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Environmental Significance in Recent Sediments Along Bay of Bengal and Palk Strait, East Coast of India: A Geochemical Approach

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ABSTRACT: The surface sediment samples were analyzed for grain size carbonates ($CaCO_3$) and organic carbon (OC) to obtain a preliminary view of its environmental conditions near Point Calimere along the southeast coast of Vedaranyam, India. The total concentrations of major elements namely, Si, Al, Fe, Ca, Mg, Na, K and P in the surface sediments of Vedaranyam coast are estimated. The element/Al ratios also are computed. The geochemical analysis for trace elements like Mn, Cr, Cu, Ni, Co, Pb, and Zn has been carried out for the surface sediments. Normalization with Al values has been done for all the trace elements and enrichment factors have been calculated. The studies indicate geogenic origin for most of the elements.

Key words: Surface sediments, Geochemistry, Trace metals, Anthropogenic, Palk Strait, Bay of Bengal, India

INTRODUCTION

Study of coastal ecosystem has attracted many researchers of the world. Sediments are important carriers of metals in the hydrological cycle and they effectively collect or release metals into the surrounding waters; thereby, they can reflect the current quality of any ecosystem. Geochemical studies lead to the understanding of the cycles, fluxes, budgets, sources and sinks of chemical elements in any particular area. Grain size parameters provide an insight in to the nature and the energy flux of the multi-various transporting agents and their preview of depositional environment. This helps in analyzing various processes effecting erosion and deposition. The earliest report on the sediments of the Bay of Bengal was presented in a number of papers (Sewell 1925, 1928, 1929 and 1932). International Indian Ocean Expedition data on the Bay of Bengal was presented in the form of an atlas (Wyrtki, 1971). The Bay of Bengal attracted a fair share of attention with regard to its sedimentation geology, notably the origin and history of the Bengal sediments (Stewart *et al.,* 1965).

According to Pragatheeswaran et al. (1986), the sediments off Chennai were more contaminated by heavy metals and organic carbon than Visakhapatnam shelf sediments.The enhanced levels of Cu, Hg and organic carbon were attributed to input from industrial sources including organo-mercurial paint industry and oil refineries. Sarma and Reddy (1988) reported on the distribution of organic carbon, total nitrogen, total phosphorus and total amino acids of Visakhapatnam harbor sediments collected each month during 1986-1987. Ramanathan et al. (1988) analyzed major and minor element geochemistry of water, suspended and bed sediments collected from the upper reaches of the Cauvery estuary to understand the geochemical processes in tropical estuarine systems.

Palanichamy et al. (1995) inferred that industrial effluents pollute the waters of Arumuganeri region, Gulf of Mannar; they also

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recorded higher suspended solids due to the discharge of effluents from the chloro-alkalinity industries and land drainage. Vanmathi (1995) concluded that heavy metals, especially cadmium, are significantly higher in Tuticorin coast than in the other coastal regions, affecting the biota in the region. Purnachandra Rao et al. (1998) studied the clay minerals and the influence of source rock and fluvial input on the shelf sediments of east coast of India. Selvaraj (1999) recorded elevated concentrations of Fe, Cu, Hg and Pb in the Kalpakkam coastal waters and sediments; he attributed the enriched levels of Pb, Cu, Cr, Cd and Zn in sediments to mainly anthropogenic input along the coast and Palar River. Enrichment of metals in bottom sediments represents a critical measure of health for any mangrove ecosystem. Previous studies along Indian coast in mangroves leaves and sediments were made by many researchers (Kotmire and Bhosale, 1979; Ramanathan, 1997; Periakali *et al.*, 2000; Lakshumanan, 2001 and Sarangi *et al.*, 2002). Studies in Mullipallam Creek were related with mangrove seedling, management, mature mangrove species, and documentation of the degradation (Selvam 2003 and Janaki-Raman *et al.*, 2007), but little is known about how mangroves, or the fauna in mangrove ecosystems affect the distribution of trace metals. In this paper, the geochemical parameters of sediments collected at Vedaranyam are presented.The study area, Vedaranyam coast, is located along the Southeast of India and has a reverse “U” shaped structure. The coastal stretch between Akkarapallivasal and Muthupet lying between 10° 15' N -10° 25’N latitude and 79° 30' E -79° 55' E longitude was considered as the study area (Table1 and Fig. 1). 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 km^2. This series consists of very dark grey brown to dark grey brown soils derived from the alluvial deposits. 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.

Table 1. Details of Seabed Sampling Stations

Sample	Latitude	Longitude	Depth (m)
S1	10°24'99"	79°53'78"	3.6
S2	10°22'82"	79°53'18"	4.7
S3	10°20'62"	79°53'52"	4.7
S4	10°17'92"	79°51'85"	4.0
S5	10°15'62"	79°50'08"	4.0
S6	10°15'66"	79°47'36"	2.9
S7	10°15'89"	79°45'62"	2.3
S8	10°16'19"	79°43'73"	2.0
S9	10°16'54"	79°41'69"	2.3
S10	10°17'28"	79°38'69"	2.2
S11	10°18'16"	79°34'69"	2.4
S12	10°19'15"	79°31'63"	2.7

MATERIALS & METHODS

Thirty six surface sediment samples were (12 samples in each season) from 12 stations during different season’s viz., Pre monsoon, Monsoon and Post monsoon were collected using Van Veen grab sampling apparatus by traveling across the study area, using fiber boat during July 2003, December 2003 and February 2004 respectively. The sampler was lowered to the Sea bottom from an armature extending off the side of the boat, via winch and cable. Sediment samples were stored in plastic bags and kept in refrigeration at -4^{oC} until analysis.

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

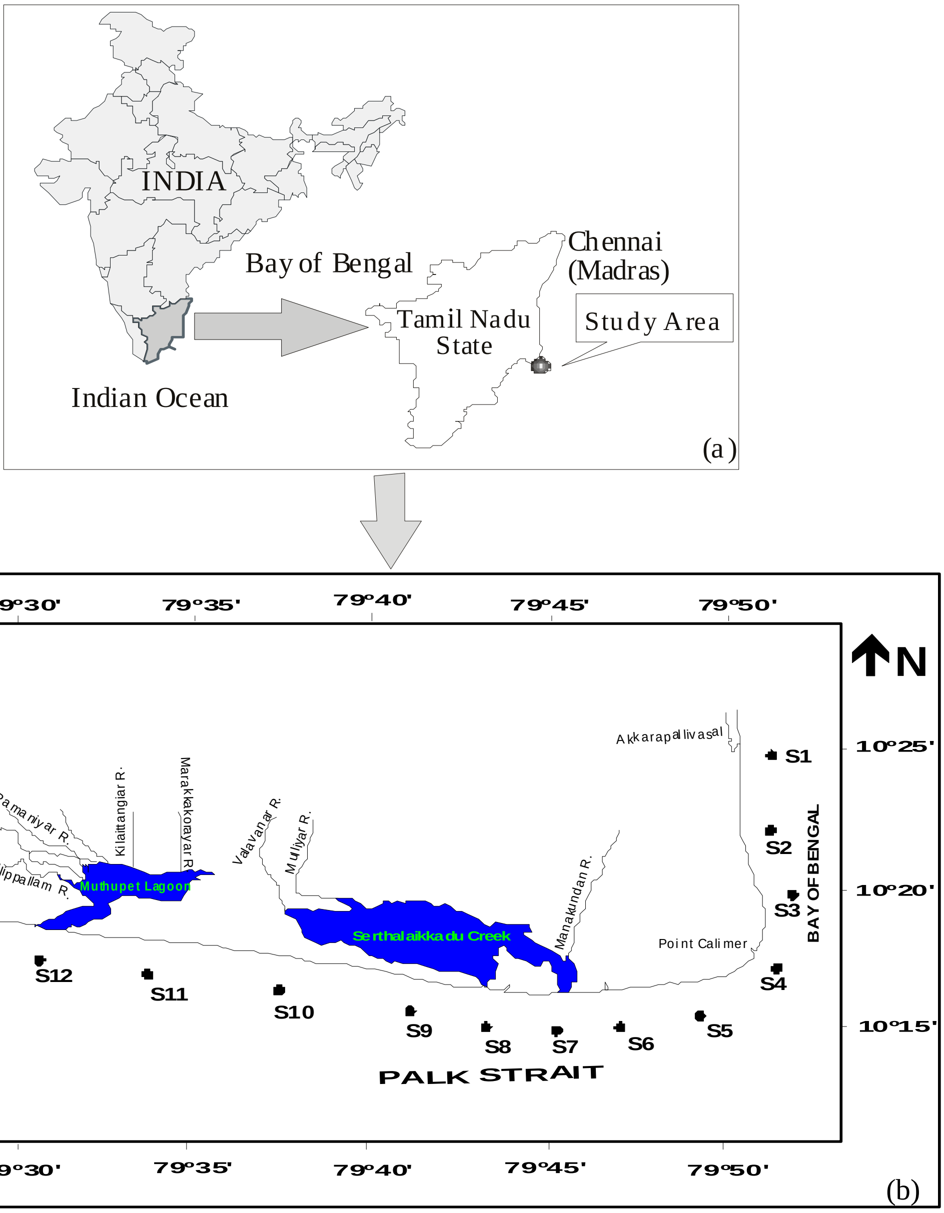

Fig. 1. Study area

using AAS (Varian Spectra AA220) which is equipped with a detritum background corrector. Further standard reference material MESS1 was used to ensure the quality control and accuracy of the analysis (Table 2).

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 and 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 aluminum in the sample, (Cx/CAl)c ratio of concentration of element x and aluminum in unpolluted sediments (Continental crustal values, Taylor and McLennan, 1985). An

Table 2. Comparison of MESS 1 values with 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 around 1.0 indicates that the sediment originates predominantly from lithogenous material, whereas an EF much greater than 1.0 indicates that the element is of anthropogenic origin (Szefer *et al.,* 1996).

RESULTS & DISCUSSION

The textural characteristics of sediments collected during different seasons are shown in table 3.The surface sediments in the study area during pre monsoon are generally clayey silt in nature. Sand varies from 0.45 to 31.26% whereas, silt and clay ranges from 54.58 to 75.91% and 7.0 to 44.41%, respectively. On an average, sand is very low (6.90%), silt is very high (62.11%) and clay is moderate (30.99%). The sedimentary type in the pre monsoon sample indicates that they are mostly dominated by clayey silt. All the sediments except S1 collected during pre monsoon show clayey silt characteristics with clay ranging from 14.9 to 44.4 % and silt from 54.6 to 64.7 %. The sediment at S1, which is sandy clayey silt, contains 15.8% sand with clay 22.1 % and silt 62.1%. The distribution pattern at S4 indicates a high percentage of sand (31.3%) with 61.8% of silt leads to sandy silt nature.

During monsoon, a variation of 1.08 – 10.84% is recorded for sand with an average of 4.09%. Silt ranges from 46.7- 74.36% with an average of 59.94%. Clay content in monsoon season varies from18.27 – 52.22% with an average of 35.96%. Except at S12, sediments from other stations during monsoon season show clayey silt characteristics. The sediments of station S12 are silty clay with 46.7 % silt and around 1% sand. The sample of station S1 records a high value for sand (10.84 %) along with silt 62.46 % and clay 26.7 %. In the sediments from other stations, clay varies from 18.27 % (S3) to 42.14% (S7). During monsoon the distribution pattern is more or less similar to that obtained for previous season, except for a general increase in silt and clay content attributable to additional sediment input from river.Sand content in the post monsoon varies from 0.18 -25.16% with an average of 6.32%; silt recorded an average of 63.35% with the range of 49.65 - 75.31%; clay content averaged to 30.33% with a range of 8.98-50.11%. The sediments collected during post monsoon season from different stations indicate sandy silt characteristics in stations S4 and S6 with sand content of 21.24% and 25.16% respectively. All other stations point out clayey silt characteristics with clay varying from 18.04 to 50.11 %. Sand percentage is very low in stations S8, S9, S11and S12.

Comparing the seasonal data on sediment characteristics, it is seen that the characteristics has changed at station S12 from clayey silt to silty clay during monsoon season as this station is located near Muthupet creek. Sand content is more in stations S4 and S6 during post monsoon season. Similar trend is observed during pre monsoon also. At stations S1 and S2, the sandy clay characteristic has changed to clayey silt type. During monsoon season, the sand content is more in most of the stations. The inflow of riverine input might have changed the sediment nature during monsoon. The distribution pattern is more or less the same except for a general increase in silt content attributable to additional sediment input from river.The calcium carbonate and organic carbon contents in the surface sediments collected during different seasons from the study area are given in Table 4. The ranges of calcium carbonate are 0.20 to 3.40%, 1.20 to 5.81%, and 2.60 to 6.61% with an average of 1.51%, 2.78% and 4.04% in pre monsoon, monsoon and post monsoon respectively .When compared to pre monsoon values, $CaCO_3$ content is higher during monsoon and the highest during post monsoon season. The station S12 (silty clay) records a maximum of $CaCO_3$ during monsoon and post monsoon.

Table 3. Characteristics of Sediments in the seabed samples

	Pre monsoon				Monsoon				Post monsoon			
Station	Sand %	Silt %	Clay %	Sediment Type	Sand %	Silt %	Clay %	Sediment Type	Sand %	Silt %	Clay %	Sediment Type
S1	15.80	62.10	22.10	Sandy clayey silt	10.84	62.46	26.70	Clayey silt	2.78	69.85	27.37	Clayey silt
S2	13.20	62.70	24.10	Clayey silt	9.55	58.47	31.98	Clayey silt	4.20	71.13	24.67	Clayey silt
S3	4.10	64.70	31.20	Clayey silt	7.37	74.36	18.27	Clayey silt	4.85	75.31	19.84	Clayey silt
S4	31.30	61.80	7.00	Sandy silt	5.09	64.61	30.30	Clayey silt	21.24	69.78	8.98	Sandy silt
S5	9.20	75.90	14.90	Clayey silt	1.51	61.31	37.18	Clayey silt	8.01	73.95	18.04	Clayey silt
S6	3.40	59.70	36.90	Clayey silt	2.75	59.14	38.11	Clayey silt	25.16	61.83	13.01	Sandy silt
S7	1.50	64.40	34.20	Clayey silt	4.24	53.62	42.14	Clayey silt	1.08	57.24	41.68	Clayey silt
S8	0.50	62.40	37.20	Clayey silt	1.14	57.65	41.21	Clayey silt	0.52	56.12	43.36	Clayey silt
S9	1.20	63.30	35.50	Clayey silt	1.21	60.13	38.66	Clayey silt	1.03	58.43	40.54	Clayey silt
S10	1.00	54.60	44.40	Clayey silt	3.15	58.04	38.81	Clayey silt	6.60	56.09	37.31	Clayey silt
S11	0.90	58.70	40.40	Clayey silt	1.17	62.84	35.99	Clayey silt	0.18	60.80	39.02	Clayey silt
S12	0.90	55.00	44.20	Clayey silt	1.08	46.70	52.22	Silty clay	0.24	49.65	50.11	Clayey silt
Mean	**6.90**	**62.11**	**30.99**		**4.09**	**59.94**	**35.96**		**6.32**	**63.35**	**30.33**	

Calcium carbonate in shelf sediments may be derived as carbonate materials and particulate matter from adjacent landmass, and through inorganic and organic precipitation from the water column. The major sources of carbonate in the sediments of the study area are the shells and broken shell fragments of organisms, mollusks and also due to dilution of biogenic calcite by detrital material in the sediments. Similar observations were made by Sebastian et al (1990), in their study on sediments of Mahe estuary, West Coast of India. The association of sand particles with $CaCO_3$ indicates the major contribution of shell fragments to the sand fraction.The study of organic carbon (OC) in the estuarine environment is important for predicting the impact of contamination. OC concentration varies from 0.41 to 2.83% during pre monsoon, 0.05 to 1.83% during monsoon, and 0.05 to 6.14% during post monsoon. The OC content is less than 1% during monsoon season in most of the stations except at stations S11 and S12. OC content is high during post monsoon and low during pre monsoon seasons. Subba Rao (1960) revealed that the shelf sediments of the east coast of India (Krishna and Godavari basins) are very fine in nature, but show very low organic matter in the silts and clays. The high organic carbon content in the sediments of the riverine part of the creek is due to fine nature of the sediments and high rate of sedimentation.The total elemental concentrations of major elements viz. Si, Al, Fe, Ca, Mg, Na, K, and P in season sediments of Vedaranyam coast are depicted in Table 5.Si is one of the most abundant elements in the earth's crust and is the major constituent in most rock forming minerals. Similarly in sediments, it is present in quartz, feldspars and clay minerals and as a wide variety of heavy and light minerals. Analytical results of SiO_2 in seabed sediments indicate that the detrital quartz present in the study is more or less evenly distributed. The mean concentration of Si during pre monsoon, monsoon and post monsoon are 29.65%, 29.29% and 29.64% respectively. Si concentration varies from 27.04 to 33.42 % with a maximum at S8 in different seasons. No significant variation in Si content is observed in the three sampling periods. Al is the third most abundant element in the earth's crust and is often associated with the broad classification of minerals called alumino silicates. These include the common sedimentary minerals phyllosilicates, feldspars and amphiboles; Buckley and Cranston (1991) inferred that the variation of Al in sediments might be associated with changes in the clay mineral content or with the content of feldspars in the sediment. Estimated results of Al in pre monsoon, monsoon and post monsoon have mean values of 8.56, 8.71, and 8.65% and ranges from 6.05 -10.48%, 7.08 – 10.62% and 7.19 – 10.73% respectively. Seasonal variation in Al concentration is not much in sediments of the study area. The higher concentration of Al in the sediments could also be due to the contribution from detrital mineral grains supplied through the Marakorayar and Karalaiyar rivers in addition to the precipitation of their dissolved species under the prevailing estuarine condition. This removal of dissolved river - borne aluminum

Table 4. Calcium carbonate and Organic carbon in Seabed sediments

	Calcium Carbonate %			Organic carbon %		
Station	**Pre monsoon**	**Monsoon**	**Post monsoon**	**Pre monsoon**	**Monsoon**	**Post monsoon**
S1	2.50	3.13	3.20	1.02	0.05	2.99
S2	2.50	2.00	5.60	1.05	0.16	2.88
S3	1.88	2.40	3.10	1.32	0.10	2.93
S4	1.40	1.60	5.60	0.41	0.84	0.05
S5	1.00	1.20	3.00	1.04	0.58	3.19
S6	0.20	2.60	3.60	1.47	0.79	6.14
S7	1.60	1.80	2.60	2.83	0.79	5.31
S8	0.40	2.40	3.00	1.55	0.31	3.19
S9	0.20	2.60	3.20	2.34	1.05	4.13
S10	1.20	3.60	3.20	1.82	0.94	5.60
S11	1.80	4.20	5.80	2.06	1.83	5.95
S12	3.40	5.81	6.61	1.77	1.68	6.09
Mean	**1.51**	**2.78**	**4.04**	**1.56**	**0.76**	**4.04**

by coagulation in the coastal areas is common (Coonley *et al.*, 1971; Holiday and Liss, 1976; Sholkovitz, 1976 and Boyle *et al.*, 1977).

Sodium is one of the poorly documented elements in the marine and estuarine sediments of the Indian coast. Sodium concentration in surface sediments collected during the pre monsoon varies from 2.43-5.39%, the average being 3.41%. Monsoon records an average of 3.53% with the concentration varying from 2.46-5.33% and post monsoon show an average of 3.82% with the variation from 2.65-5.44%. Seasonal variation for Na concentration ranges from 3.41 to 3.82 % with maximum during post monsoon. Potassium is a common rock-forming mineral and is associated with non-carbonate minerals in the coastal sediments. The more specific common mineral association of K is with the mica minerals and potash feldspars. Pre monsoon samples in the study area record an average of 1.00%, 1.05%, 1.53%, with the variation from 0.39 – 1.64%, 0.68 –1.41%, and 0.36-2.56% in pre monsoon, monsoon, and post monsoon respectively. The concentration of K in S7 and S8 is below 1 % and is the highest at S6 during post monsoon.Ca is normally present in silicate minerals at very low levels of 1%; hence, its contribution to sediment composition from detrital silicate minerals is relatively minor. The minor source of CaO in the sediments is from calcium rich shell material contributed by marine life. The larger shell fragments of more than 2 mm size were removed by sieving before analysis; hence, the contribution of Ca by shell fragments is substantially minimized. However, whole of the samples were used for $CaCO_3$ determination and so the total $CaCO_3$ content of the sample is much higher than the Ca content in the sample. Estimated concentration of Ca in pre monsoon shows an average of 4.27% with a variation of 2.62-6.20%; in monsoon it varies from 2.18-5.15% with an average of 3.91%; and in post monsoon, Ca records an average of 3.85% and ranges from 2.75-7.32%. The highest Ca concentration is recorded at S6 during post monsoon and pre monsoon seasons. During monsoon a maximum of 5.15% is recorded at S8. The concentration of Ca in the surface sediments is mostly of biogenic origin and mainly attributed to the abundance of skeletal components, which are dominated by mollusks, bryozoans, and foraminifers and, to a certain extent, to the inflow of seasonal rivers that enrich the Ca content.

Mg is present in silicate minerals at less than 1% concentration to as high as few tens of percent. In detrital silicate sediments, the Mg content is usually associated with certain phyllosilicates such as chlorites. Analytical results state an average value of 0.11% in pre monsoon, 0.13% in monsoon, and 0.10% in post monsoon. Mg in the samples varies from 0.04-0.22%, 0.07-0.23%, and 0.06-0.19% in pre monsoon, monsoon and post monsoon. The concentration is below 0.25%. Compared to other seasons, the Mg is found very much less during post monsoon season. Fe can be combined with a variety of anions to form complexes and minerals. The common mineral forms are present as silicates, oxides, sulphides and phosphates. Under a variety of natural environmental conditions, Fe also changes its oxidation state steadily with changes in the amount of oxygen and variations in pH conditions in the aqueous phases. Hence, this element provides useful information on the present and past depositional and environmental conditions (Buckley and Hargrave, 1989). Analytical results pertaining to the different seasons in the present study record an average of 1.56%, 1.54%, and 1.46% of Fe in pre monsoon, monsoon and post monsoon respectively. It varies from 1.42 to 1.61% in pre monsoon, 1.46 to 1.62% in monsoon and 0.96 to 1.64% in post monsoon.The iron concentration in the sediments shows a low value below 2% in all the seasons at all stations except at S6 (0.96%). The higher concentrations of Fe in the sediments are attributable to the contribution from detrital mineral grains supplied through adjacent rivers, in addition to precipitation of its dissolved species. The removal of dissolved river-borne iron by coagulation in estuaries is more common (Coonley *et al.*, 1971; Holiday and Liss, 1976; Sholkovitz, 1976 and Boyle *et al.*, 1977).The surface sediments clearly show that the concentration of P is the maximum at S1 in all the three seasons. In pre monsoon, P concentration varies from 0.10-0.49% with an average of 0.32%. In monsoon, it ranges from 0.38-0.77% with an average of 0.60% during post monsoon the average concentration of P is 0.65% and it varies from 0.43-0.83%.

Element/Al ratios of Pre monsoon, Monsoon and Post monsoon are presented in Tables 6.

Estimated average values of Si/Al are 3.56%, 3.44%, and 3.50% for pre monsoon, monsoon and post monsoon respectively.There is not much variation between the stations during all the seasons. The mean values of Si/Al during the seasons are observed to be slightly lower than the upper crustal value of 3.83 (Taylor and McLennan, 1985). These values are produced due to different quartz and K-feldspar (Si/Al=3.1) contents relative to illite (Si/Al=1.7), the variations being induced by variable texture and amount of opaline silica (Calvert *et al.,* 1993). In the study area, the samples with high Si/Al ratios are generally coarse grained and are manifested by a higher ratio of quartz and feldspar, as that of clays. A higher proportion of turbidite sands in these samples are, probably, the cause for higher ratios. Estimated Na/Al average in the sample indicates 0.41, 0.42, and 0.46 in pre monsoon and post monsoon respectively and the ratios show a variation of 0.30-0.89, 0.24-0.70, and 0.28-0.73 during different seasons. The Na/Al ratios are slightly higher than the CCV during all the seasons. Estimated K/Al ratios in the seasonal samples indicate average values of 0.12, 0.12 and 0.18 in pre monsoon, monsoon, and post monsoon respectively.Estimated ratios for Ca/Al in pre monsoon vary from 0.29-0.90 with 0.52 averages; in monsoon it varies from 0.25-0.72 with an average of (0.47) and in post monsoon it varies from 0.30-0.99 .The relatively higher Ca/Al ratio in the pre monsoon is mainly due to the higher $CaCO_3$ content and calcium-rich shell fragments. According to Zeller and Wray (1956), the high Ca/Al ratio could also be due to the precipitation and extraction of $CaCO_3$ separated by organisms in warm water in tropical regions. This is well supported by the high Ca/Al ratios in surface sediments of the present study. Estimated ratios of Mg/Al in the samples indicate average for pre monsoon and post monsoon as 0.01 while monsoon records 0.02.

Estimated average values of Fe/Al are 0.19, 0.18, and 0.17 for pre monsoon, monsoon and post monsoon respectively. In sediments free from authigenic Fe-bearing minerals, the Fe_2O_3/Al_2O_3 ratio is known to be reasonably constant at average of 0.18, as Fe is held in structural position with alumino-silicates (Calvert, 1976). Any iron exceeding the represented average Fe_2O_3/Al_2O_3 ratio may, therefore, be used as an approximate measure of authigenic minerals of iron and iron oxide coatings (on settling particles). Estimated P/Al ratios in pre monsoon vary from 0.01-0.06 with an overall average of 0.04 in monsoon, P/Al ratio varies from 0.04-0.10 with an average of 0.07. Post monsoon records an average of 0.08 and it ranges from 0.05-0.11. The relatively low P/Al ratios and the lack of relationship between P/Al and organic carbon suggest that organic contribution of P in these samples is of minor importance and that detrital phases mainly control the P content. These observations correlate well with earlier studies made on the slope regions off Mangalore to Ratnagiri on the west coast of India by Rao and Murty (1990), and on the east coast by Purnachandra Rao et al. (1998).If S1, S11 and S12 are excluded, a moderate increase of P/Al with increasing organic carbon concentration is observed in the samples. This suggests that P is at least partly controlled by organic supply. Hence, an additional P fraction must be present, which is likely to occur in estuarine samples because of the supply of detrital phosphorite from the neighbouring land or shelf.The major element concentrations can be summarized in the decreasing order as Si > Al > Ca > Na > K > Fe > P > Mg. There is not any change in the order with respect to different seasons.

The concentration of trace elements in the sediments is shown in Table 7. Mn is mostly found in trace elements in the lattice structures of most rock forming silicates or it occurs as major element in carbonates and oxides. Mn is precipitated as hydroxides in the estuarine and near shore areas as the less saline river water rich in Mn mixes with high saline low Mn seawater. However, the deposited Mn in sediments are re-dissolved in the pure water below the surface sediments due to the biogeochemical processes and it can also diffuse up to the oxidized sediment interface and can be precipitated as oxide or oxy-hydroxide (Buckley and Cranston, 1991). During monsoon season, Mn records a high concentration of 870 mg/kg at S4, located near the mouth of Serthalaikadu creek and a low concentration of 451.5 mg/kg at S7 (located between Serthalaikadu creek and Muthupet lagoon). In post monsoon, the high and low concentrations are observed at S8 (583.7 mg/kg) and at S6 (280.6 mg/kg) respectively. The pre monsoon concentration of Mn is more than that of monsoon and post

Table 5. Major elements in the seabed sediments

	Si (%)			Al (%)			Na (%)			K (%)		
Station	**Pr**	**M**	**Pm**	**Pr**	**M**	**Pm**	**Pr**	**M**	**Pm**	**Pr**	**M**	**Pm**
S1	30.94	30.36	30.82	7.85	7.52	7.63	2.56	2.68	2.65	0.60	1.24	1.80
S2	30.05	29.47	29.94	6.05	7.84	7.95	5.39	4.33	3.23	0.46	0.91	1.51
S3	29.35	28.77	29.23	7.70	7.90	8.01	2.56	3.31	4.06	1.38	1.41	1.55
S4	30.49	29.91	30.37	7.41	7.08	7.19	2.43	4.98	5.10	1.29	1.02	1.61
S5	28.29	27.71	28.17	9.60	10.30	10.41	2.86	2.46	2.88	1.10	0.68	1.76
S6	27.04	27.68	27.21	9.76	9.43	7.43	3.31	2.57	5.44	0.70	1.11	2.56
S7	30.05	29.47	29.94	9.00	8.67	8.78	3.26	5.33	2.70	1.64	0.94	0.36
S8	33.42	31.10	31.56	7.51	7.18	7.30	3.02	4.06	5.20	0.98	0.84	0.75
S9	31.60	31.02	31.48	8.89	8.56	8.67	2.77	2.86	3.01	0.39	1.17	1.94
S10	28.12	28.16	28.62	9.89	10.62	10.73	5.04	3.60	4.13	1.45	1.07	1.36
S11	28.24	28.13	28.59	10.48	10.15	10.26	5.06	3.29	3.57	0.68	1.13	1.66
S12	28.15	29.28	29.74	8.55	9.28	9.40	2.70	2.95	3.83	1.31	1.14	1.56
Mean	**29.65**	**29.26**	**29.64**	**8.56**	**8.71**	**8.65**	**3.41**	**3.53**	**3.82**	**1.00**	**1.05**	**1.53**

	Ca (%)			Mg (%)			Fe (%)			P (%)		
Station	**Pr**	**M**	**Pm**	**Pr**	**M**	**Pm**	**Pr**	**M**	**Pm**	**Pr**	**M**	**Pm**
S1	3.96	4.09	4.03	0.12	0.13	0.15	1.56	1.56	1.55	0.49	0.77	0.83
S2	5.45	4.82	4.32	0.09	0.09	0.08	1.60	1.49	1.36	0.24	0.52	0.58
S3	5.40	4.74	3.96	0.08	0.08	0.08	1.58	1.46	1.31	0.18	0.46	0.52
S4	4.65	5.06	3.58	0.10	0.19	0.06	1.58	1.62	1.35	0.28	0.56	0.62
S5	4.54	4.80	3.08	0.14	0.23	0.09	1.59	1.62	1.49	0.28	0.56	0.61
S6	6.20	4.75	7.32	0.12	0.22	0.19	1.54	1.62	0.96	0.41	0.69	0.74
S7	2.68	2.18	3.69	0.07	0.07	0.09	1.61	1.46	1.51	0.10	0.38	0.43
S8	2.65	5.15	2.75	0.08	0.15	0.11	1.53	1.51	1.60	0.20	0.48	0.53
S9	2.62	3.07	3.51	0.10	0.09	0.08	1.46	1.52	1.59	0.32	0.60	0.66
S10	4.14	2.62	3.23	0.22	0.12	0.10	1.59	1.52	1.61	0.41	0.69	0.74
S11	3.25	2.76	3.40	0.04	0.11	0.09	1.42	1.57	1.56	0.45	0.72	0.78
S12	5.73	2.90	3.37	0.13	0.12	0.10	1.61	1.57	1.64	0.43	0.71	0.76
Mean	**4.27**	**3.91**	**3.85**	**0.11**	**0.13**	**0.10**	**1.56**	**1.54**	**1.46**	**0.32**	**0.60**	**0.65**

Pr= pre monsoon; Pm= post monsoon; M= monsoon

Table 6. Al normalization and element for major elements in seabed sediments

	Si /Al			Na /Al			K /Al			Ca /Al			Mg /Al			Fe / Al			P / Al		
Station	**Pr**	**M**	**Pm**	**Pr**	**M**	**Pm**	**Pr**	**M**	**Pm**	**Pr**	**M**	**Pm**	**Pr**	**M**	**Pm**	**Pr**	**M**	**Pm**	**Pr**	**M**	**Pm**
S1	3.94	4.04	4.04	0.33	0.36	0.35	0.08	0.16	0.24	0.50	0.54	0.53	0.01	0.02	0.02	0.20	0.21	0.20	0.06	0.10	0.11
S2	4.97	3.76	3.77	0.89	0.55	0.41	0.08	0.12	0.19	0.90	0.61	0.54	0.02	0.01	0.01	0.26	0.19	0.17	0.04	0.07	0.07
S3	3.81	3.64	3.65	0.33	0.42	0.51	0.18	0.18	0.19	0.70	0.60	0.49	0.01	0.01	0.01	0.21	0.19	0.16	0.02	0.06	0.06
S4	4.12	4.23	4.22	0.33	0.70	0.71	0.17	0.14	0.22	0.63	0.72	0.50	0.01	0.03	0.01	0.21	0.23	0.19	0.04	0.08	0.09
S5	2.95	2.69	2.71	0.30	0.24	0.28	0.11	0.07	0.17	0.47	0.47	0.30	0.01	0.02	0.01	0.17	0.16	0.14	0.03	0.05	0.06
S6	2.77	2.93	3.66	0.34	0.27	0.73	0.07	0.12	0.34	0.63	0.50	0.99	0.01	0.02	0.03	0.16	0.17	0.13	0.04	0.07	0.10
S7	3.34	3.40	3.41	0.36	0.61	0.31	0.18	0.11	0.04	0.30	0.25	0.42	0.01	0.01	0.01	0.18	0.17	0.17	0.01	0.04	0.05
S8	4.45	4.33	4.33	0.40	0.56	0.71	0.13	0.12	0.10	0.35	0.72	0.38	0.01	0.02	0.02	0.20	0.21	0.22	0.03	0.07	0.07
S9	3.55	3.62	3.63	0.31	0.33	0.35	0.04	0.14	0.22	0.29	0.36	0.40	0.01	0.01	0.01	0.16	0.18	0.18	0.04	0.07	0.08
S10	2.84	2.65	2.67	0.51	0.34	0.39	0.15	0.10	0.13	0.42	0.25	0.30	0.02	0.01	0.01	0.16	0.14	0.15	0.04	0.06	0.07
S11	2.70	2.77	2.79	0.48	0.32	0.35	0.06	0.11	0.16	0.31	0.27	0.33	0.00	0.01	0.01	0.14	0.15	0.15	0.04	0.07	0.08
S12	3.29	3.15	3.17	0.32	0.32	0.41	0.15	0.12	0.17	0.67	0.31	0.36	0.02	0.01	0.01	0.19	0.17	0.17	0.05	0.08	0.08
Mean	**3.56**	**3.44**	**3.50**	**0.41**	**0.42**	**0.46**	**0.12**	**0.12**	**0.18**	**0.52**	**0.47**	**0.46**	**0.01**	**0.02**	**0.01**	**0.19**	**0.18**	**0.17**	**0.04**	**0.07**	**0.08**

Pr= pre monsoon; Pm= post monsoon; M= monsoon

monsoon. Generally, the concentration of Mn is high in the study area.

The geochemical reactions, which occur in near shore sediments, are mostly controlled by the physico-chemical conditions in the sediment water complex, in particular the redox potential. Hence, the low value of Mn at the riverine side and high value near the lagoonal side are due to the physico-chemical characters of the adjacent rivers and wave action. The low input of river flow, stagnant nature of the water column might control the distribution of Mn in the Creek. Further, the relationship between sediment texture and Mn also indicates the same. The Mn content at the sediment water interface is found to be highly variable in the near shore region. Manganese is very sensitive to variations in redox conditions around +340 mV and is frequently exchanged between the solid and dissolved phase if the environment fluctuates between oxic and anoxic conditions (Blazer, 1982).The total Cr concentration in pre monsoon ranges from 6.00-13.20 mg/kg with an average of 8.19 mg/kg. Monsoon records an average, slightly lower (7.33mg/kg) than pre monsoon. S11, located near the mouth of Muthupet lagoon records a high value of 13.2 mg/kg and S2, close to Vedaranyam records a minimum value of 6 mg/kg during pre monsoon. During post monsoon a maximum and minimum of 84 mg/kg and 3.5 mg/kg are recorded at S4 and S8 respectively. Samples collected during all seasons revealed the same kind of distribution pattern. In general, the concentration of Cr is high near the mouth of the estuary but less at the riverine end (Akkarapallivasal). Generally, these near shore sediments show very minimal concentration of manganese. Globally, the average concentration of Cr in river-borne solids transported in estuaries is relatively higher than that of near shore sediments (Aston and Chester, 1976).

Cu usually occurs in silicates at trace levels, but may precipitate as a major element in some specific sulphides, oxides and it also complexes readily with various organic components. Cu reveals an average of 34.52 mg/kg in pre monsoon, 28.03 mg/kg in monsoon and 24.98 mg/kg in post monsoon respectively. Cu concentration varies from 28.90-41.90 mg/kg in pre monsoon, 20.80-33.70 mg/kg in monsoon and 12.30-34.70 mg/kg in post monsoon. High and low concentrations of 41.9 mg/kg at S7 and 28.9 mg/kg at S2 are observed in pre monsoon where as a high concentration of 33.77 mg/kg at S6 and a low of 20.8 mg/kg at S10 are recorded in monsoon. Post monsoon shows a high of 34.7 mg/kg and a low of 12.3 mg/kg of Cu at S12 and S4 respectively. On an average, pre monsoon records the highest and post monsoon records the lowest. In general, Cu concentration is lesser than the continental crustal averages. Globally, the average concentration of Cu in river-borne solids transported in estuaries is relatively higher (2500 mg/kg) than that of near shore sediments (48 mg/kg) (Aston and Chester 1976). The geochemical reactions, which occur in the near shore sediments, are mostly controlled by the physico-chemical conditions in the sediment water complex, in particular the redox potential.

The average concentration of Ni is 2000 mg/kg in ultramafic rocks, 130 mg/kg in mafic rocks, 4.5 mg/kg in granitic rocks, 17 mg/kg in soils, 18 mg/kg in plant ash, and 1.5 ppb in fresh waters. Its siderophile associations are with Mg and Co in mafic and ultramafic rocks, and Co, Cu and Pb in sulphide deposits. It is present in mafic minerals. Its weathering products are Fe-oxides and nickeliferous silicates. Its aqueous species are $Ni^{2+.}$ Nickel is relatively immobile, limited to co-precipitation with limonite and hydrolysis where pH > 6.5. The distribution of Ni in igneous rocks is, as for other metals, generally closely related to the distribution of Mg and Fe (Rankama and Sahama, 1950). Ni concentrations in the study area record an average value of 33.81 mg/kg in pre monsoon, 32.85 mg/kg in monsoon and 36.55 mg/kg in post monsoon. Ni concentration of 57.5 mg/kg is recorded during pre monsoon at S5 with the lowest concentration of 12.06 mg/kg at S6. Ni concentration is the highest at S5 during all the seasons with the lowest at S11.Only during monsoon, S6 shows the lowest concentration of Ni.

Cobalt is relatively scarce in the earth's crust. The average concentration of Co in ultramafic rocks is 110 mg/kg, in mafic rocks 48 mg/kg, in granitic rocks 1 mg/kg, in soils 10 mg/kg, in plant ash 5 mg/kg, and in fresh water it is 0.1 ppb. Its chalcophile associations are Mg and Ni in mafic and particularly in ultramafic rocks. It is present in mafic minerals. Its weathering products are carbonates and hydroxides, adsorbed and co-precipitated Mn oxides or, to a less extent, Fe

Table 7. Trace elements in the seabed sediments

	Mn mg/kg			Cr mg/kg			Cu mg/kg			Ni mg/kg		
Station	**Pr**	**M**	**Pm**	**Pr**	**M**	**Pm**	**Pr**	**M**	**Pm**	**Pr**	**M**	**Pm**
S1	547.40	531.50	511.60	7.35	6.15	5.55	36.90	29.10	21.70	31.62	34.30	38.00
S2	643.80	510.50	402.30	6.00	5.70	6.15	28.90	23.30	17.40	37.14	38.30	42.00
S3	602.30	525.40	435.20	7.50	6.00	4.20	34.60	27.50	25.00	32.22	30.30	34.00
S4	552.70	870.00	450.00	6.90	6.90	84.00	32.00	26.50	12.30	40.74	41.30	45.00
S5	644.60	738.50	457.10	7.65	9.75	8.85	37.80	29.00	26.10	57.60	57.30	61.00
S6	601.50	769.60	280.60	12.00	8.85	9.45	33.20	33.70	23.60	12.06	27.56	31.26
S7	667.40	451.50	509.50	8.10	9.30	8.70	41.90	32.30	25.60	24.72	30.08	33.78
S8	657.10	547.40	583.70	7.80	7.35	3.45	36.50	32.50	30.80	29.40	27.32	31.02
S9	668.10	552.60	421.20	6.90	6.75	6.45	31.50	25.00	28.90	35.34	35.24	38.94
S10	639.40	563.20	524.10	6.15	6.45	5.70	31.10	20.80	25.50	40.98	32.78	36.48
S11	473.50	457.60	483.60	13.20	7.80	6.30	33.20	23.90	28.20	37.68	13.64	17.34
S12	628.10	531.60	528.50	8.70	6.90	6.60	36.60	32.70	34.70	26.16	26.12	29.82
Mean	**610.49**	**587.45**	**465.62**	**8.19**	**7.33**	**12.95**	**34.52**	**28.03**	**24.98**	**33.81**	**32.85**	**36.55**

	Co mg/kg			Pb mg/kg			Zn mg/kg		
Station	**Pr**	**M**	**Pm**	**Pr**	**M**	**Pm**	**Pr**	**M**	**Pm**
S1	7.50	15.15	23.25	49.26	44.61	41.93	103.30	79.60	54.50
S2	9.75	12.45	15.00	42.28	43.01	43.53	89.80	65.80	48.00
S3	19.80	13.35	6.75	44.82	43.92	41.52	193.90	99.20	44.50
S4	12.45	12.90	5.25	45.61	48.67	37.97	70.90	68.60	43.70
S5	22.35	23.55	21.45	43.41	44.19	41.10	79.40	69.10	55.90
S6	8.85	5.55	25.05	37.52	35.85	44.03	75.90	66.70	47.70
S7	20.70	19.80	12.75	41.87	46.53	47.85	93.90	68.90	56.00
S8	18.15	9.60	14.10	45.35	54.54	41.93	89.30	71.00	84.20
S9	16.05	16.20	22.50	52.62	53.12	50.06	78.00	70.30	60.70
S10	8.85	10.65	15.30	51.92	52.63	47.13	71.50	71.40	73.60
S11	13.50	12.45	15.90	43.29	50.29	49.26	73.20	71.60	72.10
S12	15.45	13.65	14.70	48.51	50.06	47.05	68.70	61.80	65.50
Mean	**14.45**	**13.78**	**16.00**	**45.54**	**47.29**	**44.45**	**90.65**	**72.00**	**58.87**

oxides. Its aqueous species are Co^{2+} and organic complexes. Cobalt is one of the more important trace elements in animal nutrition. Mobility of Co is intermediate, controlled mainly by adsorption and co-precipitation with Fe and Mn oxides. During pre monsoon Co concentration ranges from 7.5 mg/kg to 22.35 mg/kg at S5 the average being 14.45 mg/kg. Monsoon shows a range of 5.55 mg/kg at S6 to 23.55 mg/kg at S5 with an average of 13.78 mg/kg. During post monsoon the high and low concentration of 25.05 mg/kg at S6 and 5.25mg/kg at S4 occurs with an average of 16 mg/kg. There is not much variation in average Co concentration (13.78 to 16 mg/kg) during different seasons.Cobalt levels in surface sediments collected during three seasons and the corresponding average values are listed in Table 7. When compared with the average value of shale (19 mg/kg), Bulk Continental Crustal value (29 mg/kg) (Taylor and McLennan, 1985), and upper continental crustal value (17 mg/kg) (McLennan 2001), cobalt concentration is less in the sediments. The concentrations of cobalt in granites (1 mg/kg), basalts (35 mg/kg), soil (8 mg/kg), limestone (0.1 mg/kg) and sandstone (0.3 mg/kg) (Bowen, 1979), which are the main lithogenic sources for metals in marine and marginal marine sediments, are compared with the results of the study area. The comparison shows that Co concentrations in the samples of the study area are lower than the values of the geological source materials for the marine sediments. This indicates that the concentration of Co present in the sediments of the study area is associated with lithogenic origin with little contribution from external sources. The concentration does not vary much. However, maximum values are observed at the S5. A slight increase is observed during post monsoon.

Pb occurs in the nature as Pb sulphide and it is extremely insoluble, especially under reducing conditions it is readily adsorbed by organic matter. Lead is generally toxic to vegetation and animal life when present in its ionic form. Mobility of Pb is relatively low, restricted by tendency for adsorption on to Mn- and Fe-oxides and insoluble organic matter, but assisted by formation of soluble organic complexes and anion complexes. Its chalcophile associations are Ag in precious metal deposits and Fe, Zn and Cu in many other sulphide deposits and F in rock forming silicates. It is present in mica and potash feldspar. Its weathering products are cerussite, anglesite, and pyromorphite, plumbojarosite over sulphide ores, and Mn- and Fe-oxides and pyromorphite in soils. Its aqueous species are Pb^{2+}, $PbCO_3$, $Pb(OH)^+$, $Pb(OH)_2$, soluble organic matter and complex with Cl^- and HCO_3^-. The average Pb concentration in the study area in 45.54 mg/kg in pre monsoon, 47.29 mg/kg in monsoon, and 44.45 mg/kg in post monsoon. Pb concentration does not vary much during different seasons. During pre monsoon, the high concentration is recorded at S9 (52.62 mg/kg) located in between serthalaikadu and Muthupet lagoon. The lowest concentration (37.52 mg/kg) is shown at S6, serthalaikadu mouth. The high concentration is at S8 (54.54 mg/kg) and the low concentration (35.85mg/kg) is at S6. Post monsoon records a high value at S9 and a low value at S4. When compared with the average value of shale (20 mg/kg) and Bulk Continental Crustal value (8 mg/kg) (Taylor and McLennan, 1985), the lead concentration is higher in the sediments. The concentrations of lead in granites (24 mg/kg), basalts (3 mg/kg), limestone (8 mg/kg), soil (35 mg/kg) and sandstone (10 mg/kg) (Bowen, 1979) were compared with the sediments of the study area. It indicates that the lead concentrations of the samples of the study area are slightly higher than the values of geological source materials mentioned above.

Zinc is an essential trace metal and is an important component for plants and human. Its chalcophile associations are Cu, Pb, Ag, Au, Sb, As and Se in base metals and precious metal deposits, and Mg in some silicates. It is present in mafic minerals. Its weathering products are zinc sulphates, carbonates, hydrated silicates and zinc clay minerals over zinc sulphide ores, Fe^- and Mn^- oxides and organic matter in normal soils. Its aqueous species are variable partition between Zn^{2+}, $Zn(OH)_2$, soluble organic complexes and floating live organisms. The mobility of Zn is moderately high, limited by its tendency to be adsorbed by MnO_2 and by insoluble organic matter (Krauskopf, 1979). The spatial distribution patterns for the 3 periods indicate that there is much variation in the seasonal samples. Zinc concentration in the study area reveals an average of 90.65 mg/kg in pre monsoon, 72mg/kg in monsoon and 58.87 mg/kg in post monsoon. It ranges from 68.7 to 193.90 mg/kg during pre monsoon. During monsoon it ranges from 61.8 to

99.20 mg/kg and during post monsoon from 43.70 to 84.20 mg/kg. The concentration is the lowest during post monsoon season and the highest during pre monsoon season. The concentration is high at S3 except during post monsoon where S8 dominates.Trace element analysis of surface sediments during the three seasons of sampling shows the following trend: Pre monsoon Mn > Zn > Pb > Cu > Ni > Co > Cr ; Monsoon & Post monsoon Mn > Zn > Pb > Ni > Cu > Co > Cr . It is seen that the pattern remains the same for monsoon and postmonsoon seasons.Normalization of trace elements with Al values was done for all samples.The metal/Al ratios and enrichment factors for pre monsoon, monsoon and post monsoon are presented in Tables 8 – 10. The EF close to 1 point out the crustal origin, while those with factor >10 are considered to be of non-crustal source.

Mn/Al ratios in the study area range from 45.19 to 106.44 x 10^{-4} (Average= 73.16 x 10^{-4}) during pre monsoon with the highest at S4. It ranges from 45.09 to 122.91 x 10^{-4} (Average= 68.9 x 10^{-4}) in monsoon with the highest at S4. During post monsoon it ranges from 37.71 to 79.99 x10^{-4} with an average of 54.58 x 10^{-4} (highest at S8). The Mn/Al value is slightly higher during pre monsoon than in succeeding seasons. The ratio is higher than the average continental crustal value and average shale. The enrichment factor for pre monsoon, monsoon and post monsoon ranges from 0.47 to 1.11, 0.47 to 1.28 and 0.39 to 0.83 respectively. Cr/Al ratios vary from 0.62 to 1.26 x10^{-4} with respect to different stations during pre monsoon season with an average of 0.96 x 10^{-4}. It ranges from 0.61 to 1.07 x10^{-4} during monsoon and 0.47 to 11.68 x 10^{-4} during post monsoon with an average of 0.61 x 10^{-4} & 1.66x10^{-4} respectively. Cr/Al records monsoonal minimum and is high during post monsoon. High values are observed at S4 except during monsoon. Enrichment factor for Cr gives an average of 0.09 during pre monsoon, 0.08 in monsoon, and 0.16 in post monsoon.The calculated Cu/Al ratios in the study area record an average of 4.11x10^{-4} (3.15 to 4.86x10^{-4}), 3.29x10^{-4} (1.96 to 4.52x10^{-4}) and 2.90x10^{-4} (1.71 to 4.22x10^{-4}) for pre monsoon, monsoon and post monsoon respectively. The enrichment factors range from 0.62 to 0.95 in pre monsoon, 0.38 to 0.89 in monsoon and 0.34 to 0.83 in post monsoon the mean Cu/Al values of surface sediments collected during the three seasons are lower than the values of upper continental crust confirming the lower enrichment of Cu in the present study. Ni/Al ratios vary from 1.24 to 6.14x10^{-4}, 1.34 to 5.83x10^{-4}, and 1.69 to 6.26x10^{-4} with an average of 4.04x10^{-4}, 3.85x10^{-4}, and 4.31x10^{-4} for pre monsoon, monsoon, and post monsoon respectively. Enrichment factors vary from 0.16 to 0.83, 0.17 to 0.76, and 0.22 to 0.81 in pre monsoon, monsoon and post monsoon respectively. Estimated Co/Al values for different seasons range from 0.90 to 2.57x10^{-4}, 0.59 to 2.29x10^{-4}, and 0.73 to 3.37x10^{-4} for pre monsoon, monsoon and post monsoon respectively. Higher values are observed at S3 (2.57x 10^{-4}), S7 (2.27 x 10^{-4}) and at S6 (3.37 x10^{-4}) during pre monsoon, monsoon and post monsoon with an average of 1.71x10^{-4}, 1.60x10^{-4}, and 0.98x10^{-4} respectively. Enrichment factor ranges from 0.47 to 1.35 in pre monsoon, 0.31 to 1.20 in monsoon and 0.38 to 1.77 in post monsoon.

An estimate of Pb/Al ratios for various seasons shows a variation of 3.84 to 6.99x10^{-4}, 3.80 to 7.59x10^{-4}, and 3.95 to 5.93x10^{-4} respectively for pre monsoon, monsoon and post monsoon the average being 5.44x10^{-4}, 5.53x10^{-4}, and 5.21x10^{-4} . Enrichment factors in the study area record an average of 2.72, 2.77, and 2.61 in pre monsoon, monsoon and post monsoon respectively. Zn/Al ratio in the seasonal samples ranges from 6.99 to 25.01x10^{-4}, 6.66 to 12.56x10^{-4}, and 5.37 to 11.54x10^{-4} with an average of 11.01x10^{-4}, 8.46x10^{-4} and 6.86x10^{-4} in pre monsoon, monsoon, and post monsoon respectively. Enrichment factor shows an overall average of 1.02, 0.78, and 0.64 with a variation of 0.65 to 2.33, 0.62 to 1.16, and 0.5 to 1.07 in pre monsoon, monsoon, and post monsoon respectively. The Zn/Al ratios show positive correlation with Mn/Al and Fe/Al indicating co-precipitation of Zn along with Fe^{-}, Mn and oxy-hydroxides. The mean Zn/Al values of surface sediments collected during sampling periods are higher compared to the values of upper continental crust and average shale, confirming the enrichment of Zn in the study area. Comparison with the enrichment factor of average shale (Calvert and Pedersen, 1993) shows enrichment of Zn in the study area and the range from 1 to 4 indicates anthropogenic input of the element.It is interesting to note that enrichment factor values over the crust in the study area decreases in the following order for trace elements in different seasons:

Table 8. Al normalization and element enrichment factor for trace elements in seabed sediments – Pre monsoon

Station	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
							Pre monsoon							
S1	69.75	0.73	0.94	0.09	4.70	0.92	4.03	0.52	0.96	0.50	6.28	3.14	13.16	1.22
S2	106.44	1.11	0.99	0.10	4.78	0.94	6.14	0.80	1.61	0.85	6.99	3.49	14.85	1.37
S3	78.22	0.81	0.97	0.10	4.49	0.88	4.18	0.54	2.57	1.35	5.82	2.91	25.18	2.33
S4	74.6	0.78	0.93	0.09	4.32	0.85	5.50	0.71	1.68	0.88	6.16	3.08	9.57	0.89
S5	67.15	0.70	0.8	0.08	3.94	0.77	6.00	0.78	2.33	1.23	4.52	2.26	8.27	0.77
S6	61.61	0.64	1.23	0.12	3.40	0.67	1.24	0.16	0.91	0.48	3.84	1.92	7.77	0.72
S7	74.19	0.77	0.9	0.09	4.66	0.91	2.75	0.36	2.30	1.21	4.65	2.33	10.44	0.97
S8	87.44	0.91	1.04	0.10	4.86	0.95	3.91	0.51	2.42	1.27	6.03	3.02	11.88	1.10
S9	75.15	0.78	0.78	0.08	3.54	0.69	3.98	0.52	1.81	0.95	5.92	2.96	8.77	0.81
S10	64.68	0.67	0.62	0.06	3.15	0.62	4.15	0.54	0.90	0.47	5.25	2.63	7.23	0.67
S11	45.19	0.47	1.26	0.12	3.17	0.62	3.60	0.47	1.29	0.68	4.13	2.07	6.99	0.65
S12	73.49	0.76	1.02	0.10	4.28	0.84	3.06	0.40	1.81	0.95	5.68	2.84	8.04	0.74
Mean	**73.16**	**0.76**	**73.16**	**0.09**	**4.11**	**0.81**	**4.04**	**0.53**	**1.71**	**0.90**	**5.44**	**2.72**	**11.01**	**1.02**
Average shale	**96.20**	…..	**10.20**	…..	**5.10**	…..	**7.70**	…..	**1.90**	…..	**2.00**	…..	**10.80**	…..
Continental crust average	**11.54**	…..	**1.21**	…..	**6.68**	…..	**9.11**	…..	**3.04**	…..	**1.52**	…..	**0.85**	…..

Table 9. Al normalization and element enrichment factor for trace elements in seabed sediments – Monsoon

Station	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
Monsoon														
S1	70.7	0.73	0.82	0.08	3.87	0.76	4.56	0.59	2.02	1.06	5.93	2.97	10.59	0.98
S2	65.14	0.68	0.73	0.07	2.97	0.58	4.89	0.63	1.59	0.84	5.49	2.74	8.40	0.78
S3	66.5	0.69	0.76	0.07	3.48	0.68	3.83	0.50	1.69	0.89	5.56	2.78	12.56	1.16
S4	122.91	1.28	0.97	0.10	3.74	0.73	5.83	0.76	1.82	0.96	6.88	3.44	9.69	0.90
S5	71.71	0.75	0.95	0.09	2.82	0.55	5.56	0.72	2.29	1.20	4.29	2.15	6.71	0.62
S6	81.58	0.85	0.94	0.09	3.57	0.70	2.92	0.38	0.59	0.31	3.80	1.90	7.07	0.65
S7	52.1	0.54	1.07	0.10	3.73	0.73	3.47	0.45	2.28	1.20	5.37	2.68	7.95	0.74
S8	76.19	0.79	1.02	0.10	4.52	0.89	3.80	0.49	1.34	0.70	7.59	3.80	9.88	0.92
S9	64.55	0.67	0.79	0.08	2.92	0.57	4.12	0.53	1.89	1.00	6.21	3.10	8.21	0.76
S10	53.05	0.55	0.61	0.06	1.96	0.38	3.09	0.40	1.00	0.53	4.96	2.48	6.73	0.62
S11	45.09	0.47	0.77	0.08	2.36	0.46	1.34	0.17	1.23	0.65	4.96	2.48	7.06	0.65
S12	57.27	0.60	0.74	0.07	3.52	0.69	2.81	0.37	1.47	0.77	5.39	2.70	6.66	0.62
Mean	**68.9**	**0.72**	**0.85**	**0.08**	**3.29**	**0.64**	**3.85**	**0.50**	**1.60**	**0.84**	**5.53**	**2.77**	**8.46**	**0.78**
Average shale	**96.20**	**…**	**10.20**	**…**	**5.10**	**…**	**7.70**	**…**	**1.90**	**…**	**2.00**	**…**	**10.80**	**…**
Continental crustal average	**11.54**	**…**	**1.21**	**…**	**6.68**	**…**	**9.11**	**…**	**3.04**	**…**	**1.52**	**…**	**0.85**	**…**

Table 10. Al normalization and element enrichment factor for trace elements in seabed sediments - Post monsoon

Station	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
Post Monsoon														
S1	67.04	0.70	0.73	0.07	2.84	0.56	4.98	0.65	3.05	1.60	5.49	2.75	7.14	0.66
S2	50.6	0.53	0.77	0.08	2.19	0.43	5.28	0.69	1.89	0.99	5.48	2.74	6.04	0.56
S3	54.3	0.56	0.52	0.05	3.12	0.61	4.24	0.55	0.84	0.44	5.18	2.59	5.55	0.51
S4	62.57	0.65	11.68	1.15	1.71	0.34	6.26	0.81	0.73	0.38	5.28	2.64	6.08	0.56
S5	43.9	0.46	0.85	0.08	2.51	0.49	5.86	0.76	2.06	1.08	3.95	1.97	5.37	0.50
S6	37.77	0.39	1.27	0.12	3.18	0.62	4.21	0.55	3.37	1.77	5.93	2.96	6.42	0.59
S7	58.03	0.60	0.99	0.10	2.92	0.57	3.85	0.50	1.45	0.76	5.45	2.73	6.38	0.59
S8	79.99	0.83	0.47	0.05	4.22	0.83	4.25	0.55	1.93	1.02	5.75	2.87	11.54	1.07
S9	48.56	0.50	0.74	0.07	3.33	0.65	4.49	0.58	2.59	1.37	5.77	2.89	7.00	0.65
S10	48.85	0.51	0.53	0.05	2.38	0.47	3.40	0.44	1.43	0.75	4.39	2.20	6.86	0.64
S11	47.13	0.49	0.61	0.06	2.75	0.54	1.69	0.22	1.55	0.82	4.80	2.40	7.03	0.65
S12	56.25	0.58	0.7	0.07	3.69	0.72	3.17	0.41	1.56	0.82	5.01	2.50	6.97	0.65
Mean	**54.58**	**0.56**	**1.66**	**0.16**	**2.90**	**0.57**	**4.31**	**0.55**	**1.87**	**0.98**	**5.21**	**2.60**	**6.86**	**0.64**
Average shale	**96.20**	**…**	**10.20**	**…**	**5.10**	**…**	**7.70**	**…**	**1.90**	**…**	**2.00**	**…**	**10.80**	**…**
Continental crustal average	**11.54**	**…**	**1.21**	**…**	**6.68**	**…**	**9.11**	**…**	**3.04**	**…**	**1.52**	**…**	**0.85**	**…**

Pre monsoon Pb > Zn > Co > Cu > Mn > Ni >Cr
Monsoon Pb > Co > Zn > Mn > Cu > Ni >Cr
Post monsoon Pb > Co >Zn > Cu > Mn > Ni >Cr

Manganese concentration, however, does not show any relationship with coarse fraction, fine fraction, organic matter and $CaCO_3$.The lithophile associations of Mn are Mg and Fe in silicates, under mafic minerals. In the present study, Mn does not show any relationship with Fe and Mg. Hence, the lithogenic contribution of Mn cannot be estimated because of its modification due to contamination from point and nonpoint sources. However, when compared with the average value of shale (850 mg/kg) and Bulk Continental Crustal value (1400 mg/kg) (Taylor and McLennan 1985), which are considered to be the main baseline for near shore sediments, the manganese concentration is less in the study area. The results of trace metals analysis are compared with those in other coastal regions around the world (Table 11).The major oxide data for surface sediments are plotted (Fig. 2). in Al_2O_3–CaO* 1 Na_2O–K_2O (A–CN–K) compositional space (molecular proportions). In the entire sediments plot 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.,* 1996) (Fig. 3). Paleo-weathering conditions can also be determined with the help of a K_2O–Fe_2O3–Al_2O_3 ternary diagram (Wronkiewicz and Condie, 1989).The present study in comparison to the CIA of granite, typical illite, montmorillonite, average shale and kaolinite (ranges from Nesbitt and Young, 1982). Note that CIA for kaolinite is 100. CIA values for the sediments of the present study vary between 21 to 45 for pre monsoon, post monsoon and monsoon samples (Fig. 4).

CONCLUSION

The mouth of the creek is dominated by sand particles, which is due to the accretion nature of the coastal area. The fine nature of the sediment in the middle of the study area Kodikarai to Serthalaikadu creek is due to both estuarine processes and human activities. The mangroves present in the study area promote decomposition of organic matter by microbial activities, which in turn increase the fine fraction of the sediments. The low values of carbonate during sampling seasons in the middle of the shelf are due to the nature of the substratum. The major sources of carbonate materials for the sediments in the creek are shell fragments and calcareous tests of organisms. It is also due to dilution of biogenic calcite by detrital material in the sediments.The high organic carbon content in the sediments of the riverine part of the creek is due to fine nature of the sediments and high rate of sedimentation. The association of sand particles with $CaCO_3$ indicates the major contribution of shell fragments to the sand fraction. The strong positive correlation between mud sediments and organic matter is due to the terrigenous nature of the latter. There are no significant differences in the characteristics of sediment texture, $CaCO_3$ and OC contents during the different seasons. Seasonal variations of the major elements in the sea bed sediments are less. The order of major elements concentration during the seasons can be summarized as Si > Al > Ca > Na > K > Fe > P > Mg The order of the elements concentration remains same during all the seasons.

The concentration of Mn is high near the mouth of the estuary but less at the riverine end (Akkarapallivasal). The highly inconsistent Mn contents in the surface sediments of the present study upholds the idea that Mn-oxy-hydroxide flocs are transported laterally during saline bottom water inflow and deposited in quiescent parts of the estuary. Ni concentration is the highest at S5 during all the seasons with the lowest at S11. Lead concentration in the study area does not vary much during different seasons. When compared to the CCV, the lead concentration is more in the study area. The zinc concentration is highest during pre monsoon season and lowest during post monsoon. The distribution pattern of the elements during the different seasons is summarized as Pb > Zn > Co > Cu > Mn > Ni > Cr for Pre monsoon, Pb > Co > Zn > Mn > Cu > Ni > Cr for Monsoon and Pb > Co > Zn > Cu > Mn > Ni > Cr for Post monsoon. Major oxide geochemistry indicates a homogenous and un-weathered source for the sediments of the present study areas. Studies on paleo weathering indicate the source for the sediments in the study area are charnockite and tonalitic gneisses. Pre monsoon, monsoon, post monsoon samples show a relatively very low degree of alteration in sediments.

Table 11. Comparison of trace metals in sediments with various coastal regions around the world and southeast coast of India

Study areas*	Fe	Mn	Cr	Cu	Ni	Co	Pb	Zn
1	0.4-2.84	53–655	15–186	7.0–27	19–76	21–56	83–225	31–260
2	–	–	74–1480	14–937	16–134	–	19–578	54–2880
3	1.92	–	–	7.0	12	7.6	17	33
4	3.10	530	61	15	24	12	20	65
5	3.77	1098	77.3	53.47	32.63	–	50.68	322
6	3.30	410	155	190	28	8	140	250
7	3.75	–	231.5	112	34.7	–	135	176
8	–	700	87	25	36	14	21	84
9	1.26	305	177	57	24	15	16	73
10	0.8-3.18	148-329	61-120	30-62	33-55	9.2-19	11-18.5	17-35
11	2.5	431.5	75	24.81	34.27	8.85	18.72	58.53
This study (Average)	1.25	544.52	9.49	29.17	34.40	14.74	45.76	73.84

All elements are in lg-1, except Fe in %

*Study areas: (1) Gulf of Aqaba (Red Sea)–Abu-Hilal (1987); (2) Palos Verdes Peninsula, Southern California–Hershelman et al. (1981); (3)Halifax Bay–Knauer (1977); (4) China Shelf Sea–Yiyang and Ming-cai (1992); (5) Tokyo Bay–Fukushima et al. 1992; (6) Narragansett Bay–Goldberg et al. (1977); (7) Boston Harbor–Bothner et al. (1998); (8) Gulf of St.Lawerence–Loring (1978, 1979); (9) Tuticorin coast, Gulf ofMannar (Jonathan et al. 2004); (10) Chennai coast, southeast coast ofIndia–Thangadurai et al. (2005): (11)Northern part of Point calimere coast, southeast coast ofIndia–Stephen pichaimani et al. (2007)

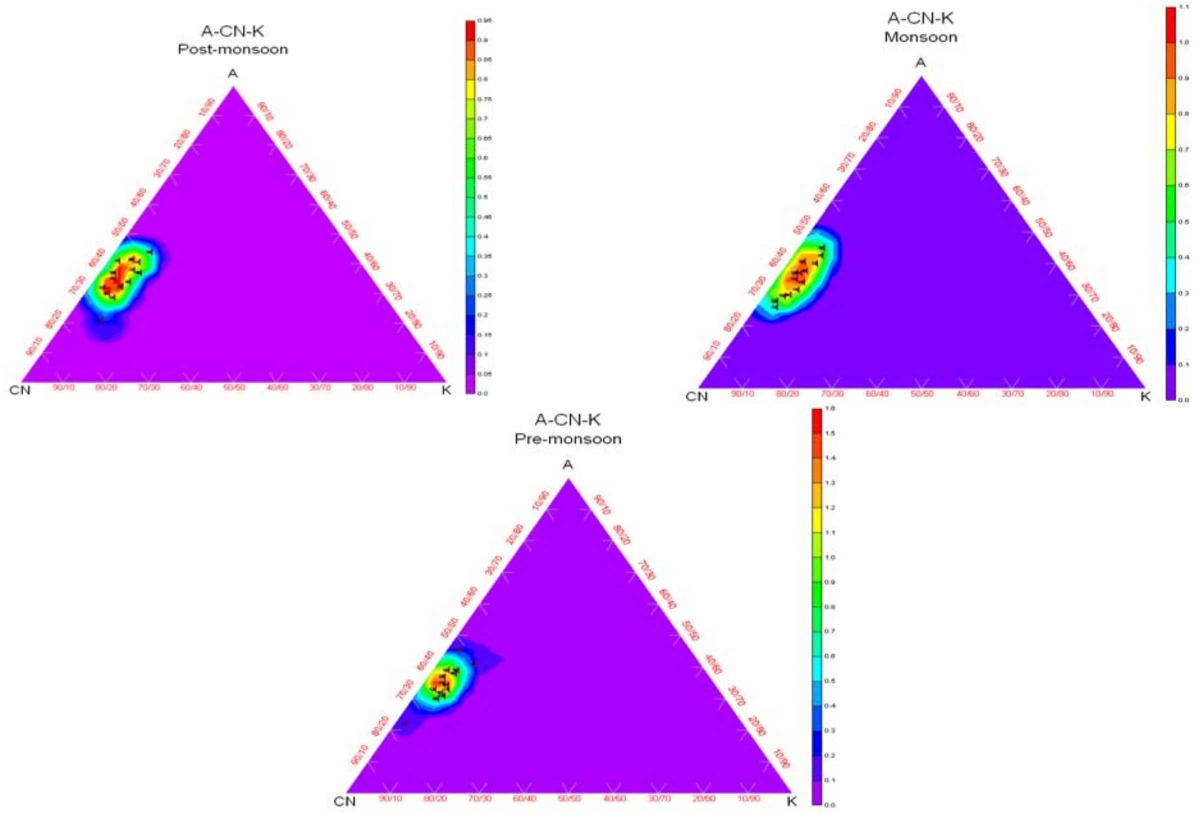

Fig. 2. The major oxide data for Seabed sediments are plotted in Al_2O_3–(CaO^* 1 Na_2O)–K_2O (A–CN–K) compositional space (molecular proportions)

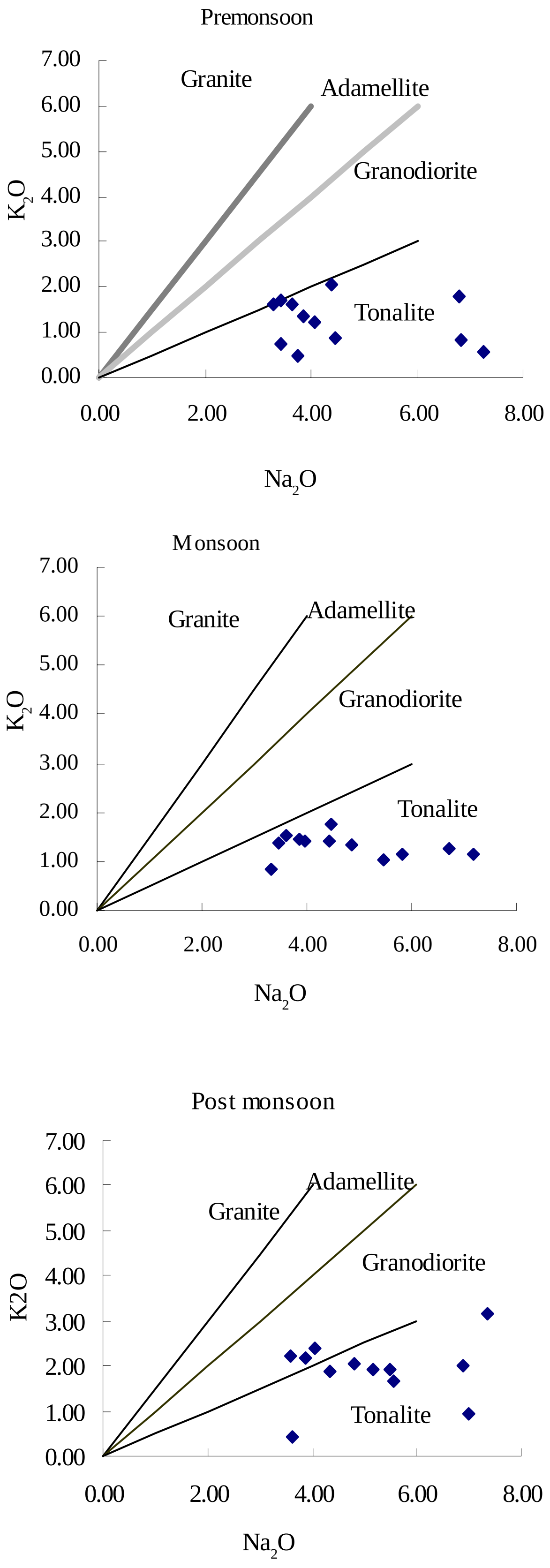

Fig. 3. Variation diagram between Na_2O and K_2O for Seabed sediments

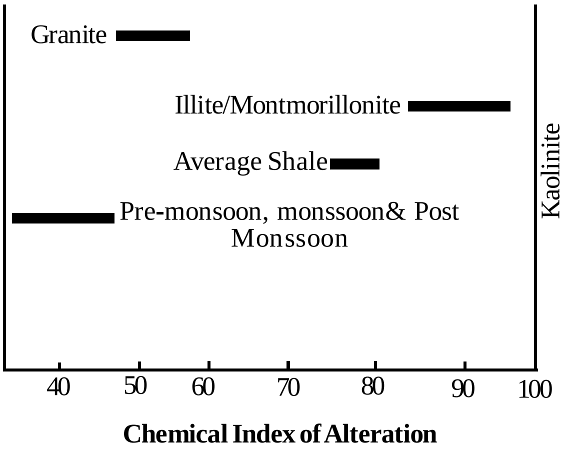

Fig. 4. Comparison of CIA of Vedaranyam with other geological materials

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