Geochemistry of Elements in Core Sediments Near Point Claimere, the Southeast Coast of India

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ABSTRACT: The core sediment samples were analysed for grain size, carbonates ($CaCO_3$), organic carbon (OC) to obtain a preliminary view of its environmental conditions near Point Calimere along the southeast coast of Vedaranyam, India.The high concentration of sand in the core is attributed to the tidal influence at the Akkarapallivasal river mouth. The sea water which enters the river suspends the flocculated sediments at the mouth and transports the fine floccules to the water column. The tidal currents also play a major role in removing the fine particles from the river mouth. The value of OC does not show any significant variation towards depth. The concentration of various major elements in the core can be summarized as Si > Al > Ca > Na > K > Fe > P > Mg and the trace elements exhibit the following order for the core samples as Mn > Zn >Cu > Pb > Ni > Cr > Co. The studies indicate lithogenic origin for most of the elements. Major and trace elements of the core sediments were estimated and normalized.

Key words: Core sediments, Geochemistry, Heavy metals, Anthropogenic, Point calimere, India

INTRODUCTION

Sediments from the marginal marine and near shore environments had been studied by a number of geologists for a considerable period of time to determine the process of deposition of ancient sediments. The nature of sediments is modified by anthropogenic activities and as the impact of these activities has increased more in the following years, sediment geochemistry had been pursued with the objective to assess coastal pollution (Van Andel and Postma, 1954; Emery, 1960; Shepard *et al.,* 1960; Strakhov, 1961; Van Andel and Shor, 1964; Van Andel and Veevers, 1967; Faganelli, *et al.,* 1987; Holm, 1988; Karbassi and Amirnezhad, 2004; Karbassi and Shankar 2005; Pekey, 2006; Abdel- Ghani and Elchaghaby, 2007; Praveena, *et al.,* 2008; Harikumar *et al.,* 2009; Mohiuddin *et al.,* 2010). Accumulation or mobilization of trace elements in the sediments of aquatic environment (Al-Masri, 2002).Sediments act as sinks and sources of contaminants in aquatic systems because of their variable physical and chemical properties (Rainey, *et al.,* 2003; Marchand, *et al.,* 2006*;* Prijiu and Narayan, 2007; Praveena, *et al.,* 2008; Sundararajan, *et al.,* 2009; Sundararajan, and Usha Natesan, 2010).

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Most of the chemical changes take place at or close to the sediment/water boundary and, for this reason, it is important to study the geochemical composition of bulk sediments (Hirst 1962; Calvert 1976). Bay of Bengal has attracted scientists and oceanographers from all over the world with regard to its sedimentation geology, in particular, origin and history of the Bengal Fan sediments (Emmel and Curray 1983; Winkler 1987). Sediments are important carriers of trace metals in the hydrological cycle and they effectively collect or release metals into the surrounding waters; thereby, they can reflect the current quality of an aquatic system (Salomons and Forstner 1984). Major elemental analysis effectively represents the composition of the solid fraction being eroded from the continents or the rock types present in the drainage basin of a river (Taylor and McLennan 1985).

Trace metal enrichment in sediments started with the industrial evolution in Indian sub-continent at the end of 19th century. As a result, the fluxes of trace metals from terrestrial areas (especially aquatic regions) have increased significantly in developing countries. Since, sediments are often the ultimate depository environment for trace metals

in the aquatic environment, the solid-phase distribution can reflect the history of metal accumulation and the weathering pattern of the sediments from adjacent regions (Förstner and Salomons 1980; Fedo *et al.,* 1996; Nesbitt *et al.,* 1996; Nath *et al.,* 2000). Normalization is done by measuring the concentrations of metals in bulk sediments and then dividing them by the percentage of 63 µm size fraction in the bulk sediments in order to obtain the concentration in the fine fraction (Krom *et al.,* 1983; Morse *et al.,* 1993; Palanques and Diaz, 1994). The aim of the present study is to identify the source and fate of metals and toxic elements in the study area, and its impact on the environment.

MATERIALS & METHODS

Akkarapallivasal river mouth (10º25'01"N latitude and 79º51'99"E longitudes) near Point Calimere

was considered as the study area (Fig. 1a, b). The coastal sands of recent age overlie the Tertiary rocks. The geomorphologic features observed in this stretch are sub aerial delta, strand plain, crevasses, chennies, cuspate bars, estuarine and swamps. The large part of the delta is occupied by their distributory flood basins comprising brown and reddish gray silty clay and fine sands. The coastline of Nagapattinam is straightened by south bound long shore currents from the Kollidam river mouth to Point Calimere. From Point Calimere to further south the coastline forms a bay. These soils occur in Nagapattinam taluk covering an extent of 37 km². The soils are very deep, moderately drained, clay to sandy clay loam in texture with deposits of sand in intermittent layers. The soils are somewhat saline in nature due to the influence of tidal waves.
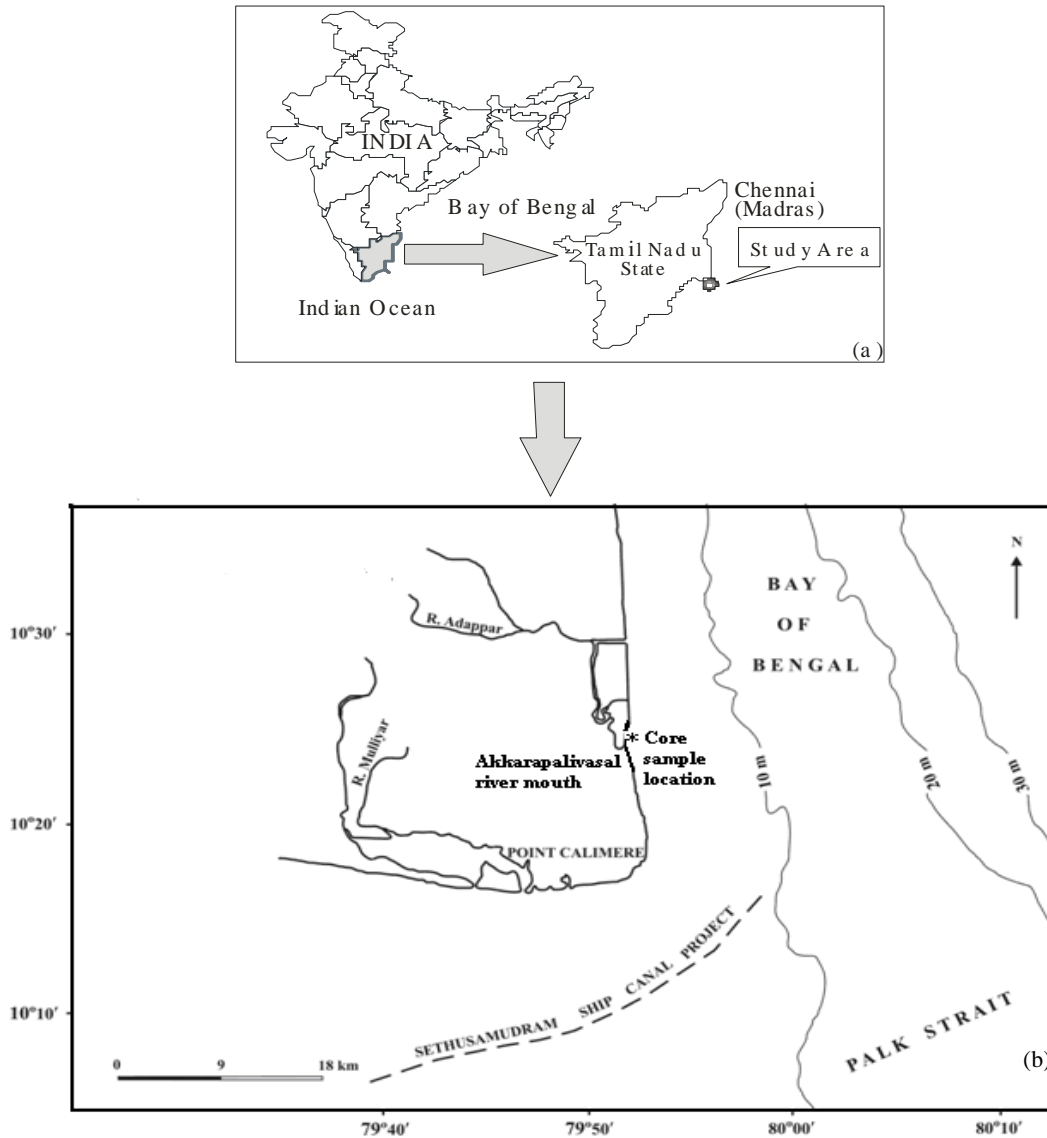

Fig. 1. Study area

Core sampling was done at one particular location during May 2003 for the present study. This location was selected as it is very close to the mouth of the river which can decipher the influence of coastal region .Collection of core samples was done from a boat using a PVC coring tube of 6.3 cm diameter and 2.5 m length, which was pre-cleaned with dilute acid. The sub-samples were sliced at 2.5 cm depth interval resulting in 18 numbers of samples. The water depth at the coring site were 1.25 m and the sub-samples were tightly packed, transported to the laboratory and stored at -4° C until further analysis. The geochemical data presented in the present study have not been corrected for compaction, as it is likely to be uniform down the length of the core (Clark *et al.,* 1998).

During the first stage of work, sand and mud (silt + clay) were estimated following the procedure of Ingram (1970).Carbonate content ($CaCO_3$) was measured following the procedure of Loring and Rantala (1992) and organic carbon (OC) was determined following the procedure of Gaudette *et al.,* (1974). Major elements (Si, Al, Fe, Ca, Mg, Na, K, and P) and trace elements (Mn, Cr, Cu, Ni, Co, Pb, and Zn) were determined after preliminary treatment and total decomposition of sediments following the procedure of Loring and Rantala (1992). The final solution was analyzed using AAS (Varian Spectra AA220) which is equipped with a detritum background corrector. Further standard reference material MESS-1 was used to ensure the quality control and accuracy of the analysis (Table 1).

The geochemical elements delivered to the creek are not only from anthropogenic sources but also by natural flux of elements from the catchment areas. One of the popular methods to distinguish the fraction of metals or enrichment is by normalization with respect to Al (Kemp *et al.,* 1976; Van Metre and Callender,1997; Loring, 1991). Moreover, Al is successfully and widely used as a normalizer and it also compensates for variations in the grain size and composition because it represents the quality of alumino silicates which is the most important carrier for adsorbed metals in the aquatic environments.The variability of the normalized concentrations is expressed as enrichment factors (EFs), which is a ratio of the content of the element in the analyzed layer to the content corresponding to the pre-industrial period: EF = (Cx/CAl)s/(Cx/CAl)c where, (Cx/CAl)s ratio of concentration of element x and aluminium in the sample, (Cx/CAl)c ratio of concentration of element x and aluminium in unpolluted sediments (Continental crustal values, Taylor and McLennan, 1985). An EF around 1.0 indicates that the sediment originates predominantly from lithogenous material, whereas an

Table 1. Comparison of published MESS-1 values with obtained data in the present study

Elements	Present results	MESS-1	Recovery (%)
SiO_2 (%)	65.40	67.50	96.89
Al_2O_3 (%)	10.34	11.03	93.74
Na_2O (%)	2.16	2.50	86.40
K_2O (%)	2.15	2.24	95.98
CaO (%)	0.67	0.67	99.26
MgO (%)	1.19	1.44	82.64
Fe_2O_3 (%)	3.72	4.36	85.32
P_2O_5 (%)	0.13	0.15	85.62
Mn (mg/Kg)	505.20	513.00	98.48
Cr (mg/Kg)	68.20	71.00	96.06
Cu (mg/Kg)	24.80	25.10	98.80
Ni (mg/Kg)	28.20	29.50	95.59
Co (mg/Kg)	10.40	10.80	96.30
Pb (mg/Kg)	33.21	34.00	97.68
Zn (mg/Kg)	180.37	191.00	94.43

EF much greater than 1.0 indicates that the element is of anthropogenic origin (Szefer *et al.,* 1996).

RESULTS & DISCUSSION

The sediment texture, down core variation and their implications on physico-chemical parameters of the core samples have been studied in detail.The grain size distribution in the core sediments is important in understanding the depositional environment history.In all the core samples, mud (silt + clay) dominates over sand, indicating relatively calm environment of deposition. There are local variations in grain size distribution within the core at different depths. The results of grain size analysis for the core samples are presented in Table 2.

Grain size results indicate a variation of 46.43-98.57% for sand with an average of 76.77%. Silt ranges from 1.23-53.37% with 23% on an average. Clay content in the core sample varies from 0.10-0.42%, with an average of 0.23%. The top portion of the core to a depth of 17.5 cm, the sediment is sandy type with sand varying from 80.76 to 98.57 %. At 15 to 17.5 cm depth, silt content is 19.04 %. At the middle portion from 17.5 to 30 cm depth, it is only silty sand with an exception of sandy silt at 20 to 22.5 cm depth. At a depth of 30 to 32.5 cm sand (87.5%) exists with 12.08 % silt and 0.42% clay. At the bottom portion from 32.5 to 40 cm depth, silty sand is seen with silt ranging from 27.71 to 43.59 % and at the bottommost portion at a depth of 40 to 45 cm it is sandy in nature (80-88 %). The high concentration of sand in the core is attributed to the tidal influence at the Akkarapallivasal river mouth. The sea wa-

Table 2. Characteristics of Sediments in the core

Depth in cm	Sand %	Silt %	Clay %	Sediment Type
0-2.5	98.57	1.23	0.20	Sand
2.5-5	95.36	4.44	0.20	Sand
5-7.5	92.35	7.45	0.20	Sand
7.5-10	92.85	6.95	0.20	Sand
10-12.5	93.54	6.26	0.20	Sand
12.5-15	87.05	12.75	0.20	Sand
15-17.5	80.76	19.04	0.20	Sand
17.5-20	63.50	36.30	0.20	Silty sand
20-22.5	46.43	53.37	0.20	Sandy silt
22.5-25	50.48	49.26	0.25	Silty sand
25-27.5	54.33	45.36	0.31	Silty sand
27.5-30	71.02	28.62	0.36	Silty sand
30-32.5	87.50	12.08	0.42	Sand
32.5-35	71.92	27.74	0.34	Silty sand
35-37.5	56.15	43.59	0.26	Silty sand
37.5-40	72.11	27.71	0.18	Silty sand
40-42.5	87.88	12.02	0.10	Sand
42.5-45	80.00	19.86	0.14	Sand
Mean	**76.77**	**23.00**	**0.23**	

ter which enters the river suspends the flocculated sediments at the mouth and transports the fine floccules to the water column. The tidal currents also play a major role in removing the fine particles from the river mouth.

Calcium carbonate concentration ranges from 0.40 to 3.00%. The average concentration of calcium carbonate is 1.31%. Down core variations of $CaCO_3$ are plotted in Fig. 2b. The $CaCO_3$ content in the core increases from 0.6 % to 2.2 % at a depth of 5 to 7.5 cm and then decreases to 1.2 % at a depth of 10- 12.5 cm. It again increases to 2.6 % from 20 to 22.5cm. Beyond that it decreases suddenly from 25 to 27.5 cm and stays almost steady upto a depth of 37.5 cm. About 3% $CaCO_3$ content is observed at a depth of 42.5 cm. The decreasing trend of the concentration of calcium indicates dissolution of carbonate due to transient drop in the pore water pH. The principal reason for this may be partial decalcification process (Oenema *et al.,* 1988) due to transient drop in pore water pH. It may also due to biological productivity and its variation through course of time.

Organic carbon (OC) concentration varies from 0.25 to 3.60%, as shown in Fig. 2a. Average organic carbon for the core is 1.31%. A good amount of organic matter is supplied by river runoff and considerable volume of

organic debris is retained on the overlying water column. An abundant supply of organic matter in water column, relatively rapid rate of accumulation of fine-grained inorganic matter, and low oxygen content of the waters immediately above the bottom sediments would favor high organic matter in the bottom sediments. In the core, the OC content is high in the middle part (22.5-25 cm) there after the OC content varies in a zigzag fashion between 1.26 and 2.59% up to a depth of 35 cm and then decreases. The relatively higher concentrations of OC in top layers reveal the adsorption and incorporation of organic materials from the polluted water column above. The low (minimum) concentration at 0 to 2.5 cm depth is perhaps due to the domination of decomposition over production. The value of OC does not show any significant variation towards depth. The low values indicate domination of decomposition over production. The mean value of OC content in the core is 1.31%, which coincides with the reported values (Murthy and Veerayya 1972; Paropakari 1979; Jonathan 2001; Sundararajan 2001).

The major elements in the core sediments of Vedaranyam coast are presented in Table 3. Si values record a mean concentration of 27.03% ranging from 24.29 to 30.45%.It clearly indicates that the Si content is decreasing up to 25 cm and again it is increasing.
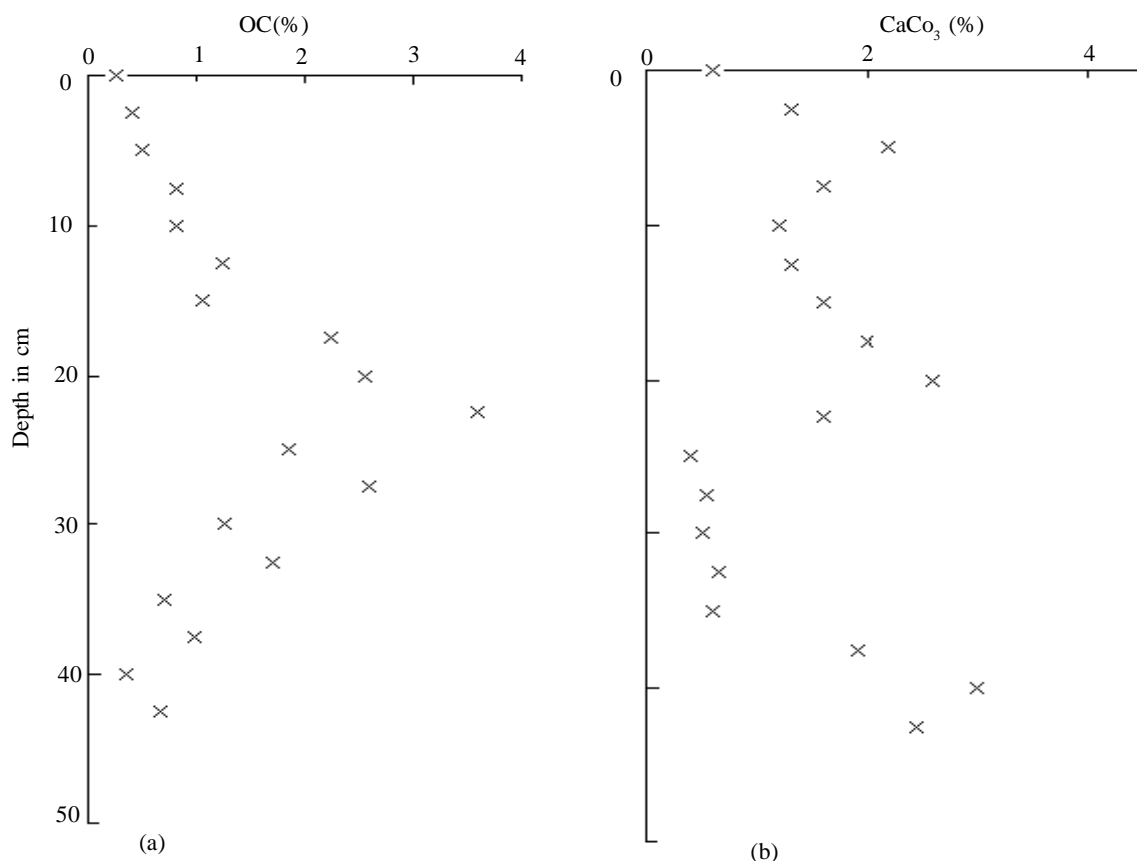
Fig. 2. Down core variation of OC and CaCO$_3$

Towards the bottom of the core there is not much variation in Si concentration. The average sand content encountered in this core shows similar trend. The core is very near to the coast and the influence of tide is more. Estuarine removal of dissolved silica was reported by Liss (1976). Hence the contribution from detrital mineral grains and estuarine mixing in the removal of Si has been considered in the present study. The fluvial process and human induced activities are more in this area (Selvaraj *et al.,* 2005).

The average Al concentration in the core is 8.80% and ranges from 6.04 to 11.94% (Tables 3). The concentration varies with depth and relatively low concentration of 6.54% is observed on the surface of the core (0- 2.5cm). A gradual increase of Al is observed from 7.5-22.5 cm (11.97%); thereafter, it decreases with depth. Na concentration in the core varies from 2.11 to 5.53%, the maximum of 5.53% being recorded at 35 to 37.5 cm depth. Upto a depth of 15 to 17.5 cm, almost a steady Na is observed between 2.61 and 2.96%. The bottom portion shows slightly higher % of Na from 3 to 5.5%.The middle and bottom portions contain lesser amount of K mostly below 2%, whereas at the surface up to a depth of 15 cm it varies from 2.29 to 2.72%.

The concentration of Ca in the core records an average of 7.15% with a variation of 4.42-9.77%. Ca content varies from 4.42% at 35-37.5 cm depth to 9.77% at 10-12.5 cm depth with an average of 7.15%. The top portion shows high % of Ca compared to middle and bottom segments.Mg % is very less about 0.1%. Core samples record an average of 1.34% of Fe in the core. It varies from 1.00-1.60%. In the core sediments of the study area, phosphorous show moderate variations in concentration. The analytical results for the core are enumerated in Table 3. Pconcentration varies from 0.26-0.79% with an average of 0.60%.

Element/Al ratios of the core sediment samples are presented in the depth profile of element/Al ratios for each element (Figs 3 &4) Estimated average values of Si/Al are higher 3.21, ranging from 2.08-4.66 for the samples in the core (Fig. 3 a). Low ratios in certain samples of the core sediments indicate presence of higher amount of Al; similar low ratios were also reported in the Sulu Sea and in the shallow sediments of South China Sea, and were attributed to variations in texture of the sediments and opal silica (Calvert *et al.,* 1993). The lower Si/Al ratio and higher sand content in many samples indicate poor concentration of quartz and other silica rich minerals. In the core Si/Al ratios are very much lower than the CCV.

Table 3. Major elements in the core samples

Depth in cm	Si%	Al%	Na%	K%	Ca%	Mg%	Fe%	P%
0-2.5	30.45	6.54	2.91	2.29	6.75	0.06	1.00	0.79
2.5-5	29.23	6.69	2.81	2.61	8.02	0.04	1.18	0.70
5-7.5	25.59	8.82	2.67	2.72	8.74	0.00	1.31	0.65
7.5-10	27.64	6.04	2.76	2.61	9.52	0.10	1.46	0.58
10-12.5	24.29	8.35	2.96	2.39	9.77	0.19	1.49	0.56
12.5-15	24.56	9.23	2.86	2.32	9.44	0.17	1.43	0.65
15-17.5	26.13	9.35	2.84	2.08	9.05	0.14	1.27	0.74
17.5-20	27.46	9.92	2.53	1.76	8.45	0.13	1.31	0.53
20-22.5	28.21	10.66	2.11	1.38	7.69	0.11	1.31	0.41
22.5-25	24.78	11.94	2.93	1.72	6.65	0.09	1.33	0.58
25-27.5	26.37	10.81	3.61	1.86	5.08	0.05	1.28	0.79
27.5-30	26.00	10.81	3.26	2.01	4.98	0.07	1.38	0.65
30-32.5	26.74	9.75	2.87	2.17	4.97	0.07	1.40	0.53
32.5-35	27.47	8.68	3.93	1.87	4.75	0.07	1.32	0.41
35-37.5	27.46	8.59	5.53	1.65	4.42	0.06	1.16	0.26
37.5-40	27.83	8.15	5.25	1.53	6.12	0.10	1.33	0.65
40-42.5	27.95	7.62	5.06	1.30	7.13	0.12	1.60	0.72
42.5-45	28.42	6.51	5.27	1.38	7.15	0.12	1.51	0.54
Mean	**27.03**	**8.80**	**3.45**	**1.98**	**7.15**	**0.09**	**1.34**	**0.60**
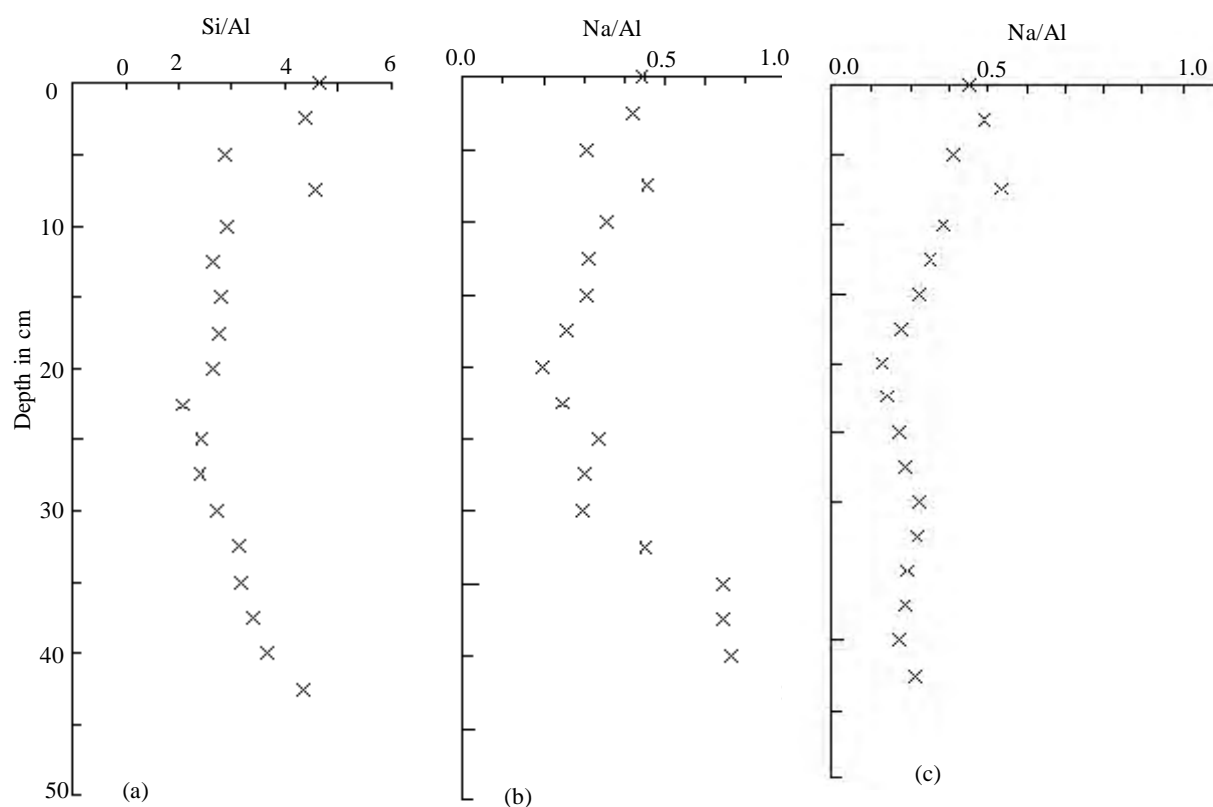
Fig. 3. Down core variation of Al normalization Si, Na, K

Ca/Al

Depth in cm

(a)

Mg/Al

Depth in cm

(b)

Fe/Al

Depth in cm

(c)

P/Al
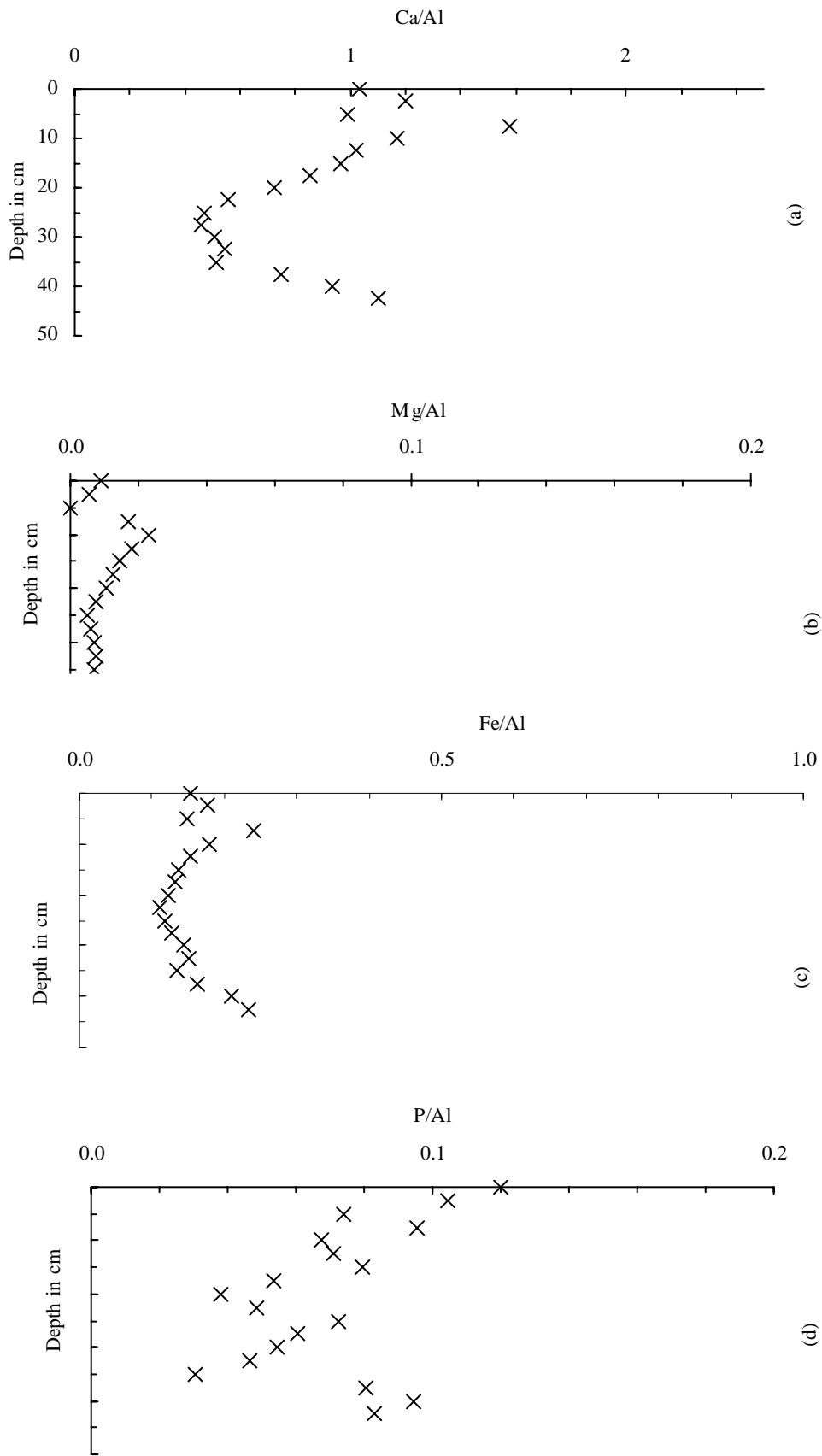
Depth in cm

(d)

Fig. 4. Down Core variation of Al normalization for Ca, Mg, Fe and P

The Na/Al average in the core samples shows a higher of value of 0.41 than the CCV of (0.39), and the ratios of Na record a variation of 0.20-0.81(Fig. 3 b). Towards bottom of the core from 32.5 cm to 45 cm depth, the Na/Al ratios are higher than the CCV. Estimated K/Al ratios in the core samples indicate low values of 0.24 (Fig. 3c). At the surface of the core, up to a depth of 20 cm and from 37.5 to 42.5 cm depth, the Cu/Al ratios are higher than CCV. The ratios for Ca/Al vary from 0.46-1.58 with 0.85 as average which is higher than the continental constant values (Fig. 4 a). Mg/Al ratios indicate an average of 0.01 in the core. (Fig. 4 b). Fe/Al ratios in core sample reveal moderate values, which fall within the continental crustal values (Fig. 4 c).

The P/Al ratios vary from 0.03-0.12 with an overall average of 0.07. For the core retrieved, P/Al ratios and their variations in the sub samples are presented in (Fig. 4d). The lower ratios of P/Al in the core samples reveal low concentrations of P in the analyzed sediments, which are controlled by the detrital phase and are mostly attributed to the absence of low organic carbon and oxygen minimum condition. In the core P/Al ratios are higher than the CCV at all depths. The explanations put forward by Rao and Murthy (1990) in their studies on the west coast of India and Purnachandra Rao et al. (1998) on the east coast are applicable in the present study. The concentration of various major elements in the core can be summarized as Si > Al > Ca > Na > K > Fe > P > Mg.

Core sediments in the study area record an average of 436.13 mg/kg of nondetrital Mn in the core. It varies from 243.21 to 730.40 mg/kg (Table 4) .The lowest is recorded at the surface of the core. The Mn profiles described above can be represented qualitatively as a two-layer system, where the boundary between the upper and lower units corresponds to the observed minimum in the profile, a depth where maximal Mn remobilization occurs (Li *et al.,* 1969; Calvert and Price 1972, Elderfield 1979). The upward increase in Mn concentration above the boundary is related to the vertical migration of Mn by diffusion and advection, resulting from the concentration gradient and burial compaction of solid Mn phases, such as oxides, carbonates, and sulphides (Calvert and Price 1972; Elderfield 1979). In areas of high sedimentation rate, the core sediment is less. As sedimentation proceeds, the surface sediment containing both Fe and Mn oxide phases is buried and microbial oxidation of sedimentary organic matter results in the reduction and dissolution of the oxide phases at depth. With compaction, the dissolved Mn migrates toward the sediment water interface (Heaton and Dayal 1985).

Table 4. Trace elements in the core samples (mg/Kg)

Depth in Cm	Mn	Cr	Cu	Ni	Co	Pb	Zn
0-2.5	243.00	3.75	75.80	68.30	9.15	40.93	78.20
2.5-5	297.10	8.55	59.30	56.50	11.40	41.51	68.90
5-7.5	351.80	13.50	43.40	44.70	13.05	37.26	59.00
7.5-10	406.70	14.85	56.60	39.40	13.05	40.88	72.70
10-12.5	461.30	16.35	71.80	33.80	13.20	44.49	86.60
12.5-15	404.20	17.40	67.30	33.10	14.25	49.17	84.50
15-17.5	346.80	18.15	64.90	32.10	15.00	53.79	82.30
17.5-20	483.30	17.85	54.90	21.10	10.95	50.83	77.50
20-22.5	619.70	18.15	35.70	7.20	7.50	47.92	73.00
22.5-25	476.60	17.40	31.00	14.10	13.35	40.54	70.50
25-27.5	331.40	16.20	32.40	22.80	19.05	33.13	67.20
27.5-30	384.20	15.90	32.90	23.90	19.35	37.95	67.60
30-32.5	436.70	15.00	34.40	25.40	19.80	42.78	67.30
32.5-35	383.40	9.45	32.30	44.70	18.15	42.64	54.40
35-37.5	330.00	3.75	30.10	64.00	13.50	42.56	41.10
37.5-40	530.30	11.25	35.80	57.60	11.85	46.15	62.40
40-42.5	730.40	18.15	41.10	50.90	9.90	49.27	84.20
42.5-45	633.50	19.20	40.60	54.22	13.35	47.76	74.50
Mean	**436.13**	**14.16**	**46.68**	**38.55**	**13.66**	**43.86**	**70.66**

The concentration of Cr varies from 3.75 to 19.20 mg/kg with a mean concentration of 14.16 mg/kg in the core. In the core at the surface up to 5.5 cm depth and from 32.5 to 37.5 cm depth, the Cr concentration is less than 10 mg/kg. From 7.5 – 32.5 cm depth, the concentration lies between 13.5 and 18.15 mg/kg. Towards the bottommost portion, the concentration increases again from 11.25 to 19.2 mg/kg. Estimated concentration of Cu record an average of 46.68 mg/kg and it varies from 30.10 to 75.80 mg/kg. Analytical results of Ni in the core from the study area vary from 7.20 to 68.30mg/kg, with an average of 38.55 mg/kg. Ni concentration is between 7.2 and 68.3 mg/kg, the highest is at the surface and the lowest is at a depth of 20-22.5 cm. The bottom portion shows higher concentration of Ni compared to middle and top portions. Even though the values of Ni show lithogenic origin and low concentration in the present study, they are still rich enough to suggest anthropogenic contribution. This is confirmed by comparison of the present data with the Adyar estuary (Achyuthan *et al.,* 2002), where Ni concentration of 18 to 38 mg/kg had been reported. They had also suggested that Adyar estuary had been highly contaminated with respect to Ni due to anthropogenic activity. The values observed in the creek are more than those of Adyar estuary, indicating that near shore sediments of Vedaranyam is also contaminated by Ni. Estimated Co concentration ranges from 7.50 to 19.80 mg/kg, and an average of 13.66 mg/kg, for the core. The Co concentration in the core varies from 7.5 mg/kg at a depth of 20-22.5 cm to 19.8 mg/kg at 30-32.5 cm depth.The middle portion of the core from 15-17.5 cm depth, and from 27.5-30 cm depth with the exception of 7.5 mg/kg at 20-22.5 cm depth, the concentration is more compared to the top and bottom portions. Analytical results of nondetrital Pb in the study area ranges from 33.13 to 53.79 mg/kg, with an average of 43.86 mg/kg in the core (Table 5). In the core, the concentration of Pb varies from 33.13 to 53.79 mg/kg. The lowest is recorded at 25-27.5 cm depth in the middle portion of the core and the highest (53.79 mg/kg) is also recorded in the middle of the core at 15-17.5 cm depth. The zinc concentration varies from 41.10-86.60 mg/kg. The low and high values are recorded at 35-37.5 cm and 10-12.5cm depths respectively. The average concentration of Zn is 70.66 mg/kg. The trace element content discussed above exhibit the following order for the core samples: Mn > Zn >Cu > Pb > Ni > Cr > Co.

Normalization of trace elements with Al values was done for all samples taken from the core. The metal/Al ratios and enrichment factors for the analyzed trace metals are shown (Figs. 5 & 6) with respect to CCV. Mn/Al ratios in the study area range from 30.67 to 97.32×10^{-4}, with an average of 51.31×10^{-4}. The down core profiles with variations for Mn/Al ratios are shown

(Fig. 5 a). Enrichment factors for the core samples ranges from 0.32 to 1.01. The normalization values are very much above the CCV in the core.The EF values for Cr based on average shale do not show very high concentrations.Cr/Al ratios vary from 0.44 to 2.95×10^{-4} with an average of 1.63×10^{-4}, for the core. The Cu/Al ratios in the study area record an average of 5.66×10^{-4} .Enrichment factor ranges from 0.51 to 2.27. Down core profile of Cu/Al are shown in Figure 5c. The down core variations in Cu/Al ratios are almost the same. The values at the surface upto a depth of 15 cm are slightly higher than the CCV. Ni/Al ratios vary from 0.68 to 10.45×10^{-4}, with an overall average of 4.84×10^{-4}, for the core samples. Computed Ni/Al ratios as seen in the down core profile (Fig. 6 a). Enrichment factors vary from 0.09 to 1.36.The average for the core is 0.63. Estimated Co/Al values for the core samples ranges from 0.70 to 2.16×10^{-4}, with an overall average of 1.58×10^{-4}, (Figure 6 b). Enrichment factors for Co are well below 1indicating low concentrations. The Enrichment factors value ranges from 0.37 to 1.14; Co/Al ratios do not vary much down the core. Estimate of Pb/Al ratios for the core samples vary from 3.07 to 7.34×10^{-4}, with an overall average of 5.18×10^{-4}. The down core profile variations of Pb/Al ratios are represented in Fig. 6 c. The Pb/Al ratios of the core are high, with minor variation between samples which shows the periodical change in the input of this metal and its anthropogenic nature. Enrichment factors record an average of 2.59, for the core samples. It varies from 1.53 to 3.67. Pb/Al ratios vary in a zigzag manner with increase and decrease down the core.

The overall observation of Pb/Al ratios in the study area indicate that external atmospheric inputs has played a major part in the increase of Pb over the crustal average and it is also well supported by the very high EF values. The variations in EF values, which range from 1.0 to 4.9, also confirm this inference.

Zn/Al ratio in the core samples ranges from 4.79 to 12.04×10^{-4}, with average of 8.36×1010^{-4}.The down core variation of Zn/Al ratio with reference to the crustal values is shown in Fig. 6 d. Enrichment factor also shows an average of 0.77, with a variation of 0.44 to 1.11. The Al normalization values are very much higher (2-7 times) than the CCV. The mean EF values are above 1, which indicates that influence of anthropogenic input is very less. The element/Al ratios and the enrichment factors for majority of the analyzed sediments are more or less higher than the crustal average. Universally, the Enrichment factors above 1 for many of the metal reveal enrichment and this is taken into consideration for the study area. By applying the above rule to the study area, the analyzed elements specify that except Mn, all the elements are above the crustal

Table 5. Al normalization and element enrichment factor for trace elements in the core samples

Depth in cm	Mn/Al (X10⁻⁴)	EF	Cr/Al (X10⁻⁴)	EF	Cu/Al (X10⁻⁴)	EF	Ni/Al (X10⁻⁴)	EF	Co/Al (X10⁻⁴)	EF	Pb/Al (X10⁻⁴)	EF	Zn/Al (X10⁻⁴)	EF
0-2.5	37.18	0.39	0.57	0.06	11.6	2.27	10.45	1.36	1.4	0.74	6.26	3.13	11.97	1.11
2.5-5	44.42	0.46	1.28	0.13	8.87	1.74	8.45	1.1	1.7	0.9	6.21	3.1	10.3	0.95
5-7.5	39.9	0.41	1.53	0.15	4.92	0.97	5.07	0.66	1.48	0.78	4.23	2.11	6.69	0.62
7.5-10	67.35	0.7	2.46	0.24	9.37	1.84	6.53	0.85	2.16	1.14	6.77	3.39	12.04	1.11
10-12.5	55.24	0.57	1.96	0.19	8.6	1.69	4.05	0.53	1.58	0.83	5.33	2.66	10.37	0.96
12.5-15	43.77	0.45	1.88	0.18	7.29	1.43	3.58	0.47	1.54	0.81	5.32	2.66	9.15	0.85
15-17.5	37.09	0.39	1.94	0.19	6.94	1.36	3.43	0.45	1.6	0.84	5.75	2.88	8.8	0.81
17.5-20	48.71	0.51	1.8	0.18	5.53	1.08	2.13	0.28	1.1	0.58	5.12	2.56	7.81	0.72
20-22.5	58.14	0.6	1.7	0.17	3.35	0.66	0.68	0.09	0.7	0.37	4.5	2.25	6.85	0.63
22.5-25	39.92	0.41	1.46	0.14	2.6	0.51	1.18	0.15	1.12	0.59	3.4	1.7	5.91	0.55
25-27.5	30.67	0.32	1.5	0.15	3	0.59	2.11	0.27	1.76	0.93	3.07	1.53	6.22	0.58
27.5-30	35.54	0.37	1.47	0.14	3.04	0.6	2.21	0.29	1.79	0.94	3.51	1.76	6.25	0.58
30-32.5	44.78	0.47	1.54	0.15	3.53	0.69	2.6	0.34	2.03	1.07	4.39	2.19	6.9	0.64
32.5-35	44.15	0.46	1.09	0.11	3.72	0.73	5.15	0.67	2.09	1.1	4.91	2.46	6.26	0.58
35-37.5	38.42	0.4	0.44	0.04	3.5	0.69	7.45	0.97	1.57	0.83	4.96	2.48	4.79	0.44
37.5-40	65.07	0.68	1.38	0.14	4.39	0.86	7.07	0.92	1.45	0.77	5.66	2.83	7.66	0.71
40-42.5	95.85	1	2.38	0.23	5.39	1.06	6.68	0.87	1.3	0.68	6.47	3.23	11.05	1.02
42.5-45	97.32	1.01	2.95	0.29	6.24	1.22	8.33	1.08	2.05	1.08	7.34	3.67	11.45	1.06
Mean	**51.31**	**0.53**	**1.63**	**0.16**	**5.66**	**1.11**	**4.84**	**0.63**	**1.58**	**0.83**	**5.18**	**2.59**	**8.36**	**0.77**
Avshale	**96.2**	.....	**10.2**	.....	**5.1**	.....	**7.7**	.....	**1.9**	.....	**2**	.....	**10.8**	.....
Continental Crust Average	**11.54**	.....	**1.21**	.....	**6.68**	.....	**9.11**	.....	**3.04**	.....	**1.52**	.....	**0.85**	.....
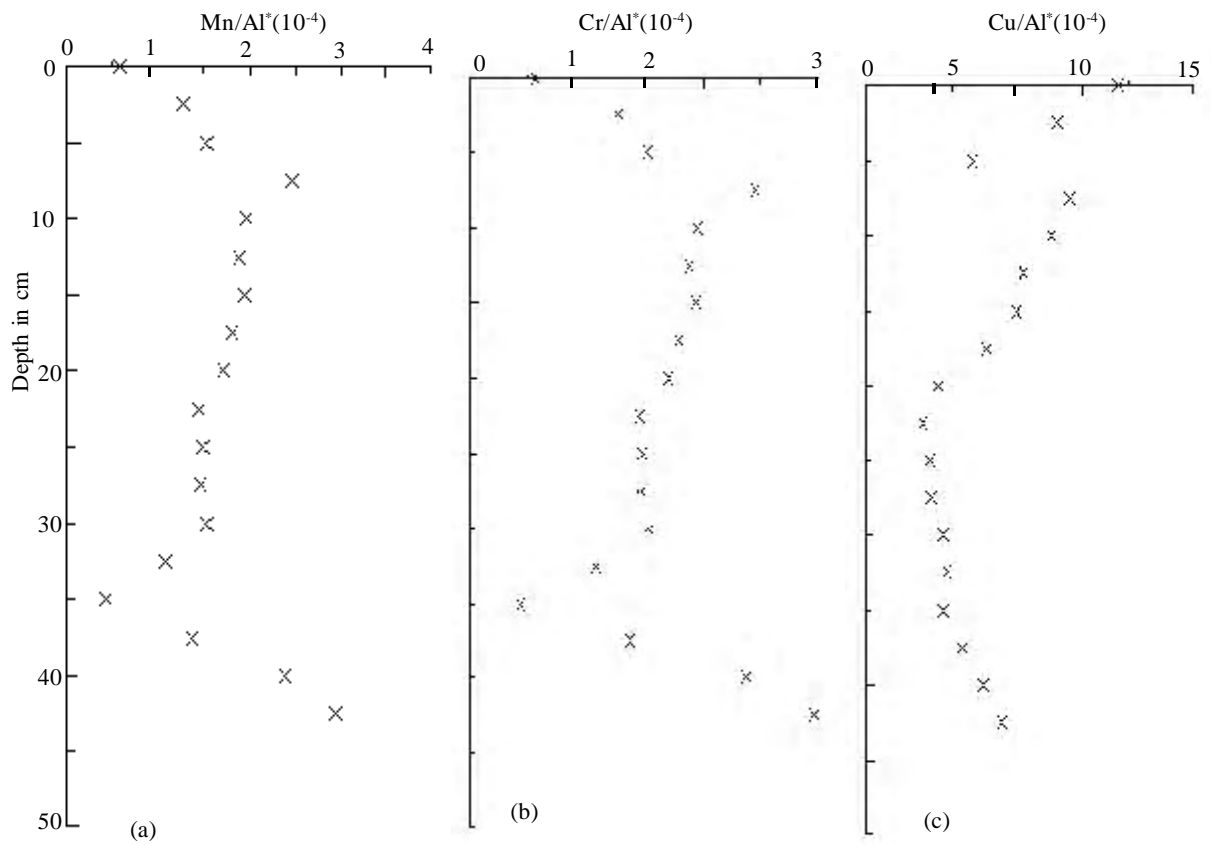
Fig. 5. Down Core variation of Al normalization Mn, Cr and Cu
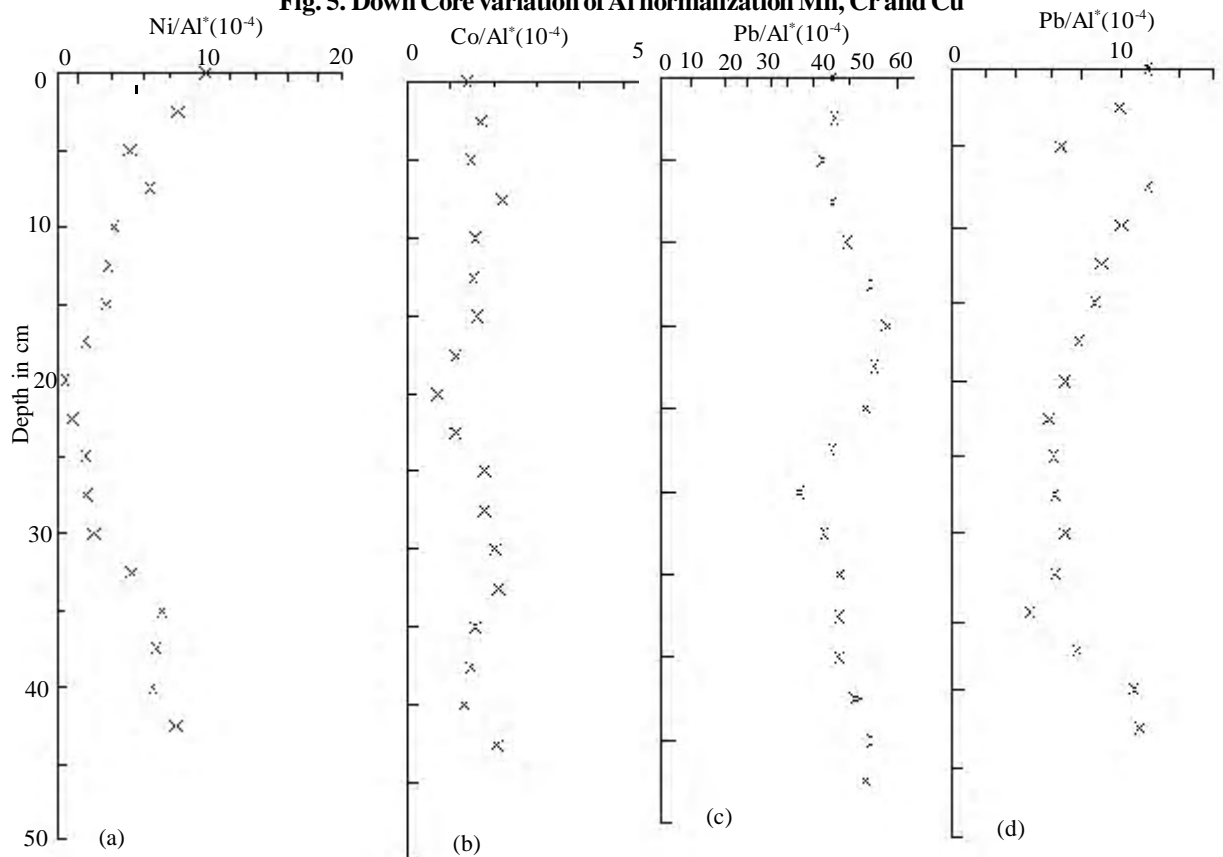
Fig. 6. Down Core variation of Al normalization for Ni, Co, Pb and Zn

value demonstrating external input. Similar inferences had also been observed for many coastal regions like Neches estuary, Texas (Ravichandran *et al.,* 1995), Gulf of Mannar (Jonathan *et al.,* 2004), Kalpakkam, south east coast of India (Selvaraj *et al.,* 2004) and Cuddalore, south east coast of India (Ayyamperumal *et al.,* 2006). The higher enrichment factor of all the metals in the study area exhibits sediment contamination due to the anthropogenic activities around the mangrove region. This is also supported by Warren, 1981; Szefer and Skwarzec 1988; Mac Donald et al. 1991; Van Geen and Luoma 1999.It is interesting to note that the enhancement order of enrichment factor values over the crust in the study area decreases in the following order for toxic trace elements Pb > Cu > Co > Zn > Ni > Mn > Cr . The analyzed results correlate well with earlier studies indicating that higher enrichment factor values show an external contamination in the study area. These elements dominating the study area suggest that various anthropogenic activities had taken place and the results also support the inference (Table 6).

The major oxide data for surface sediments and core sediments are plotted in Al_2O_3–CaO* 1 Na_2O–K_2O (A–CN–K) compositional space (molecular proportions) in all the sediments plot (Fig. 7 and 8) on a trend parallel to the Al_2O_3–CaO*+Na_2O join, suggesting that the sediments represent the products from granite and charnockite sources (Fedo *et al.,* 1995). The present study is compared to the CIA of granite, typical illite, montmorillonite, average shale and kaolinite (Nesbitt and Young 1982). Note that CIA for kaolinite is 100.CIA values for the sediments of the core, shows a relatively very low degree of alteration in sediments (Fig. 9). In this core sample CIA values show wide range from un-weathered to high degree of weathering.

CONCLUSION

The core samples are dominated by sand and have higher concentration of organic carbon and depleted $CaCO_3$ concentration. The samples with high Si/Al ratio are generally coarser grained and this is manifested by a higher ratio of quartz + feldspar relative to clays. The higher concentrations of Al and Fe in the sediments are also due to the detrital mineral grains supplied through adjacent rivers. The behavior of Na and

Table 6. Comparison of trace elements with various estuarine and coastal regions from east coast of India (mg/kg)

Location	Mn	Cr	Cu	Ni	Co	Pb	Zn
Present Study							
Core (Range)	243-730	3.75-19.2	30-75.8	7.2-68	7.5-19.8	37.26-53.79	41.1-86.6
Average	436.13	14.16	46.68	38.55	13.66	43.86	70.66
(1)Hugli estuary	502.61	49.89	19.19	27.52	14.34	29.31	80.02
(2)Sunderban mangrove region	495-862	28.8-49.3	21.5-64.1	26.5-44.5	10.4-15.9	13.7-24.9	26-162
(3)Godavari estuary	1059	2.2	47.8	25.7	28.8	55.8	-
(4) Kalpakkam, Bay of Bengal	356	57	20	30	9	16	71
(5)Shallow cores, Bay of Bengal	529	84	26	64	-	-	-
(6)Bed sediments of river Palar	1131	338	64	-	-	45	-
(7)Intertidal sediments, SE coast of India	51-2005	11-394	0-105	-	-	5-130	13-144
(8)Core sediments a) Adyar estuary, SE coast of India (0-10.5 cm)	345	318	-	426	10	2	168
b) Muttukadu (0-5 cm)	409	48	-	49	8	1	68
c) Mamallapuram (0-1 cm)	777	87	-	53	9	13	106
d) Marakkanam (0-1 cm)	442	58	-	12	7	11	87
(9)Surface sediments, Gulf of Mannar	296	167	-	24	7	16	73
(10)Core sediments Ennore creek (0-2.5 cm), SE coast of India	391	643	-	49	11	17	105
(11) Surface sediments, Palk strait	730	10.4	69.6	25	13.5	43.8	67.6

1) Chatterjee et al., (2007); 2) Sarkar et al., (2004); 3) Ray et al., (2006); 4) Selvaraj et al., (2004); 5) Sarin et al., (1979);

6) Mohanachandran (1988); 7) Mohanachandran and Subramanium (1990); 8) Achyuthan et al., (2002); 9) Jonathan and Ram-

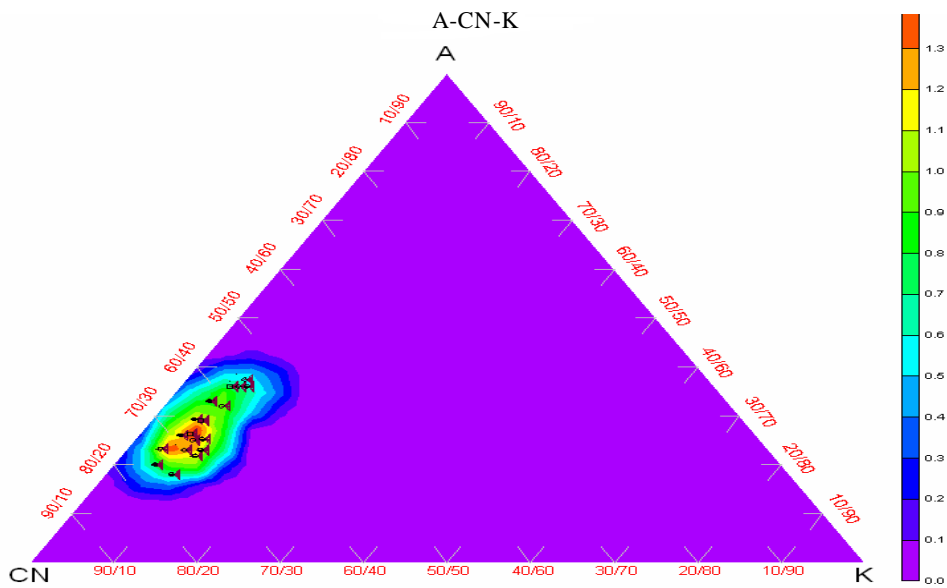Mohan (2003); 10) Selvaraj et al., (2003); 11) Sundararajan and Usha Natesan (2010).

Fig. 7. The major oxide data for Core sediments are plotted in Al_2O_3–$(CaO* 1 Na_2O)$ K_2O (A–CN–K) compositional space (molecular proportions)
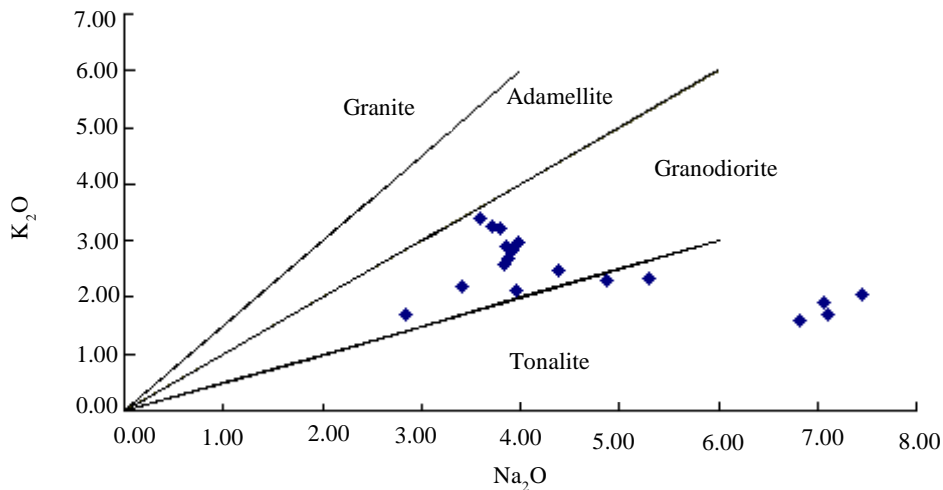

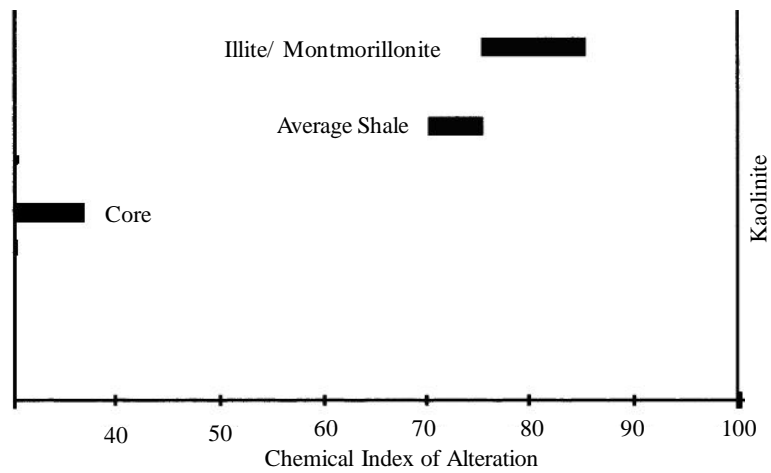**Fig. 8. Variation diagram between Na_2O and K_2O for core sediments**

Fig. 9. Comparison of CIA of Vedaranyam with other geological materials

K indicates the dominance of K-feldspar over plagioclase feldspar. The variation of high Mg/Al ratio in the sand fraction and top layers of the core samples indicates the presence of skeletal fragments, ooids and coral debris. In addition, the higher ratios of Mg/Al in the present study could be due to the precipitation of Mg with an increase in pH and the eddy currents in the coastal zone. The concentration of various elements in the core can be summarized as Si > Al > Ca > Na > K > Fe > P > Mg.

The highly inconsistent Mn concentration in surface sediments of the present study upholds the idea that oxyhydroxide flocs of Mn are transported laterally during saline bottom water inflow and deposited in quiescent parts of the estuary. When compared to the contamination in other parts of the world, the concentration of trace metals in near shore sediments and core is not alarming. High rate of sedimentation and non-decomposition of OM are characterized by the core C1. The distribution pattern of various trace elements in the core is shown as Pb > Cu > Co > Zn > Ni > Mn > Cr .Studies on provenance indicate the source for the sediments in the study area are charnockites and tonalitic gneisses. Core samples show a relatively very low degree of alteration in sediments.

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