31	32	30	29	30	28	23	26
Zn	152	108	122	132	120	126	122	126	132	98
As	3	4	3	3	1	1	1	8	6	6
Rb	22	24	24	22	9	8	9	63	63	59
Sr	204	228	201	181	195	251	181	200	361	271
Y	19	20	21	18	7	7	7	24	19	22
Zr	109	124	120	117	42	44	43	45	44	45
Nb	33	35	34	31	12	12	12	11	10	11
Mo	5	2	<1	<1	3	<1	1	<1	1	3
Ag	2.0	<0.2	<0.2	<0.2	<0.2	0.2	<0.2	0.8	0.6	1.2
Cd	1.0	1.5	1.0	0.5	1.0	0.5	<0.5	<0.5	0.5	0.5
Ba	250	330	290	290	270	440	290	320	640	430
Hf	1.99	2.10	2.33	2.18	0.53	0.53	0.47	1.54	1.57	1.48
Ta	1.43	1.40	1.59	1.40	0.25	0.25	0.23	0.84	0.74	0.86
Pb	516	780	70	110	26	24	30	30	28	30
Bi	8	2	<2	10	<2	<2	2	<2	8	4
Th	5.61	5.29	5.27	5.47	1.29	1.37	1.33	10.72	10.08	9.59
U	1.31	1.05	1.18	1.38	0.29	0.27	0.30	2.56	2.00	2.23

Table 3 Major and trace element composition of the bed sediments of Periyar river and it's estuarine area on the SW coast of India (sample nos. 11 to 20).

Sample No.	11	12	13	14	15	16	17	18	19	20
Water Depth (m)	12	4	3	5	4	4	3	5	5	3
Sediment Type	Sandy silt	Sandy mud	Mud	Sandy silt	Mud	Silty sand	Silty sand	Sand	Sand	Sand
SiO_2 (%)	49.80	60.92	53.92	58.75	46.83	75.30	65.20	78.87	82.16	87.40
TiO_2	0.72	0.70	0.90	0.92	0.98	0.60	0.62	1.19	0.30	0.23
Al_2O_3	14.76	12.33	15.53	15.33	18.13	9.83	14.16	8.87	7.20	5.38
Fe_2O_3	6.57	5.82	7.31	6.03	9.12	2.82	4.89	3.06	2.38	1.62
MnO	0.05	0.04	0.05	0.05	0.06	0.03	0.04	0.06	0.01	0.01
MgO	2.55	2.02	2.27	1.99	2.17	0.80	1.25	0.57	0.33	0.21
CaO	5.14	1.68	1.58	1.99	1.45	1.54	2.12	1.36	0.95	0.61
Na_2O	2.63	2.29	1.95	2.77	1.77	1.78	2.42	1.61	1.23	0.82
K_2O	2.00	1.62	1.89	2.71	2.35	2.47	3.43	2.72	2.25	1.99
P_2O_5	0.28	0.37	0.42	0.30	0.61	0.16	0.35	0.12	0.21	0.11
LOI	14.42	12.68	14.52	9.63	16.59	3.25	5.21	1.71	2.57	1.53
Li (ppm)	20.4	14.1	25.7	19.8	23.9	3.0	0.8	0.8	0.4	2.2
Be	1.5	1.5	1.5	2.0	1.5	1.0	1.5	0.5	0.5	0.5
Sc	26	22	32	31	47	7	4	4	3	3
V	75	58	75	70	101	36	59	48	41	34
Cr	143	120	149	120	170	56	82	47	49	39
Co	16	12	16	13	18	8	12	4	4	3
Ni	60	49	61	46	63	15	27	10	7	6
Cu	21	22	34	27	51	11	17	5	6	9
Zn	82	358	648	720	1130	206	426	106	186	132
As	1.8	1.1	1.9	1.3	1.4	0.3	0.1	0.1	0.1	0.2
Rb	20	15	24	28	29	16	12	12	9	10
Sr	445	231	273	372	263	375	452	327	257	225
Y	12	14	27	21	26	6	4	3	2	4
Zr	74	91	136	214	130	75	85	85	21	38
Nb	20	19	30	33	38	13	13	13	5	7
Mo	5	<1	3	3	<1	1	2	4	2	1
Ag	0.6	0.2	0.8	0.2	<0.2	<0.2	<0.2	0.2	0.2	<0.2
Cd	0.5	3.5	6.0	7.5	20.0	3.5	5.5	1.0	2.0	1.0
Ba	770	540	640	1050	870	1130	1430	1160	930	1130
Hf	1.7	2.3	2.2	3.2	2.5	1.6	2.6	2.6	0.8	0.9
Ta	0.9	0.9	1.1	0.8	1.3	0.4	0.6	0.6	0.3	0.2
Pb	24	22	42	36	62	26	46	22	22	20
Bi	2	<2	<2	6	8	8	<2	<2	2	6
Th	3.7	5.8	6.9	12.2	13.1	8.6	10.7	10.7	5.9	7.0
U	0.7	1.3	2.0	1.4	3.1	0.9	0.6	0.6	0.8	0.5

Table 4 Major and trace element composition of the bed sediments of Muvattupuzha river and it's estuarine area on the SW coast of India (sample nos. 21 to 35).

Sample No.	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35
Water Depth (m)	7	7	5	5	5	5	4	3	5	5	5	4	5	5	5
Sediment Type	Clay	Clay	Clay	Sandy clay	Clay	Clay	Clay	Sandy clay	Silty sand	Silty sand	Silty sand	Sand	Silty sand	Muddy Sand	Clay
SiO_2 (%)	42.59	41.58	46.09	63.92	43.59	43.78	48.20	73.73	85.19	69.00	75.03	79.73	69.31	66.96	45.08
TiO_2	1.07	0.89	0.85	0.64	1.02	0.97	1.03	0.70	0.81	1.21	0.64	0.40	0.61	1.37	1.27
Al_2O_3	18.33	16.15	15.19	11.11	17.73	17.61	17.05	6.83	4.41	11.12	10.75	8.45	13.06	10.68	15.35
Fe_2O_3	10.16	8.82	8.16	5.17	9.59	9.65	9.11	3.54	2.03	4.81	3.33	2.28	4.50	6.32	8.81
MnO	0.05	0.04	0.04	0.03	0.08	0.07	0.06	0.03	0.02	0.05	0.03	0.03	0.04	0.08	0.08
MgO	3.01	3.33	2.94	1.94	3.30	3.09	2.73	0.92	0.51	1.29	0.74	0.51	0.98	0.99	1.90
CaO	1.03	2.58	2.35	1.66	1.66	1.22	1.22	0.29	0.17	1.79	1.62	1.19	1.57	0.60	0.69
Na_2O	0.84	2.76	2.09	2.30	1.21	0.64	1.20	0.24	0.33	1.78	1.67	1.33	1.80	0.62	0.46
K_2O	1.46	1.47	1.30	1.33	1.51	1.41	1.65	0.56	0.37	1.80	2.21	2.03	2.36	1.42	1.55
P_2O_5	0.45	0.47	0.38	0.23	0.51	0.47	0.35	0.12	0.07	0.11	0.08	0.04	0.10	0.11	0.08
LOI	20.89	21.97	19.35	11.63	20.07	19.54	16.86	12.62	4.46	7.49	4.22	3.03	6.17	11.14	24.40
Li (ppm)	41	23	26	9	24	22	9	3	1	1	1	4	4	7	20
Be	2.0	1.5	1.5	1.0	2.0	1.5	2.0	1.0	0.5	1.0	1.5	1.0	1.5	1.0	2.0
Sc	37	34	40	6	31	28	16	5	5	5	3	12	12	19	31
V	103	92	87	52	101	93	90	45	32	62	48	34	59	89	128
Cr	212	195	192	107	216	200	179	79	49	87	64	48	78	107	176
Co	21	10	15	13	19	15	17	8	3	12	8	4	10	13	25
Ni	89	81	80	45	93	85	73	32	14	29	20	14	29	42	70
Cu	56	28	29	17	34	30	28	15	9	13	9	6	13	17	27
Zn	316	110	90	66	140	118	118	44	24	48	28	18	40	48	70
As	2.2	2.5	1.9	0.8	1.8	1.6	0.8	0.4	0.2	0.3	0.2	0.5	0.5	0.9	2.4
Rb	20	21	17	12	20	18	14	5	11	11	11	20	20	15	26
Sr	163	220	176	210	172	143	212	73	56	254	254	240	228	119	89
Y	17	18	16	8	16	14	11	4	5	5	3	6	6	7	13
Zr	120	106	145	77	88	89	84	63	82	84	96	87	84	206	185
Nb	28	28	27	17	29	26	19	16	18	18	8	12	11	29	38
Mo	3	6	4	3	2	2	3	1	<1	4	3	<1	2	<1	3
Ag	2.6	<0.2	<0.2	0.2	<0.2	0.4	<0.2	<0.2	0.4	0.4	<0.2	<0.2	<0.2	<0.2	0.6
Cd	2.0	0.5	<0.5	<0.5	0.5	<0.5	<0.5	1.5	0.5	1.0	<0.5	0.5	<0.5	1.5	<0.5
Ba	350	330	250	440	330	290	470	170	120	680	820	710	810	410	140
Hf	2.4	2.1	3.2	2.0	2.3	2.3	2.5	1.9	2.6	2.5	2.8	1.5	1.5	4.9	3.5
Ta	1.3	1.2	1.3	0.8	1.3	1.2	1.0	1.0	0.9	0.9	0.4	0.4	0.4	1.1	1.9
Pb	342	28	54	22	30	32	34	12	10	18	22	18	18	20	18
Bi	10	<2	4	6	<2	14	2	<2	<2	<2	<2	6	4	<2	10
Th	5.9	5.1	4.5	5.9	5.3	5.2	5.2	4.2	10.1	10.0	5.7	7.1	7.1	16.2	9.7
U	2.0	1.2	1.2	1.0	1.4	1.8	1.6	1.1	1.2	1.1	0.7	0.7	0.7	1.2	2.3

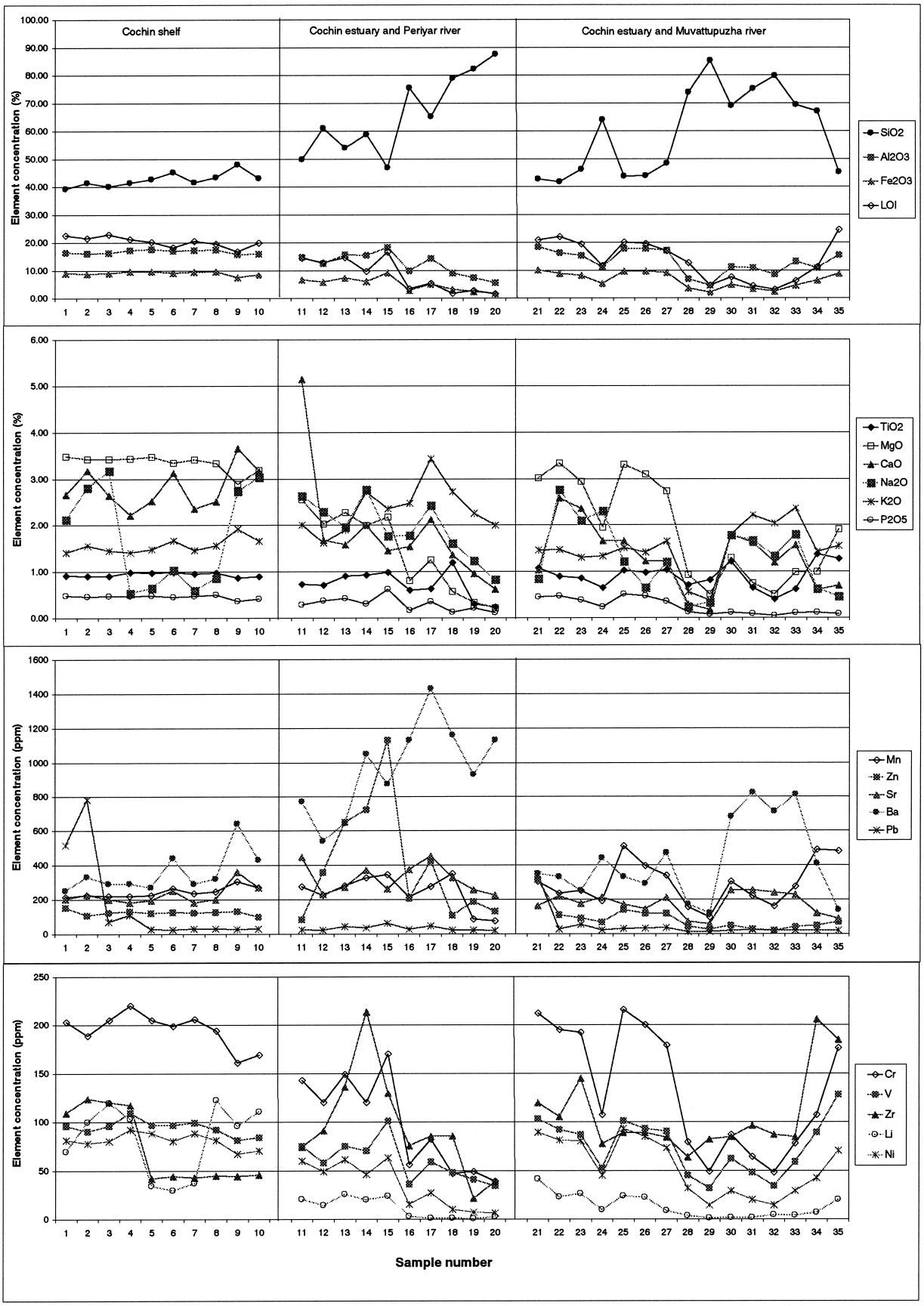

Fig. 2 Variation of major and trace elements in the bed sediments of Cochin inner shelf, estuary, Periyar and Muvattupuzha rivers on the SW coast of India.

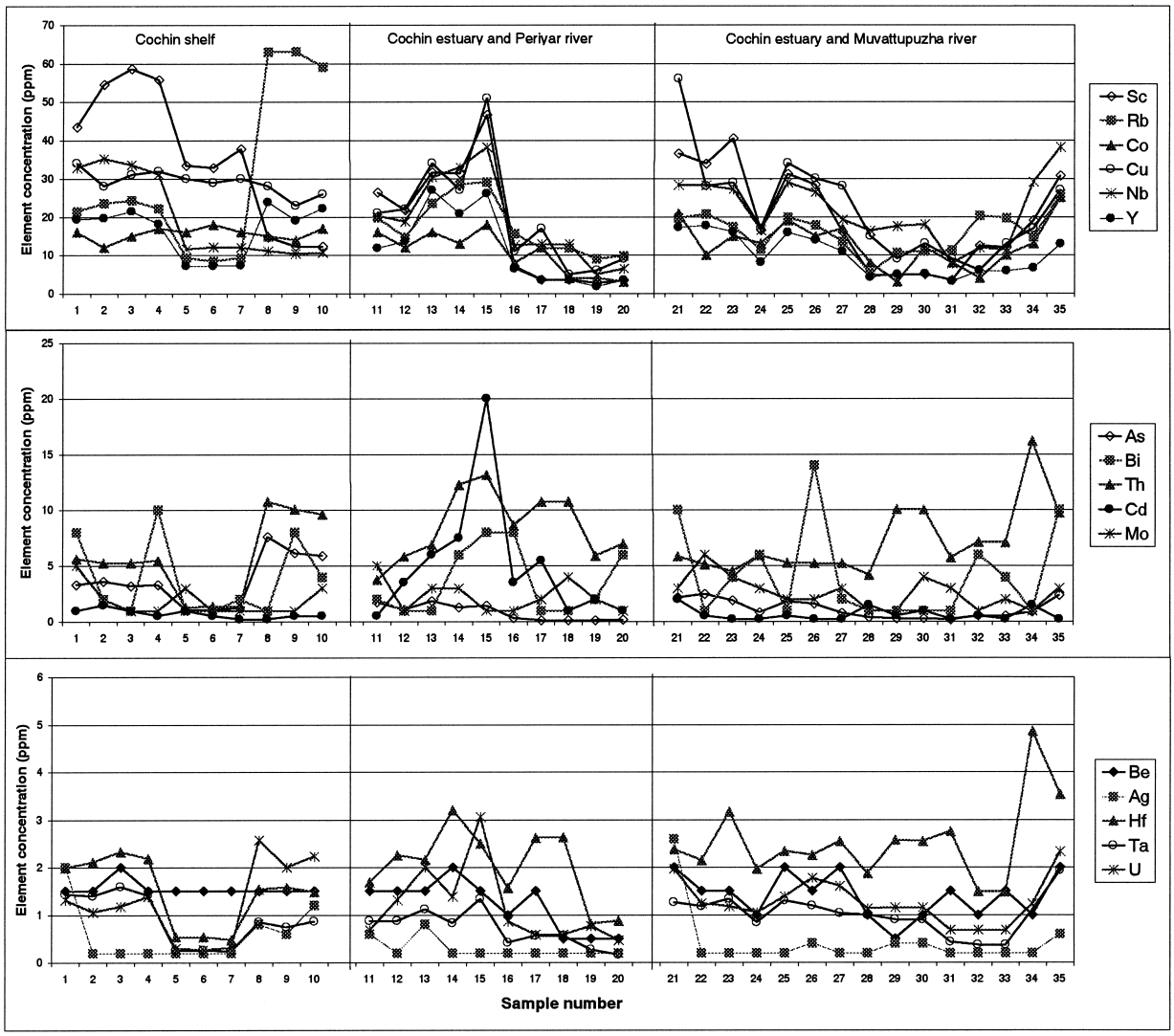

Fig. 2 Continued.

Periyar River and it's estuarine area

Sediments exhibit a decreasing trend towards the fresh water zones in case of TiO_2, Al_2O_3, Fe_2O_3, MnO, MgO and LOI. In this estuary - river system, most of the samples show very high concentration of K_2O and SiO_2 and are depleted in MgO, LOI, Fe_2O_3, Al_2O_3 and TiO_2 than the nearby shelf, estuarine or river areas.

Muvattupuzha River and it's estuarine area

SiO_2 and K_2O contents show a marked increase in the riverine sediments whereas Al_2O_3, Fe_2O_3, MnO and MgO concentrations are higher in the estuarine samples than the riverine ones and a distinct enrichment of these elements is found in the river-estuary mixing zone. The river samples register a slight increasing trend in the above elements towards the fresh water zones. The estuarine sediments are rich in CaO, Na_2O, P_2O_5 and LOI and these elements register a clear decreasing trend towards the river. TiO_2 is comparatively enriched in the river-estuary mixing zone. The last two stations (Nos. 34 & 35) exhibit a different trend and these samples contain higher concentration of Al_2O_3, Fe_2O_3, TiO_2, MnO and LOI and lower SiO_2, CaO and Na_2O than the rest of the Muvattupuzha river sediments.

5.2 Trace elements

Shelf sediments

Most of the trace elements such as Li, Sc, V, Cr, Co, Ni, Cu, As, Rb, Ta and Pb show a distinct enrichment in the shelf sediments than the estuarine or riverine sediments in the study area. The elements like Sc, V, Cr, Cu, Zn, Zr, Nb, Cd, Hf, Ta and Pb are clearly enriched in the offshore areas whereas As, Rb, Sr, Y, Ba, Th and U are comparatively more in the nearshore zone. Abnormally high concentration of Pb (780 ppm) is noticed in the offshore area. No significant trend is observed in the aerial distribution of any other trace elements in the area.

Periyar River and it's estuarine area

All trace elements except Ba and Sr are found en-

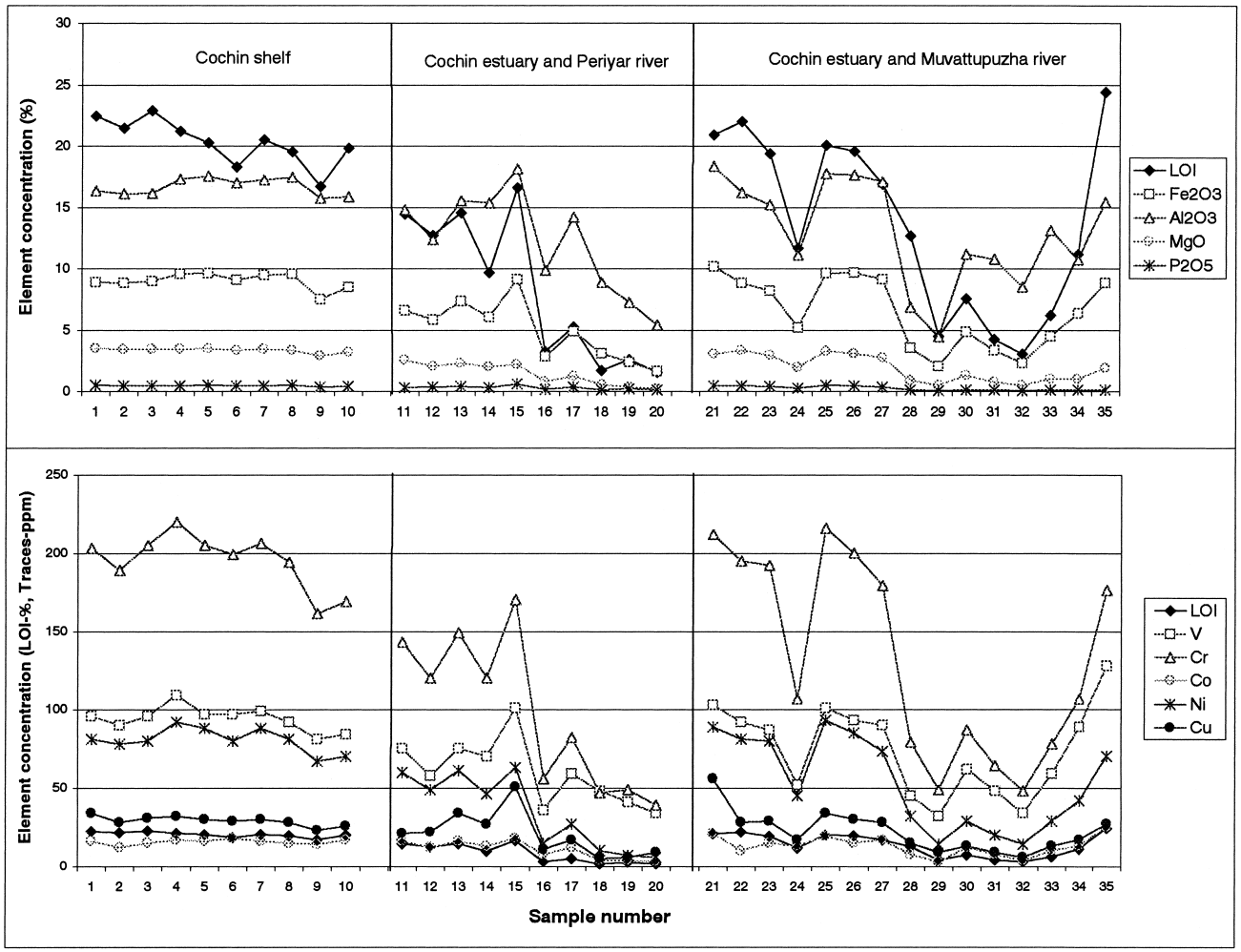

Fig. 3 Affiliation of some major and trace elements with the organic rich sediments in the study area.

riched in the estuarine areas of the Periyar river than it's fresh water zones. The elements like Sc, V, Cr, Cu, Zn, Sr, Rb, Y, Zr, Nb, Cd, Ba and U register an increasing trend from the estuarine mouth to the fresh water — estuary mixing zone. Some of the sampling sites in this estuary - river system give very high concentration of Zn, Sr, Cd and Ba.

Muvattupuzha River and it's estuarine area

The contents of Li, Sc, V, Cr, Co, Ni, Cu, Zn, As, Y, Nb, Mo, Ta and Pb are higher in the estuarine samples than the river samples. Coarse grained river sediments are found enriched in Ba and Sr. Fine grained river sediments collected from the meandering cone of the Muvattupuzha river show high contents of V, Cr, Co, Ni, Cu, As, Zr, Nb, Hf, Ta and Th. Some of the sediment samples of this estuary - river system contain relatively high concentrations of Zn, Ba, Pb and Bi.

6. Discussion

The texture of the sediments varies considerably in the study area. The river sediments are generally silty sand to sand, estuarine sediments are sandy silt to clay and inner shelf sediments are principally mud in nature. The last two samples in the Muvattupuzha River are muddy sand and clay. The geochemical distribution patterns of various elements in the study area indicate that the texture of the sediments is the major controlling factor on sediment geochemistry. The finer sediments like clay, mud, sandy mud, sandy silt and silty sand from the inner shelf, estuary and river show enrichment of most of the major and trace elements in comparison with the sandy river sediments. The particle size has a significant role in the accumulation and exchange process of elements between sediments and water in fresh water — sea water mixing. The higher concentration in the fine sediments is due to the increase in specific surface area and to the surface properties of clay minerals (Biksham *et al.,* 1991).

The loss on ignition increases from rivers through estuaries to shelf indicating the source of organic matter is primarily detrital in nature. The thick tropical vegetation in the catchment areas of rivers and estuaries, presence of some mangrove patches on estu-

Table 5 Comparison of average concentrations of enriched elements in the study area with the global units and nearby geological environments.

	1 Cochin inner Shelf	2 Cochin estuary (north)	3 Cochin estuary (south)	4 Periyar river	5 Muvattupu-Zha River	6 Average shale	7 Upper crust	8 Cochin Mangalore shelf	9 Coonda-pore shelf	10 Cauvery river
Fe_2O_3 (%)	8.98	6.97	8.03	2.95	4.58	6.75	4.42	7.05	7.43	2.52
K_2O	1.56	2.11	1.34	2.57	1.68	3.20	3.45	2.63	N A	1.33
MgO	3.34	2.20	2.66	0.63	0.99	2.49	2.24	1.58	N A	1.82
P_2O_5	0.46	0.40	0.37	0.19	0.08	0.16	0.15	0.48	N A	N A
TiO_2	0.93	0.84	0.90	0.59	0.90	0.76	0.52	0.82	N A	N A
Cd (ppm)	0.7	7.5	0.7	2.6	0.6	0.30	0.1	N A	N A	N A
Bi	3.8	3.6	4.9	3.6	3.4	N A	0.12	N A	N A	N A
Cr	195	140	173	55	87	90	35	N A	159	122
Ni	81	56	72	13	31	68	19	105	66	30
Zn	124	588	125	211	39	95	52	89	51	26
Sr	227	317	171	327	177	300	316	238	N A	200
Ba	355	774	329	1156	527	580	668	N A	N A	444
Pb	164	37	69	27	18	20	17	N A	6	10

(1,2,3,4,5) present study; (6) Turekian and Wedepohl, (1961); (7) Wedepohl, (1995); (8) Paropkari, (1990); (9) Pandarinath and Narayana, (1998); (10) Subramanian et al, (1985); N A - No data available.

arine banks, high rate of primary production in tropical estuaries and shelfs, prevailing anoxic condition and fine particle size of sediments are important factors responsible for the higher concentration of organic matter in the estuary and shelf. Major elements like Fe_2O_3, Al_2O_3, MgO and P_2O_5 and trace metals Cu, Ni, Co, Cr and V exhibit strong association with LOI distribution pattern (Fig. 3). Li *et al.*, (2000) have observed close associations of trace elements with clay minerals and organic content in the sediments of Pearl river estuary, China. Trace metal enrichment in estuarine and marine sediments also results from the presence of metal scavenging phases like Fe/Mn hydoxides during estuarine mixing. According to Cronan (1969), Fe/Mn hydroxides help in the removal of several trace elements from natural waters by lattice substitution and surface adsorption process. The higher content of some of the trace metals in Cochin inner shelf and estuary resulted from the physico — chemical flocculation of Fe and Mn hydroxides in the near shore region and estuary (Paropkari, 1990 ; Padmalal *et al.*, 1997). Sholkovitz (1978) has emphasized the role of flocculation in the enrichment of some of the trace elements during estuarine mixing.

According to Dhanunjaya Rao (1989), the total heavy mineral content in the beach sands of the area comprises more than 15%, containing ilmenite, garnet, rutile, sillimanite and little monazite and zircon. The heavy mineral concentration results from the hinter land geology, laterization of gneissose rocks, presence of small streams and the sorting by waves and tides. The heavy minerals such as ilmenite and rutile are important Ti bearing minerals on the west coast of India (Mallik, 1972). The moderately high concentration of TiO_2 in comparison with the world average (Table 5) throughout the study area could be attributed to the heavy minerals present in the area.

There are many factories such as a major fertiliser plant producing K-P-N fertilisers, an oil refinery, a rare earth element processing factory and zinc smelters on the banks of the Periyar river and a news print factory on the Muvattupuzha riverbank. Besides these, the high dependency on chemical fertilisers and pesticides in agriculture in the catchment areas of both rivers and estuary and the increased population pressure and fast urbanization giving rise to the heavy sewage effluents, which are the possible anthropologic factors leading to the high concentration of some of the major and trace elements in the study area. Sediment samples from the Cochin inner shelf and estuary show moderately high concentration of some of the elements like Fe_2O_3, MgO, P_2O_5, Ba and Cr and abnormally high concentration of Zn, Pb, Cd and Bi in comparison with the world average values and

the shelf and river sediments from south India (Table 5). Periyar river sediments possess very high contents of trace elements like Zn, Ba, Cd and Bi whereas Muvattupuzha River shows excess concentration of only Cd and Bi. There are many studies dealing with the contamination of aquatic system by the artificial release of heavy metals (Smith, 1977 ; Forstner, 1979). The spatial distribution of the above elements indicates that all the sampling units in the study area are more or less anthropologically contaminated with the lower reaches of the Periyar river and northern part of Cochin estuary showing a maximum. An acute Pb contamination is also noticed in the inner shelf area. However, a significant portion of the dissolved phase of various elements, especially heavy metals in each sample has been washed off during the initial washing of the sediment samples. Hence it is assumed that the original contribution from anthropological sources could be much higher than the present assessment.

7. Conclusions

Geochemical study of bottom sediments from parts of Periyar and Muvattupuzha rivers, Cochin estuary and the adjoining nearshore continental shelf indicates that the fine grained sediments are enriched in most of the major and trace elements investigated such as MgO, CaO, Al_2O_3, TiO_2, Fe_2O_3, Na_2O, P_2O_5, K_2O, MnO, Li, Sc, V, Cr, Co, Ni, Cu, Zn, As, Rb, Ta, Zr, Nb and Pb and depleted in SiO_2 than the coarser sediments. The spatial distribution patterns of various elements in the study area indicate that the texture is the major controlling factor on sediment geochemistry. Other possible factors include organic matter content and the presence of metal scavenging phases like Fe/Mn hydoxides during estuarine mixing. Some of the nearshore shelf, estuarine and river sediments posses high content of TiO_2 due to the presence of heavy minerals in the area. The distribution patterns of the elements like Fe_2O_3, MgO, P_2O_5, Ba, Cr, Zn, Pb, Cd and Bi indicate that all the three sampling units are anthropologically contaminated. The Periyar river and its estuarine area show a maximum heavy metal contamination in the study area. The statistical analysis of geochemical data and mineralogical studies will be further carried out to delineate the natural sediment chemistry and anthropologic contribution in these aquatic systems.

Acknowledgements : The research was funded by Japan Science and Technology Corporation (JST) and was carried out at the Geological Survey of Japan, Tsukuba. The author is highly grateful to the host researcher, Dr. Yoshio Watanabe for helpful discussions and assistance and guidance in various analyses. He is also indebted to Dr. N. Imai of GSJ and Dr. M. Yamamoto of Hokkaido University for their help during laboratory analysis. He thanks Drs. Y. Matsuhisa and Y. Saito of GSJ for their critical review and constructive suggestions for the improvement of the manuscript.

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Received March 22, 2001
Accepted July 18, 2001

熱帯インド南西沿岸における河川–汽水–沿岸域底質堆積物の地球化学

Shajan Kuttickat Paul

要　旨

インド南西岸，Kerala 州沿岸域の Periyar, Muvattupuzha 川及び Cochin 汽水域周辺の底質堆積物の地化学的検討を行い，元素の分布と濃集パターン，起源，そして元素分布の規制要因と環境からの混入について検討した．河川堆積物試料は砂質シルトないし砂で，汽水性および沿岸堆積物はシルト質砂から泥である．検討の結果，堆積物粒度組成が元素分布の主要な規制要因であることが明らかになった． 汽水性ならびに沿岸堆積物では Mn, Ca, Al, Ti, Fe, Na, P, K, Mg, Li, Sc, V, Cr, Co, Ni, Cu, Zn, As, Rb, Ta, Zr, Nb, Pb そして灼熱減量組成に富み，Si に乏しい．有機物に富む試料でも同様な Fe, Al, Mg, P, Cu, Ni, Co, Cr そして V の挙動を示す．その他の可能性のある元素濃集要因として，Fe/Mn 水酸化物による金属元素の吸着と重鉱物の濃集があげられる．Fe, Mg, P, Zn, Ba, Pb, Cd, Bi そして Cr は多くの試料で濃集しているが，これは全ての試料に人為的汚染が生じており，特に Periyar 川とその河口域にもっとも大きな重金属類の濃集が認められる．

（要旨翻訳：渡部芳夫（深部地質環境研究センター））