Geochemical variations of major and trace elements in recent sediments, off the Gulf of Mannar, the southeast coast of India

M.P. Jonathan · V. Ram-Mohan · S. Srinivasalu

Abstract The Gulf of Mannar along the Tuticorin coast is a coral base of the southeast coast of India. To obtain a preliminary view of its environmental conditions, geochemical distribution of major elements (Si, Al, Fe, Ca, Mg, Na, K, P), trace elements (Mn, Cr, Cu, Ni, Co, Pb, Zn, Cd) and acid leachable elements (Fe, Mn, Cr, Cu, Ni, Co, Pb, Zn, Cd) were analyzed in surface sediment samples from two seasons. Geochemical fractionation confirmed the lithogenic origin of metals, which were mainly associated with the detrital phase. The sediments in the gulf are sandy with abundant calcareous debris, which controls the distribution of total and acid leachable elements. Enrichment factors relative to crust vary by a magnitude of two to three and the presence of trace metals indicates the input of Cr, Pb, Cd, Cu and Zn in both forms through industrial activities. Factor analysis supports the above observation with higher loadings on acid leachable elements and its association with $CaCO_3$. The increase in concentration of trace metals (Cr, Pb, Cd, Cu, Co, Ni, Zn) along the Gulf of Mannar indicates that the area has been contaminated by the input from riverine sources and the industries nearby. The present study indicates that other sources should be evaluated in the long-term monitoring program.

Keywords Tuticorin · Surface sediments · Geochemistry · Trace metals · Anthropogenic · Gulf of Mannar · India

Received: 3 September 2002 / Accepted: 25 August 2003
Published online: 29 October 2003
© Springer-Verlag 2003

M.P. Jonathan (✉) · V. Ram-Mohan · S. Srinivasalu
School of Earth and Atmospheric Sciences, Department of Geology,
University of Madras, Guindy Campus, 600025 Chennai, India
E-mail: mp_jonathan7@yahoo.com
Tel.: +91-44-22350344
Fax: +91-44-22350344

Introduction

Geochemical studies of surface sediments along the coastal zone have been extended in the last few decades due to the growing awareness of coastal pollution and its impact on the ecosystem. The sediments at the sea bottom play an important role in the pollution scheme of a coastal ecosystem, as they are less susceptible to movement than the water column. When the effluent loaded water meets the coastal zone, various physico-chemical reactions take place and a large part of the pollutant, in one form or other, settles down, or is adsorbed by the oceanic sediments depending upon the physico-chemical conditions. In the past few years, there have been numerous instances of man-induced metal contamination to inland and coastal sediments. Once the metals are released to the environment, they are transferred to the sediments through adsorption onto suspended matter and subsequent sedimentation (Hart 1982). The adsorption and sedimentation processes of metals mainly depend on the composition including grain size, carbonate content, level of organic matter, Fe-Mn oxyhydroxides, etc. According to Oakley and others (1980), trace metals in estuarine and marine sediments are partitioned between different phases depending on the amount of each phase and the strength of adsorption. The bioavailability of trace elements in marine sediments, however, depends in part on the mineral phase on which the elements are bound (Bryan and Langston 1992). The geochemical cycle of wastes from various sources discharged in the coastal environment is determined to a large degree by their interaction with sediments. As a result, sediments act as integrators and amplifiers of concentration of many elements in the waters, which pass over and transport them and play a vital role in the shallow coastal areas.

Thus, coastal marine sediments serve as an ultimate sink for metals discharged into the aquatic environment (Luoma and Bryan 1981; Hornberger and others 1999). It is therefore, important to understand how anthropogenic activities change the concentrations of potentially toxic metals and thereby affect benthic organisms. Though the Gulf of Mannar off the southeast coast of India is declared as a bio-reserve, geochemical characters of bulk sediments in the inner shelf of the gulf are lacking. This study will provide the first, detailed comprehensive account of the major and trace element geochemistry of sediments.

DOI 10.1007/s00254-003-0898-7

Previous studies

Studies of the inner shelf sediments have revealed that the areas of environmental stress caused by anthropogenic activities are contaminated with heavy metals some of which are toxic. Based on examination of the Namibian shelf sediments, major and trace element geochemistry reflects the complex intermixture of several sedimentary components of minor metal enrichments (Calvert and Price 1983). Boston harbor and San Francisco sediments have been adversely affected by domestic and industrial anthropogenic inputs from their associated population centers (White 1972; Fitzgerald 1980; Van Geen and Luoma 1999a). Extensive study on the geochemical characteristics of surface sediments of Halifax harbor revealed that heavy metals have accumulated over a period of time and they reflect the changes in industrial activity, urban growth, changes in the use of metals in paints and domestic and industrial chemicals (Buckley and others 1995). Results of surface sediment analysis for major and trace elements from fifteen Japanese coastal sites recorded higher concentrations of heavy metals than from open seas (Yiyang and others 1988). Detailed study on the surface sediments and mineralogical composition of Sulu Sea and South China sea revealed that the sediments are carbonate rich and the compositional variability of the sediments is controlled to some extent by variations in sediment supply from adjacent land mass (Calvert and others 1993). Taliadouri and Varnavas (1995) observed an increase in trace metal concentration in surface sediments from Thermaikos Gulf, mainly attributable to sewage outfall, the industrial zone and the river input.

Partition of total element concentrations into their non-detrital and detrital contributions allows certain deductions to be made regarding the site of the elements as well as their sources and pathways by which the metals have entered the marine environment. The heavy metals in detritus elements represent that part of the total concentration held in the lattice of silicate minerals, discrete oxide, sulfide minerals and compounds (Hirst 1962; Loring and Nota 1968; Loring 1976). The acid soluble contribution represents some proportion of the element that was initially leached from its source rock or released in dissolved form from industrial sources and incorporated during weathering, transportation and deposition into the sediments.

Studies on the Indian shelf region are limited when compared to other regions of the world. Considerable work has been carried out on the sediments of the west coast of India by Gogate and others (1976), Paropkari and others (1978) and Bhosle and others (1978), whereas, the inner shelf of the Bay of Bengal off the east coast has received very much less attention. Overall, the geochemical characters of surface sediments of the Bay of Bengal, indicate that the metal distribution is mainly controlled by their sediment texture and studies along the Visakhapatnam coast (Satyanaryana and others 1985; Raman 1995), Puri to Port Novo (Mohapatra and others 1992), central east coast of India (Rao and Sarma 1993) and the Madras coast (Pragatheeswaran and others 1986) were limited to the northern part of the east coast of India. The southern part of the east coast of India from Madras is practically not monitored, even though, it is heavily industrialized along the coastal stretch.

Study area

The Gulf of Mannar is a transitional zone between the Arabian Sea and Indian Ocean proper and is connected with the Bay of Bengal through a shallow sill, the Palk Strait. The area under investigation off Tuticorin in the Gulf of Mannar presents great interest because it is an industrial belt consisting of many major industries involved in the production of chemicals, petrochemicals and plastics. In addition, a major harbor, thermal power plant, heavy water plant and human activities from around Tuticorin to Tiruchendur have altered the ecosystem prominently. The gulf consists of several coral reef islands and of the 21 coral islands present along the coastline between Tuticorin and Pamban, most of them are close (2 to 18 km) to the main land (Fig. 1). In the Gulf of Mannar, pearl oysters known as pearl banks lie about 12 to 20 km from the coast at a depth of 15 to 25 m. As per the overall industrial scenario, many large and small-scale industries have developed along the coastal zone in recent years.

Geologic setting

The area investigated forms the southern part of the South Indian Granulite facies terrain, which includes part of Madurai Block (MB) and the Kerala Khondalite Belt (KKB). The southern part of MB is represented by charnockites in the western part and gneisses in the eastern part which are inter-banded with supracrustals chiefly of meta-sedimentary sequences mainly made up of quartzite, carbonate and metapelite with a minor metabolic component. KKB is bounded by the Cardamon Hills in the north and the Nagerkoil Charnockite Massif in the south, which consists of high-grade supracrustals. The MB and KKB, which are separated by the Achankoil Shear Zone (AKSZ), are mostly similar in geochronologic characteristics (Santhosh and others 1992; Harris and others 1994). A narrow strip of Cenozoic sedimentary formations about 10 to 12 km wide occurs all along the coast, comprising Tertiary carbonate and Holocene sediments (Fig. 1).

The Gulf of Mannar receives riverine input through a number of small rivers and streams of which the Tambraparni River is the major source. The minor rivers are the Gudar, Vaipar, Karamaniar and Nambiyar, which flow during monsoon periods. Garnet, ilmenite, zircon, magnetite, rutile and clayey sand are observed along the coastal dunes and at the mouths of these rivers.

The catchments of these rivers and streams draining the area comprise crystalline rocks of Precambrian age and Holocene to Recent sedimentary formations on the coastal margins. The physiographical features present a raised beach with a sand bar parallel to the coastline north of Tiruchendur. Beach, coastal ridges, cliff coastline, sand dunes, beach terraces, spits, salt marshes and teri sands are some of the geomorphic features observed in the study area.

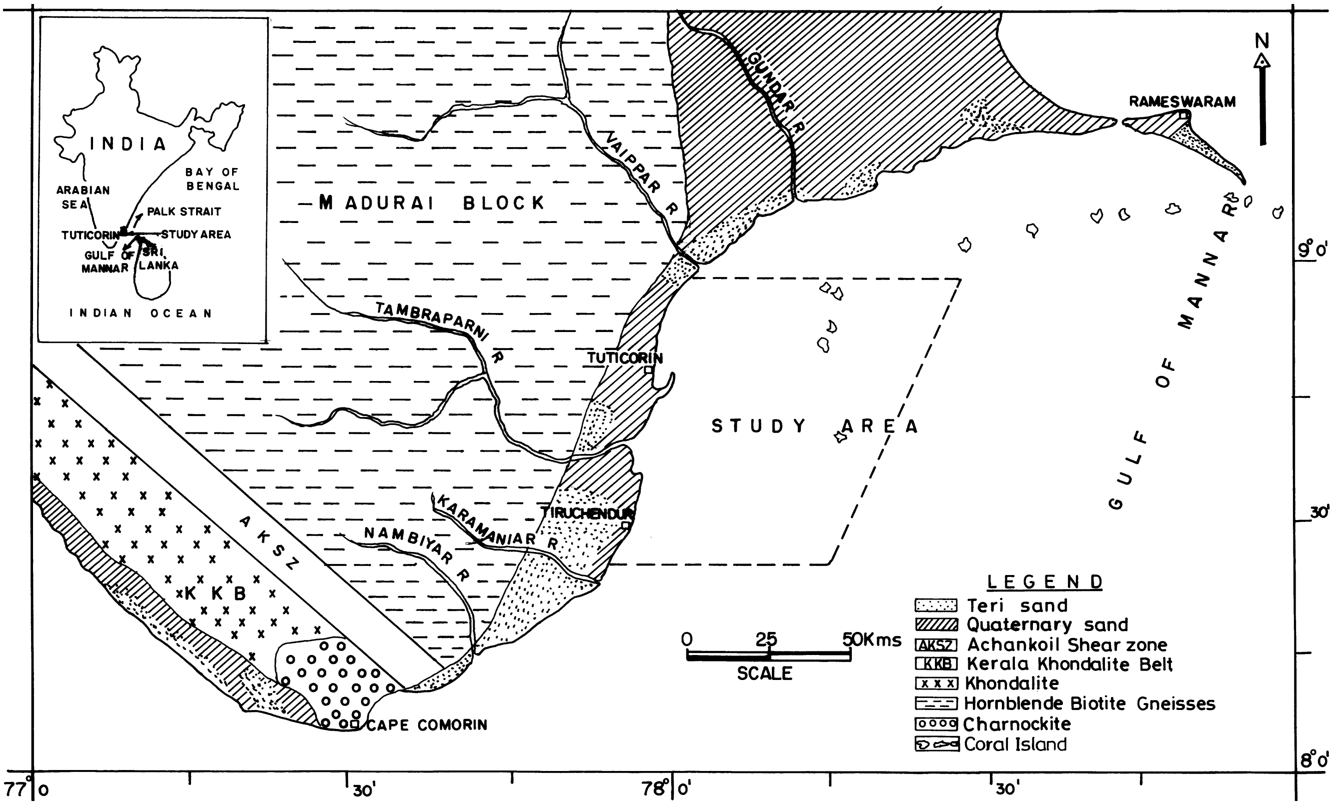

Fig. 1
Geological map of the study area and its adjoining areas, southeast coast of India

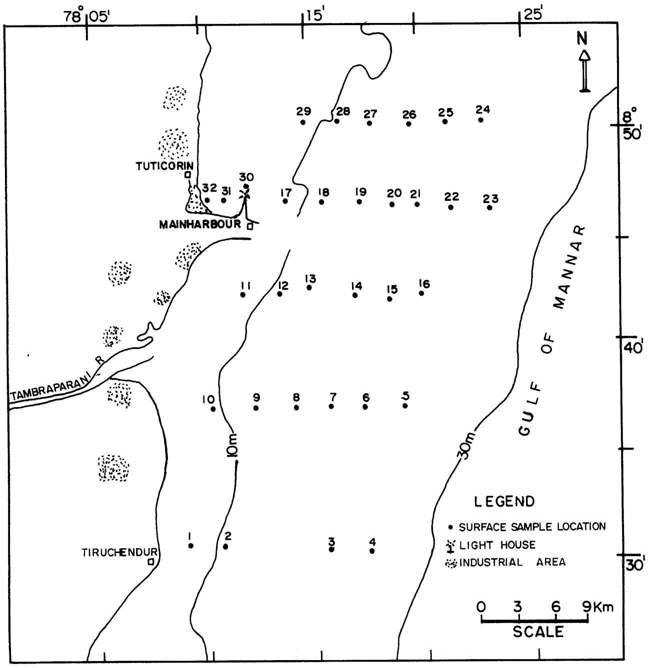

Fig. 2
Surface sample locations in the Gulf of Mannar

Materials and methods

Surface sediment samples were collected in two different oceanographic cruises during 1996 and 1997 and 32 surface sediment samples were collected in each season (64 samples) and only the averages of all major and trace metal concentrations are presented in this paper (Fig. 2). The sediment samples were collected using the Petersen grab and the samples were analyzed for sediment texture, major and trace metals. Textural studies on the sediments were performed for sand, silt and clay distributions (Ingram 1970). Determination of calcium carbonate ($CaCO_3$) was performed following the procedure of Loring and Rantala (1992). Organic carbon (OC) was determined by exothermic heating and oxidation with potassium dichromate and concentrated H_2SO_4, followed by titration of excess dichromate, with 0.5 N ferrous ammonium sulfate solution (Gaudette and others 1974). Major element analysis of Si, Al, Fe, Na, K, Ca, Mg and P was determined after preliminary treatment and decomposition of sediments following the procedure of Loring and Rantala (1992). Si and Al were determined by fusing the powdered sample with NaOH in a nickel crucible; all other major elements were determined by total decomposition method with HF, HNO_3 and HCl in a sealed Teflon vessel (Teflon bomb). Determination of acetic acid leachable metals was preferred in the present study as it is one of the weakest chemical treatments that can effectively remove the weakly bound part of the total metal concentrations in the sediments (Loring and Rantala 1988). Further, it leaves the silicate lattices intact and does not attack the resistant iron and manganese materials or organic compounds (Hirst 1962; Agemian and Chau 1976; Luoma and Jenne 1976). Two grams of dry sediment samples were used for acetic acid leaching of sediments where 25% v/v HOAc was added and separated for acid leachable trace element analysis (Loring and Rantala 1992).

Finally, the total and acid leachable trace elements (Mn, Cr, Cu, Ni, Co, Pb, Zn, Cd), were analyzed by flame AAS (Varian Spectr AA 200) equipped with a deuterium background corrector. The flame was employed, except in the instance of Cd, which requires the use of a graphite furnace because of its much lower concentration. Suitable internal chemical standards (Merck Chemicals, Germany) were used to calibrate the instrument. All the reagents used were analytical grade of high purity. Reference materials MAG-1 from National Research Council of Canada were used for the present study to ensure the accuracy of the analysis and our values lay within 1.5–3.4% from the values reported by Govindaraju (1989).

To establish the natural processes and the source of pollution (Bridgman 1992), R-mode factor analysis with rotation was applied to the whole data set. Factor analysis is a useful explanatory tool in multi-variate stastical analysis, and it can be applied to discover and interpret relations among variables (samples) or to test hypotheses. The general purpose of factor analysis is to determine a way of condensing the information in a number of original variables into a smaller set of new composite dimensions with minimum loss of information. An important concept in factor analysis is the rotation of factors. Several different approaches (Varimax, Quatrimax) are available for performing factor rotations. The Varimax rotation of Kaiser (1958) has proved to be very successful as an analytic approach in many cases and has, therefore, been applied for the present study.

Results and discussion

Textural characteristics of sediments

The sediments of the Gulf of Mannar surrounding Tuticorin coast consist of calcareous sand and gravels, derived from coral/algal reefs and benthic macro fauna and other terrigenous detritus depending on the local source. The sediments in the present study area are a heterogeneous mixture mainly composed of quartz sand, biogenic carbonate and shell fragments. The sediments collected in the present study range from sand to sandy clay silt (Table 1), with 11 to 91% of sand, 7 to 75% of silt and 1 to 23% of clay. Clay silt sediments containing 10–23% clay were observed

Table 1
Sample locations, textural characters, calcium carbonate and organic carbon distribution in surface sediments off the Gulf of Mannar

Sample number	Latitude	Longitude	Sand (%)	Silt (%)	Clay (%)	Sediment type	$CaCO_3$(%)	Org.C (%)
1	8°30′15″	78°09′48″	87	11	2	Sand	75.00	0.54
2	8°30′23″	78°11′20″	91	7	2	Sand	63.10	0.67
3	8°30′17″	78°16′47″	56	36	8	Silty sand	36.96	1.70
4	8°30′02″	78°17′28″	60	38	2	Silty sand	45.80	0.69
5	8°37′41″	78°18′15″	52	43	5	Silty sand	56.46	0.84
6	8°37′48″	78°16′13″	45	51	4	Silty sand	55.70	0.88
7	8°37′38″	78°16′58″	59	39	2	Silty sand	44.73	0.38
8	8°37′45″	78°13′18″	86	13	1	Sand	52.46	0.30
9	8°37′45″	78°11′43″	85	13	2	Sand	28.63	0.33
10	8°37′46″	78°10′02″	15	67	18	Sandy clay silt	47.65	2.22
11	8°42′47″	78°11′48″	15	75	10	Sand	53.22	1.68
12	8°42′48″	78°13′45″	88	10	2	Sand	16.03	0.50
13	8°42′49″	78°15′01″	84	14	2	Sand	30.85	0.25
14	8°42′47″	78°16′30″	75	23	2	Silty sand	49.31	0.51
15	8°42′45″	78°18′15″	73	23	4	Silty sand	39.80	0.21
16	8°42′38″	78°19′42″	85	10	5	Sand	36.04	0.34
17	8°47′19″	78°13′30″	86	12	2	Sand	27.55	0.08
18	8°47′20″	78°15′02″	83	15	2	Sand	39.07	0.30
19	8°47′17″	78°16′26″	84	14	2	Sand	29.47	0.26
20	8°47′20″	78°18′01″	57	40	3	Silty sand	15.57	0.33
21	8°47′21″	78°19′33″	53	44	3	Silty sand	16.58	0.21
22	8°47′19″	78°21′18″	47	48	5	Sandy silt	47.93	0.59
23	8°47′15″	78°22′48″	57	41	2	Silty sand	36.16	0.91
24	8°50′44″	78°22′35″	56	42	2	Silty sand	47.43	0.63
25	8°50′40″	78°21′01″	85	14	1	Sand	32.68	0.34
26	8°50′45″	78°19′21″	85	14	1	Sand	38.59	0.38
27	8°50′47″	78°17′45″	91	7	2	Sand	28.02	0.50
28	8°50′38″	78°16′15″	55	39	6	Silty sand	21.32	1.37
29	8°50′41″	78°14′40″	14	68	18	Clay silt	14.78	1.85
30	8°47′32″	74°11′47″	17	68	15	Sandy clay silt	22.64	1.86
31	8°46′30″	78°11′02″	14	69	17	Clay silt	6.78	3.63
32	8°47′36″	78°10′08″	11	66	23	Clay silt	2.79	4.14
Mean	–	–	61	34	5	–	36.22	0.92

in the near shore regions (stations 29–32) and near Tambraparni River estuary (stations 10 and 11). Sand dominated regions were observed in the entire study area with 45 to 91% and, in the northern part, silty sand with 40–48% of silt was observed at stations 20–24 which are opposite to the main harbor. The silty nature could be due to the formation of a spit and construction of a jetty for the Tuticorin harbor, which shelters the area from the action of currents, which transport the sediments. The increase in sand content in the entire study area indicates that currents from the abrasion zone transport the finer sediments once they reach the coastal zone (Szefer and Skwarzec 1988). Moreover, the coarse grained nature of the coastal region reflects the turbulent conditions of deposition (Francois 1988). However, increase in fine sediments along the coast in certain samples is an indication of fresh water input with finer particles that settle to the bottom when current and wind speeds reduce (Thomson-Becker and Luoma 1985).

Calcium carbonate and organic carbon

Distribution of $CaCO_3$ in the gulf indicates a calcium carbonate range from 2.79–75%. Accumulation of $CaCO_3$ was observed in the entire southern part of the study area (stations 1–19). The high terrigenous input of $CaCO_3$ from a land source is indicated by 47–53% of $CaCO_3$ at the two estuarine stations 10 and 11. The high $CaCO_3$ values in the southern part indicate that the major source of carbonate materials is the shell fragments and input from adjacent land mass where Tertiary limestones and calcareous sandstones extend in the southern region (Ray and others 1990; Armstrong Altrin Sam 1998). A small, closely spaced group of samples in the northern transect forms a separate trend of low $CaCO_3$ from 2.79 to 22.64% (stations 28–32). The very low values of $CaCO_3$ in the northern part are attributed to the fine nature of sediments, which do not support biogenic activity. From stations 20–27, low (15.57%) and high (47.93%) values were observed at alternate stations with increase in sand and the flow of wastewater from coastal industries, which brings the noncarbonate materials, and gives the low and high values. Relatively high values of carbonates in the southern part may be due to the strong currents leading to nondeposition of terrigenous materials (Rao 1978).

Distribution of organic carbon in the samples is influenced to a significant degree by the diluting effect of $CaCO_3$ present in the study area. The distributions of OC shows that the concentrations in the samples of the estuarine region (1.68–2.22%) and the northern transect (1.37–4.14%) are high where, $CaCO_3$ contents are lower and the dominance of mud also indicates that they are attached to finer particles. Data from most of the samples fall into a single relationship, but during periods when sediment was finest in certain samples, the substantial variation in organic carbon concentration is evident. The high inputs of terrigenous material from the adjacent land mass and industrial effluents nearby have increased the OC values

Table 2
Average concentration of major elements (%) in surface sediments off the Gulf of Mannar

Sample number	Si (%)	Al (%)	Na (%)	K (%)	Ca (%)	Mg (%)	P (%)
1	26.77	1.63	0.82	0.17	15.49	5.91	0.49
2	26.76	1.35	0.67	0.17	14.58	4.71	0.38
3	28.29	1.92	1.11	0.25	12.92	6.65	0.32
4	28.67	2.03	0.74	0.28	11.04	8.14	0.32
5	27.25	3.08	1.04	0.38	12.09	5.83	0.38
6	25.96	3.99	1.19	0.46	13.67	6.13	0.49
7	27.79	5.92	0.96	0.92	7.23	6.42	0.39
8	27.21	5.40	0.77	1.29	5.47	8.31	0.27
9	31.26	5.98	0.96	1.25	2.43	3.26	0.21
10	23.53	8.49	1.56	1.35	7.17	7.79	0.41
11	27.16	4.92	0.90	1.44	7.41	6.68	0.35
12	32.04	4.82	0.93	1.58	4.13	4.07	0.15
13	30.63	4.62	1.15	1.58	5.71	4.46	0.13
14	30.90	5.94	0.64	1.41	4.32	3.86	0.19
15	32.78	5.16	1.34	1.74	2.19	4.71	0.15
16	32.38	4.82	0.64	1.37	3.40	4.29	0.13
17	35.02	3.77	0.45	0.55	1.04	3.43	0.11
18	32.79	3.74	0.57	0.91	4.44	4.28	0.17
19	32.12	5.95	0.67	0.91	2.31	5.19	0.17
20	32.16	4.73	0.67	0.85	3.53	4.97	0.19
21	28.74	8.04	1.15	1.63	1.64	5.40	0.17
22	29.49	4.78	0.87	0.83	7.05	5.40	0.24
23	27.17	4.94	0.84	0.67	11.12	4.46	0.33
24	27.49	7.30	1.33	1.33	7.96	4.63	0.24
25	28.82	6.35	0.82	0.83	4.44	6.51	0.26
26	29.43	4.80	1.15	0.85	9.11	4.46	0.24
27	29.03	4.89	0.97	0.85	5.59	6.86	0.25
28	30.11	4.45	0.82	0.77	8.26	4.20	0.27
29	26.55	7.52	0.59	0.77	1.83	5.83	0.41
30	24.14	5.97	0.72	0.78	8.75	3.56	0.17
31	25.18	9.55	2.98	1.30	0.24	1.12	0.57
32	20.54	15.79	2.79	1.07	2.19	3.43	0.58
Mean	28.69	5.39	1.03	0.95	6.52	5.15	0.29

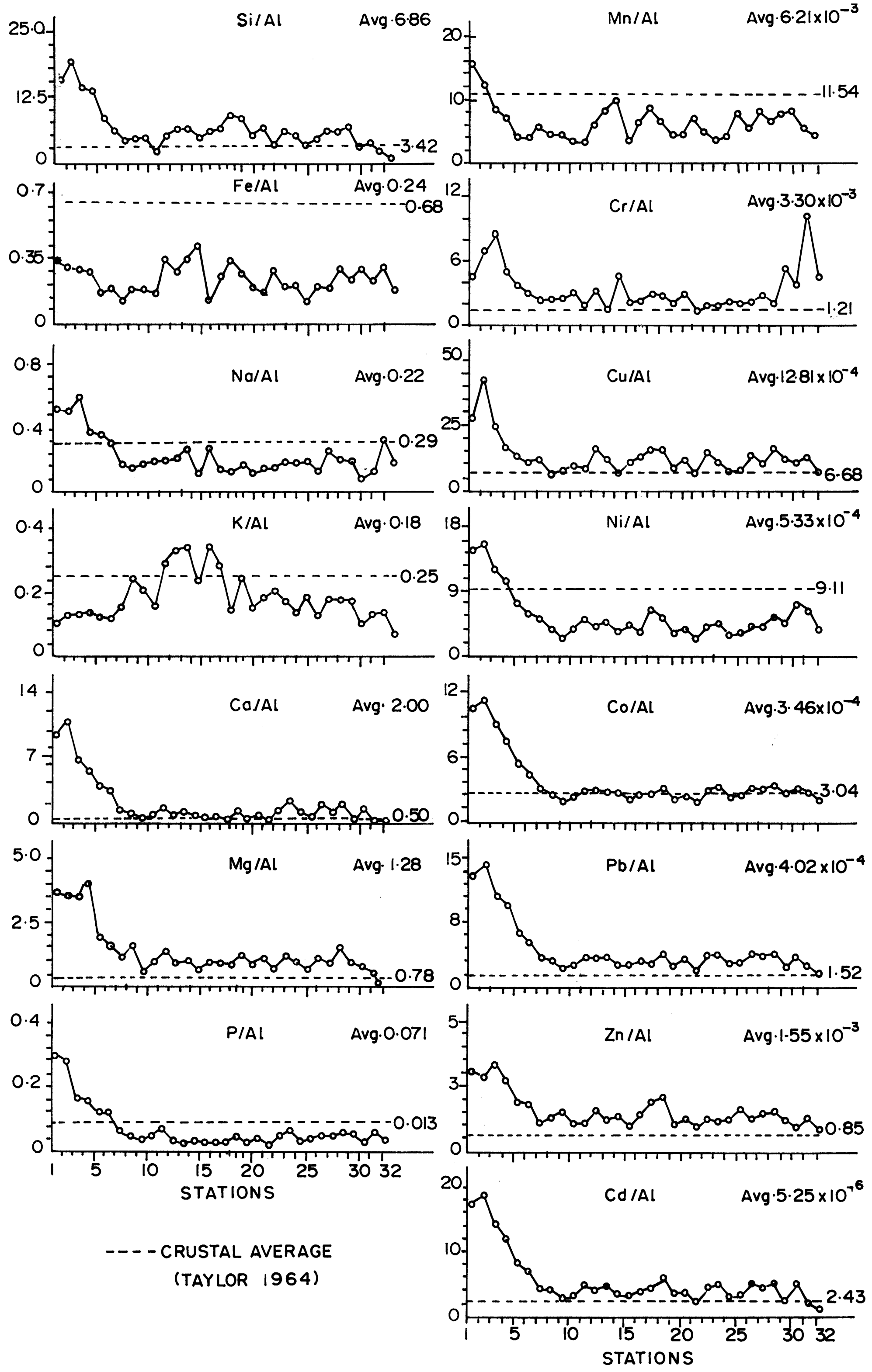

Fig. 3
Al normalized elements compared with crustal average in surface sediments off the Gulf of Mannar

close to the shore; the clayey silt and sandy silt sediments in these areas also support the deposition of organic debris (Rajamanickam and Setty 1973). The low values of OC (0.08–0.91%) in the entire study area (except stations 10, 12 and 28–32) are often accompanied by the time integrating nature of marine sedimentation and mixing processes at the sediment water interface where the rate of delivery as well as rates of degradation by a microbial-medicated process can be high (Canuel and Martens 1993). The sandy and shallow nature of the coastal region also supports the above inference (Rozonov and others 1974).

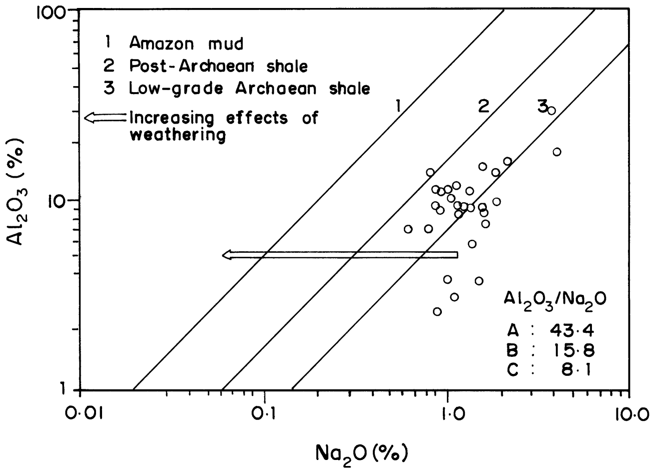

Fig. 4
Weathering pattern of surface sediments off the Gulf of Mannar

Major elements

The wide variability of the carbonate contents of the samples examined makes the interpretation of chemical data somewhat difficult as variable mixtures of carbonate and silicates are dealt with. In an attempt to compensate for the natural variability of major and total trace elements in sediments, normalization was done so that any anthropogenic metal contributions could be detected and quantified. Loring (1991) indicated that the natural mineralogical and granular variability is best compensated by the geochemical normalization of major and trace metal data. Al remains the most successful and widely used normalizer and compensates for variations in grain size and composition because it represents the quality of alumino silicate, which is the most important carrier for adsorbed metals in near shore sediments. Moreover, in the crust, metal to aluminium ratios are less affected by human activities (Schropp and others 1990). According to Salomons and Forstner (1984), the contamination in an area can be inferred from the enrichment factor (EF), which is the ratio between metal/Al in the sample and metal/Al in the average shale or crust and this provides an effective tool to evaluate sediment quality and aids in making comparisons between different areas. The behavior of major and minor elements by means of element/Al ratios has been examined as it has shown that variations in such ratios can be interpreted in terms of the texture and mineralogy of sediments (Calvert 1976).

The average concentrations of major elements (Si, Al, Na, K, Ca, Mg and P) are presented in Table 2 and the Al normalized values are represented in Fig. 3. Si concentrations in the surface sediments are more or less uniform and the entire region indicates the presence of higher quartz content, except in the estuarine region (24.96–27.16%) and in the near shore regions of the northern part (18.41–24.25%). Si/Al ratios indicate high values in the southern part (16.00–25.46) where Al values are very low. The low Si/Al ratio (1.26–6.74) indicates that these variations could be due to variations of quartz in the sediments (Calvert and others 1993). The high Si/Al ratio (8.85–19.82) in the southern part could not only be due to the presence of free quartz and sand-rich sediments but also due to the productive overlying waters (Rao and Sarma 1993) and as most of the samples are generally coarse grained, this indicates a higher ratio of quartz + feldspar relative to clays. Al concentration shows moderate values from 3.08 to 8.49% in the estuarine and middle parts, while very high values are observed in certain regions of the northern part (9.55–15.79%). Al concentration is rich in the area, except the southern most transect, wherein limestone and greywacke occur along the coast. In addition, the strong dirunal winds and seasonally high inflows from Tambraparni River would aid mixing and result in an increase of Al content (Summers and others 1996). The association of Al with fine-grained sediments suggests that they are detrital minerals dominated by phyllosilicates (Buckley and Cranston 1991).

Sodium and potassium concentrations in the area are low with mild enrichment in the southern part indicating the influence of river input. Sodium and potassium concentrations from stations 7 to 16 clearly indicate the influence of river input with higher values from 0.64 to 1.56 and 0.92 to 1.74%, respectively. High concentrations of Na are encountered in the northern part near a major industrial outfall region (stations 31 and 32) with 2.98 and 2.74%. The high concentration of Na in these samples is mostly due to the high ash content used in the coal fired thermal power plant and the results correlate with earlier studies made by Henry and Knapp (1980). The behavior of Na and K largely reflects the distribution of K and plagioclase feldspars in the sediments. In spite of high Na/Al ratio (0.30–0.58) in the southern part (stations 1–6), the K/Al ratios have lower values, whereas the highest K/Al ratios are found at estuarine stations 11–16 (0.28–0.24) indicating the dominance of K-feldspars.

Calcium and magnesium concentrations reveal a higher average (6.52 and 5.15%) than for other coastal regions along the southeast coast of India. High values of Ca and Mg in the southern part of the area are probably due to the inflow of the Tambraparni River and the seasonal rivers south of Tiruchendur enriching the Ca content in the sediments as they flow through the limestone beds of Kudangulam (Hashimi and Nair 1976; Ray and others 1990). It is apparent that calcium carbonate and Ca are more abundant on the southern side off Tuticorin where the shelf is widest and shell debris is the main constituent. Relatively low values of carbonates and Ca in the northern part may be either due to strong currents leading to nondeposition of terrigenous material or because the supply is limited and does not extend to cover the relict sediments of the northern part. The sharp increase of carbonate content suggests that the terrigenous material abruptly ends in the middle part and is not deposited on the northern side. In the southern part, calcium carbonate is mainly of biogenic origin as indicated by the abundance of skeletal components, which are dominated by mollusks, bryozoa, corals, foraminifers, ostracods and echinoids. The high Mg content in sediments observed in the southern part of Tuticorin indicates that among the different processes, biological processes play an important role. Organisms that secrete carbonate skeletons incorporate varying amounts of Mg into the skeleton and this is in

Table 3

Average concentration of total and acid leachable elements ($\mu g.g^{-1}$) in surface sediments off the Gulf of Mannar

Sample number	Fe ($\mu g.g^{-1}$)		Mn ($\mu g.g^{-1}$)		Cr ($\mu g.g^{-1}$)		Cu ($\mu g.g^{-1}$)		Ni ($\mu g.g^{-1}$)		Co ($\mu g.g^{-1}$)		Pb ($\mu g.g^{-1}$)		Zn ($\mu g.g^{-1}$)		Cd ($\mu g.g^{-1}$)	
	T	Nd	T	Nd	T	Nd	T	Nd	T	Nd	T	Nd	T	Nd	T	Nd	T	Nd
1	5,400	384	251	150	76	6.20	46	6.05	24	9.50	17	7.45	21	4.65	50	3.95	0.28	0.24
2	4,100	256	165	105	94	6.55	58	6.80	21	9.15	15	7.10	19	4.80	39	3.25	0.25	0.23
3	5,600	504	160	92	162	7.05	48	6.35	23	8.90	17	7.15	20	4.50	64	3.70	0.27	0.23
4	5,700	358	144	100	101	6.45	34	5.15	21	8.75	15	6.20	19	4.45	56	3.40	0.24	0.22
5	5,400	291	122	52	115	6.00	42	5.80	22	7.55	16	6.15	19	4.35	59	3.10	0.25	0.21
6	7,700	322	160	57	119	6.65	44	5.20	23	7.05	17	6.00	20	4.65	73	3.25	0.27	0.22
7	7,200	493	329	60	133	5.00	70	10.05	30	4.45	17	6.75	19	3.90	65	3.35	0.24	0.17
8	10,300	182	243	86	128	3.75	35	4.05	20	2.65	13	5.15	16	3.50	68	2.60	0.21	0.15
9	11,400	120	265	59	144	1.90	44	5.90	14	3.25	10	1.90	12	1.75	88	1.45	0.15	0.08
10	13,900	713	287	113	250	5.05	76	11.05	30	8.25	18	6.75	19	3.65	91	3.55	0.25	0.18
11	16,900	234	157	69	87	4.25	40	6.80	24	7.60	13	5.00	16	3.50	51	5.60	0.22	0.17
12	13,800	135	291	40	153	3.05	77	11.30	19	4.15	13	4.25	15	2.00	76	3.85	0.18	0.12
13	15,900	207	376	166	71	3.70	55	8.50	21	6.90	12	4.75	15	3.00	55	5.40	0.20	0.16
14	25,100	199	572	107	267	2.70	39	4.80	19	5.20	15	5.80	14	2.60	79	2.30	0.19	0.12
15	6,400	172	175	60	111	2.80	54	6.95	21	4.10	10	4.00	12	2.10	50	1.65	0.15	0.10
16	12,400	144	309	30	105	2.35	61	9.70	15	4.45	11	3.90	13	2.15	66	1.75	0.17	0.11
17	12,700	133	317	22	105	1.35	58	6.95	23	2.25	9	2.40	9	1.50	72	1.15	0.15	0.08
18	10,100	180	240	32	101	2.55	57	9.05	19	3.15	11	4.45	13	2.55	77	1.65	0.21	0.14
19	11,600	168	253	9	116	2.05	49	8.15	17	3.90	11	4.10	13	2.00	61	1.55	0.20	0.14
20	8,100	131	193	11	131	3.30	52	6.85	16	4.50	10	3.10	14	2.10	57	1.60	0.16	0.15
21	23,000	156	523	8	105	3.60	50	7.25	17	4.20	13	3.40	13	1.95	76	1.95	0.16	0.10
22	9,600	176	222	26	83	5.15	67	10.0	18	6.90	13	4.60	16	3.10	58	2.70	0.20	0.16
23	9,900	199	168	38	84	6.20	53	7.15	21	7.90	15	6.45	17	3.45	57	2.90	0.23	0.15
24	8,700	231	299	75	154	5.55	51	7.80	20	6.90	15	6.50	18	3.30	89	2.95	0.21	0.18
25	12,800	169	468	79	122	5.20	47	7.00	19	6.10	14	5.55	16	3.00	99	2.80	0.19	0.15
26	9,000	154	255	88	97	5.45	61	9.05	19	7.80	14	5.50	17	3.75	60	3.20	0.22	0.19
27	14,100	157	376	75	124	4.80	49	7.25	18	6.50	14	5.40	16	3.40	70	2.90	0.20	0.15
28	10,600	191	284	84	81	5.80	67	9.85	23	6.60	14	5.15	16	3.65	71	3.15	0.21	0.19
29	22,000	202	553	179	387	2.70	86	18.20	33	4.30	19	3.85	15	1.95	96	6.00	0.17	0.10
30	14,000	274	466	251	219	4.85	59	10.05	40	7.90	17	6.10	19	3.55	63	4.15	0.28	0.19
31	28,900	679	502	212	963	1.85	110	23.85	58	6.30	24	5.00	21	2.35	132	8.00	0.16	0.12
32	29,400	747	640	288	682	2.30	99	20.05	55	6.05	29	5.40	19	2.60	162	16.20	0.13	0.11
Mean	12,553	271	305	88	177	4.25	57	8.84	24	6.04	15	5.16	16	3.12	73	3.59	0.21	0.16

T total metal concentration; *Nd* acid leachable elements agreement with the present analysis of the sediments (Rao 1978); moreover, coralline algae and foraminifers can also contribute Mg to the sediments.

The higher concentration of Mg is attributed to Mg^{2+} by the ion exchange process with Ca^{2+} and the skeletal fragments and organisms from the skeletal debris are made up of high Mg-calcite contributing Mg to the present sediments and the dissolution of Mg in the shelf sediments is also available for reprecipitation (Rao 1978). Comparing the northern and southern part, Ca and Mg concentrations vary from 2.19 to 15.49 and 3.43 to 8.31% from stations 1–16; whereas, in the northern part except for a few pockets, lower values are seen (1.04 to 11.12 and 1.12 to 6.86%). The average concentration of Ca in the southern part (stations 1–16) is 8.08% and in the northern part 4.97% (stations 16–32).

Phosphorous in the southern part (stations 1–11) of the study area is high (0.32–0.49%) except at stations 8 and 9. In the middle part of the study area, from stations 12 to 21, the concentration records low values from 0.11 to 0.19% and, in the northern part, from stations 22 to 28, moderate concentrations are observed (0.24 to 0.33%). P/Al indicates a higher value (0.12–0.30) in the southern part (stations 1–6) indicating that the higher concentration of P was fixed in association with iron and the supply of detrital phosphate or phosphatized limestone from neighboring land, and that it is newly formed. The low P/Al ratios reveal low concentrations of P in the analyzed sediments, which are controlled by the detrital phase and are mostly attributed to the low organic carbon concentrations (Rao and Murty 1990; Purnachandra Rao and others 1998).

To know the source of metal input from the land source a plot of Al_2O_3 vs Na_2O (Fig. 4) was drawn. It indicates that most of the sediments fall in the field between post-Archean shale and low-grade Archean shale, while a few samples fall in the field of low-grade Archean shale. This indicates that the sediments have been derived from a partially weathered source and from the near shore continental margins. As the samples show much variation in the composition from post-Archean shale to low-grade Archean shale field, it can be inferred that the sediments exhibit variable influence of weathering in the source region.

Distribution patterns of trace elements in sediments

The concentrations of the metals Fe, Mn, Cr, Cu, Ni, Co, Pb, Zn and Cd in the sediments of the Gulf of Mannar are substantially higher at stations close to the coast in the northern (stations 29-32) and the southern regions (stations 1–7) (Table 3). The range and magnitude of concentrations of trace metals, except Fe and Mn, in the northern side, are similar to those observed in the southern side (stations 1–7) of the Gulf of Mannar. Samples obtained in the middle stations tend to have lower concentrations.

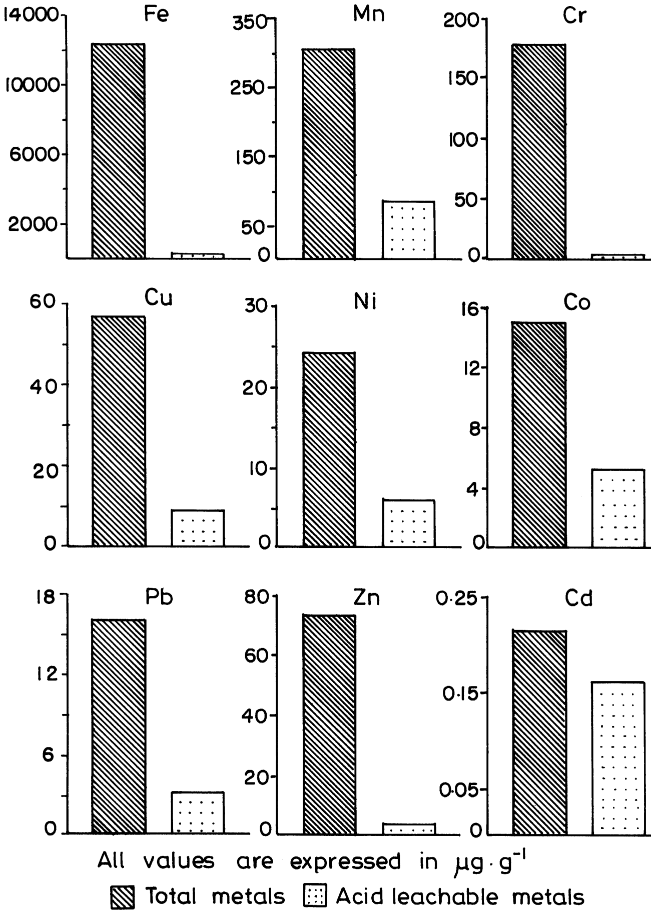

Fig. 5
Concentrations of total + acid leachable ($\mu g.g^{-1}$) from surface sediments off the Gulf of Mannar

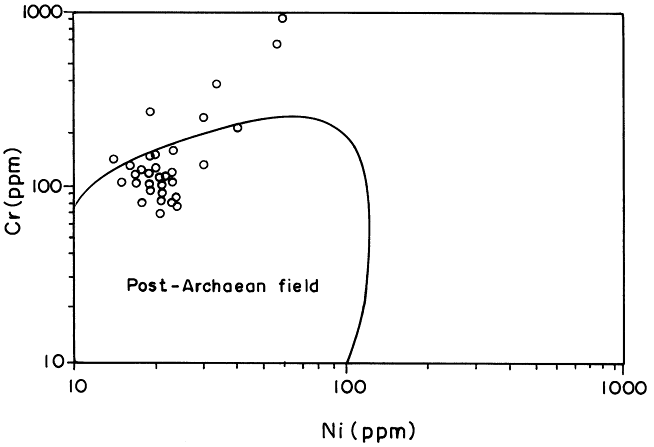

Fig. 6
Cr vs Ni plot indicating the nature of the source of sediments off the Gulf of Mannar

Concentrations of total Fe and Mn are low in the southern side (stations 1–7), which is dominated by high $CaCO_3$ and sand content, whereas the estuarine region (stations 8–14) indicates high values of total Fe (10300–25100 $\mu g.g^{-1}$) and Mn (157–572 $\mu g.g^{-1}$). Very high values of total Fe and Mn are observed at stations 14 and 21 and in the near shore region stations 29–32 in the northern side. It seems likely that the Fe enrichment results from reduction of Fe in the sediments during the oxidation of organic matter (Francois 1988). The low Fe/Al ratio (0.12–0.42) in the present study indicates that authigenic Fe-bearing minerals are held in the structural positions (Calvert 1976).

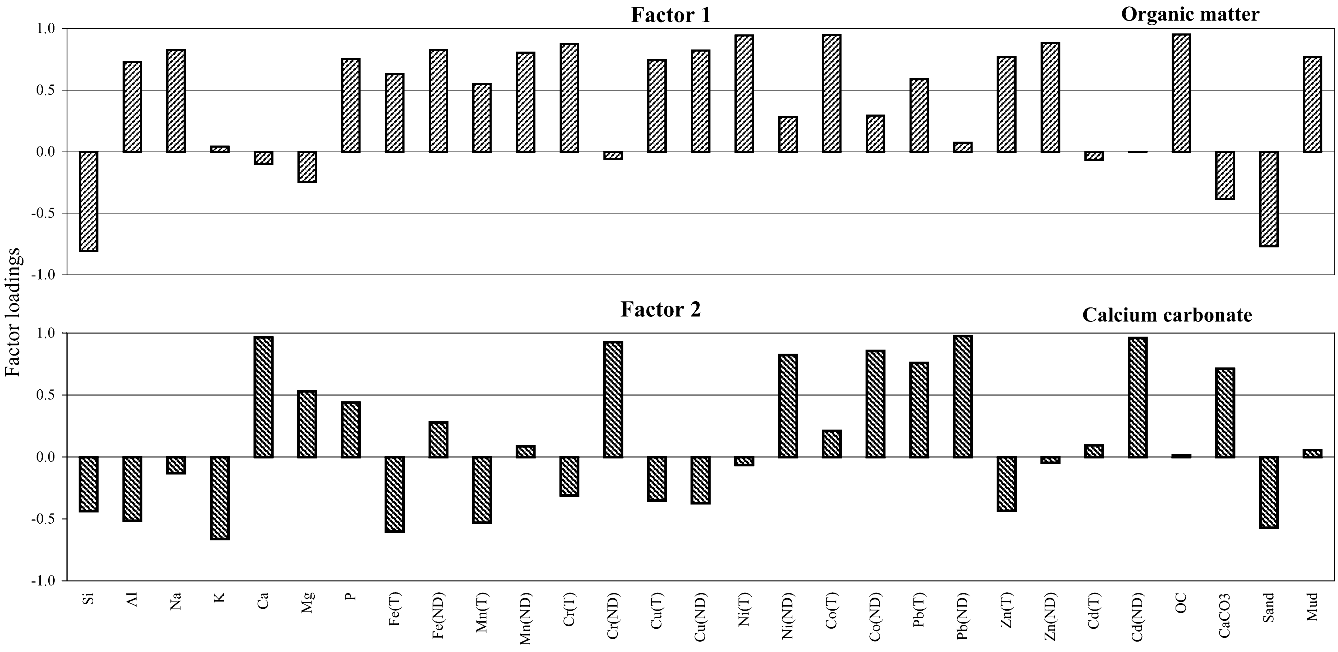

Fig. 7
Results of factor analysis (R-mode) showing the elemental composition of the two primary factors accounting 76.4% of the total variance

The concentrations of metals Cr (71–963), Cu (34–110), Ni (14–58), Co (9–29), Pb (9–21), Zn (39–162) and Cd (0.13–0.28 $\mu g.g^{-1}$) are similar in the Gulf of Mannar with high and low values at near shore stations and at certain middle parts of the shelf. The very high concentrations of trace elements in stations 29–32 and stations 10, 14 and 21 indicate greater mixing at the shallowest depth and the similar concentration of metals in other stations indicate the sandy nature. It is probable that winnowing has prevented greater accumulation of fine-grained material and that the waves from storms refract through the coastal region (Bothner and others 1998).

Iron can be converted to complex hydroxy compounds that may eventually precipitate (Riley and Chester 1971). This would lead to the co-precipitation of other metals in the water column and so increase the concentration of many metals in the sediments. A number of river borne metals (Fe and Mn) precipitate rapidly upon entering the sea and other trace metals (Co, Zn, Ni, Cu, Cr) could precipitate in a linear manner with time (Lowman and others 1966). In fact, many minerals present in marine sediments are capable of adsorbing large quantities of certain trace elements from the water column (Krauskopf 1956; Turekian 1971). In this regard, the continual resuspension of bottom sediments occurring in the Tambraparni estuary and the northern part of Tuticorin may serve to scavenge and concentrate metals that are naturally present in the water column as well as those introduced by industrial discharges. This mechanism could account for the increase in metal concentration and a combination of these factors may explain the increased levels of all metals found in the samples collected from the estuarine as well as the northern parts of the Gulf of Mannar (Knauer 1977).

The distribution pattern of metal/Al ratio of trace element resembles the distribution pattern discussed earlier showing elevated concentrations at the southern side, river mouth, and at stations 29–32 in the north. Anthropogenic contribution of metals and the role of Fe-Mn oxides, grain size and $CaCO_3$ become major factors affecting the distribution of metals in the region.

When comparing the crustal averages (Taylor 1964) with that of the present study, higher values are observed with K indicating the dominance of potash feldspar; in addition, as the study area is rich in calcareous shell debris, Mg/Al and P/Al also indicate a three-fold increase in the averages than the crustal values. Trace metal averages indicate a two-fold increase of Cu, Zn and Cd, three-fold increase of Pb and Cr and a marginal increase of Co over the crustal averages. Mn and Ni averages are lower than the crustal values.

The calculated EF values for all surface sediments reveal higher values in the southern region, which is strongly influenced by the anthropogenic introduction of trace elements with the skeletal carbonate fragments. The EF values in the Gulf of Mannar decrease in the following order:

Elements	Cr>	Pb>	Cd>	Cu>	Zn>	Co>	Fe>	Ni>	Mn
EF values	2.73	2.65	2.16	1.92	1.82	1.14	0.68	0.59	0.54

This enhancement order indicates higher anthropogenic input of metals such as Cr, Pb, Cd, Cu, and Zn in the coastal sediments. These elements are most probably derived from various activities of thermal power plant operation, harbor activities, large industrial input along the coast and from the Tambraparni River. Similar enrichment of EF values was observed in the Baltic, Boston harbor and San Francisco Bay sediments (Warren 1981; Szefer and Skwarzec 1988; Mac Donald 1991; Van Geen and Luoma 1999b).

Table 4
Correlation coefficient for major, trace and acid leachable elements off the Gulf of Mannar

	Si	Al	Na	K	Ca	Mg	P	Fe (T)	Fe (Nd)	Mn (T)	Mn (Nd)	Cr (T)	Cr (Nd)	Cu (T)
Si	1.00													
Al	−0.48	1.00												
Na	−0.57	0.71	1.00											
K	0.17	0.50	0.28	1.00										
Ca	−0.33	−0.59	−0.21	−0.68	1.00									
Mg	−0.16	−0.30	−0.34	−0.23	0.40	1.00								
P	−0.80	0.31	0.60	−0.36	0.35	0.11	1.00							
Fe (T)	−0.29	0.78	0.53	0.51	−0.64	−0.42	0.19	1.00						
Fe (Nd)	−0.73	0.47	0.74	−0.11	0.14	0.03	0.77	0.29	1.00					
Mn (T)	−0.28	0.72	0.37	0.36	−0.57	−0.37	0.09	0.85	0.22	1.00				
Mn (Nd)	−0.70	0.48	0.55	−0.04	0.02	−0.24	0.52	0.50	0.60	0.57	1.00			
Cr (T)	−0.51	0.71	0.81	0.17	−0.40	−0.47	0.58	0.73	0.66	0.60	0.67	1.00		
Cr (Nd)	−0.38	−0.47	−0.15	−0.59	0.91	0.52	0.32	−0.60	0.14	−0.47	−0.02	−0.39	1.00	
Cu (T)	−0.35	0.63	0.65	0.19	−0.40	−0.50	0.41	0.55	0.54	0.51	0.50	0.76	−0.34	1.00
Cu (Nd)	−0.42	0.69	0.69	0.20	−0.44	−0.48	0.47	0.67	0.54	0.59	0.60	0.86	−0.39	0.95
Ni (T)	−0.69	0.64	0.77	0.01	−0.16	−0.36	0.66	0.59	0.77	0.52	0.81	0.88	−0.17	0.75
Ni (Nd)	−0.56	−0.24	0.16	−0.48	0.79	0.23	0.47	−0.25	0.40	−0.25	0.35	−0.02	0.80	−0.07
Co (T)	−0.86	0.60	0.74	−0.16	0.12	−0.11	0.84	0.49	0.83	0.48	0.78	0.77	0.14	0.62
Co (Nd)	−0.60	−0.18	0.13	−0.44	0.78	0.37	0.53	−0.28	0.51	−0.16	0.33	0.00	0.79	−0.07
Pb (T)	−0.80	0.02	0.44	−0.43	0.67	0.22	0.78	−0.10	0.69	−0.07	0.52	0.32	0.68	0.19
Pb (Nd)	−0.50	−0.44	−0.04	−0.61	0.93	0.50	0.48	−0.52	0.32	−0.45	0.16	−0.24	0.91	−0.30
Zn (T)	−0.45	0.86	0.73	0.25	−0.50	−0.35	0.44	0.73	0.55	0.70	0.53	0.82	−0.42	0.66
Zn (Nd)	−0.69	0.69	0.74	0.05	−0.10	−0.22	0.65	0.60	0.67	0.50	0.79	0.72	−0.11	0.63
Cd (T)	−0.36	−0.54	−0.26	−0.58	0.89	0.46	0.27	−0.56	0.20	−0.46	0.07	−0.35	0.82	−0.36
Cd (Nd)	−0.37	−0.52	−0.11	−0.64	0.92	0.45	0.37	−0.59	0.25	−0.51	0.10	−0.29	0.89	−0.31
Org. C	−0.75	0.65	0.77	−0.01	−0.08	−0.24	0.70	0.58	0.79	0.41	0.75	0.83	−0.06	0.69
Ca CO_3	−0.04	−0.60	−0.37	−0.34	0.71	0.52	0.13	−0.62	−0.05	−0.59	−0.25	−0.52	0.56	−0.60
Sand	0.70	−0.55	−0.51	−0.06	0.05	0.04	−0.56	−0.46	−0.60	−0.29	−0.52	−0.58	−0.04	−0.50
Mud	−0.70	0.55	0.51	0.06	−0.05	−0.04	0.56	0.46	0.60	0.29	0.52	0.58	0.04	0.50

T total metal; *Nd* nondetrital metals

Partition of the sediments shows (Fig. 5) that 0.68–9.00% of total Fe, 1.53–69.44% of total Mn, 0.19–8.16% of total Cr, 11.57–21.68% of total Cu, 18.62–47.33% of total Co, 9.78–43.57% of total Ni, 11.19–25.26% of total Pb, 1.60–10.98% of total Zn, and a high acid leachable fraction of 53.33–93.75% of total Cd is nondetrital. The acid leachable fraction in the study area decreases in the following order:

Elements	Cd>	Co>	Mn>	Ni>	Pb>	Cu>	Zn>	Cr>	Fe
Average (%)	75.91	35.08	28.91	25.31	19.15	15.39	4.94	2.40	2.21

These nondetrital proportions indicate that Cd makes up for 75.91% of the total Cd. The nondetrital fractions of Cr, Co, Pb, Cd and Ni indicate a positive relationship with $CaCO_3$, Ca and Mg indicating their association with calcareous shell debris and it appears that calcium carbonate plays a significant role in the determination and distribution of the nondetrital elements. In general, the nondetrital metals are controlled by their inclusion in and their association with amorphous or weakly crystalline Fe-Mn compounds, ion exchange positions, and organic matter as well as grain size (surface area) of the material. In the sediments, ion-exchange positions in the alumino-silicates and titaniferous minerals (Cd, Co, Ni) appear to contribute significantly to the nondetrital fraction.

The total Cr/Ni plot (Fig. 6) reveals that a very good positive correlation exists and most of the sediments fall in the field of post-Archean shale, while a few samples fall in the field of late Archean shale. The Cr and Ni abundances are too high to be explained simply by provenance and some anthropogenic input might have enriched the values. However, the level of enrichment reflects differing source composition.

Factor analysis and inter-element relationship

A 29×29 correlation matrix from the bulk sediments was computed giving 29 components, contributing 100% of the total variance. Based on the point of inflection, two common factor loadings, along with percent of total, cumulative percent variance and Eigen values were derived (Sahu 1973). The factor scores were computed from original raw data measurements and the rotated factor loadings were produced to create an entirely new set of smaller number composite variables.

Distribution of total and acid leachable elements in the present study indicates a general trend in relation to sediment texture and calcium carbonate distribution in the area. In the case of the first rotated factor of major and other elements, it contributes 43.6% of the total variance, 12.66 of Eigen value, and depicts the strong influence of Al, Fe (t and nd), Mn (t and nd), Cr (t), Cu (t and nd), Ni (t), Co (t), Pb (t), Zn (t and nd), organic carbon and mud. Within this association, sand, Si and to a certain extent $CaCO_3$ operate against the dominant variables in this factor (Fig. 7). This explains the general association of major and trace elements as a single source with finer fraction and organic matter. The strong loading on trace elements explains crustal erosion as well as atmospheric fall out as the source. Of the variables, Co, Cr and Ni came

Cu (Nd)	Ni (T)	Ni (Nd)	Co (T)	Co (Nd)	Pb (T)	Pb (Nd)	Zn (T)	Zn (Nd)	Cd (T)	Cd (Nd)	Org. C	$CaCO_3$	Sand	Mud
1.00														
0.82	1.00													
−0.06	0.17	1.00												
0.69	0.86	0.40	1.00											
−0.10	0.21	0.79	0.49	1.00										
0.23	0.50	0.78	0.73	0.84	1.00									
−0.32	0.01	0.80	0.28	0.87	0.79	1.00								
0.73	0.69	−0.20	0.69	−0.12	0.14	−0.35	1.00							
0.72	0.81	0.23	0.85	0.20	0.45	0.04	0.70	1.00						
−0.38	−0.08	0.70	0.11	0.80	0.67	0.88	−0.49	−0.18	1.00					
−0.33	−0.06	0.81	0.18	0.81	0.75	0.94	−0.43	0.04	0.90	1.00				
0.77	0.90	0.31	0.87	0.24	0.53	0.07	0.71	0.84	−0.05	0.01	1.00			
−0.63	−0.41	0.41	−0.21	0.55	0.29	0.67	−0.59	−0.37	0.66	0.62	−0.39	1.00		
−0.59	−0.71	−0.27	−0.66	−0.16	−0.43	−0.06	−0.46	−0.58	−0.05	−0.03	−0.81	0.28	1.00	
0.59	0.71	0.27	0.66	0.16	0.43	0.06	0.46	0.58	0.05	0.03	0.81	−0.28	−1.00	1.00

to the sediments through normal crustal weathering and the other four variables (Mn, Cu, Pb, Zn) came from anthropogenic sources like industrial effluents and emissions (Kelin and others 1974).

The second rotated factor accounts for 32.8% of the total variance, 76.4% of cumulative variance and 9.50 of Eigen value. This factor loading indicates that $CaCO_3$ controls the distribution of most of the trace metals with high loadings in nondetrital Cr, Ni, Pb, Cd and both forms of Co with $CaCO_3$, Ca and Mg, suggesting that the shell debris is Mg rich and that the metals are also closely associated with them. The coralline sediments indicate that substantial portions of these elements occur in fractions, which are leachable by dilute acid treatment; it is also indicative that they are anthropogenic elements brought out by the activities along the coastal region (Förstner and Patchineelam 1980; Abu-Hilal 1987). The variables giving a negative loading in this factor are Al, K, Fe (t), Mn (t) and sand, which suggests that the sediments contain K-feldspar and the Fe and Mn hydroxides are associated as surface coatings.

From the correlation matrix it is evident that mud reveals good correlation with total Cr (0.58), Cu (0.50), Ni (0.71), Co (0.66) and with organic carbon (0.81) and very low relation to total Pb (0.43) and Zn (0.46) (Table 4). The low relationship of mud is seen with total Fe (0.46) and Mn (0.29), therefore, the highest concentration occurs in the offshore sandy muds and muds. The positive covariance of detrital Cr, Cu, Ni, Co, Zn to Al and sometimes-partial inclusion of these metals in the fine-grained fraction indicate the dominance of aluminophyllosilicate minerals. The positive correlation of Fe with Mn, Zn, Cr, Cu, Co and Ni indicate that they are attached to the Fe, Mn oxyhydroxides. The positive relationship of total Ni, Cr, Co, Pb and acid leachable Mn, Co and Zn with mud and organic carbon and, in addition factor 1, also indicates high loadings on P. The increase and association of P and other elements could indicate an anthropogenic source such as sewage sludge mixing in the study area (Smith 1977; Brian and others 1982; Furrer and others 1983).

Acetic acid extractable Fe shows positive correlation with total Cr, Ni, Co, Pb, Zn and nondetrital Mn, Cu, Co and Zn as well as organic carbon and mud. It indicates that the weak acid leachable Fe is mainly available in the form of oxic phase/oxide coatings on sediment particles (Rao and Murty 1990). The role of Fe-Mn oxides and anthropogenic contribution of metals becomes a major factor in affecting the distribution of metals in the Gulf of Mannar (Subramanian and Mohanachandran 1990). The similar pattern of positive relationship of nondetrital Mn with other trace metals also suggests that they are associated with Mn-oxyhydroxides in the inner shelf region off Tuticorin and it could be incorporated or adsorbed on growing MnO_2 particles (Spencer and others 1968; Buckley and Winters 1992). The significant positive correlation of nondetrital Zn, Cu and to a little extent Ni, with mud and organic carbon illustrates the increase in nondetrital concentrations of these elements with decreasing grain size (increasing surface area) of the sediments. The positive correlations of nondetrital Zn, Cu and

Table 5
Comparison of elements in sediments with various other coastal regions around the world

Areas*	Al (%)	Fe (%)	Mn (μg.g^{-1})	Cr (μg.g^{-1})	Cu (μg.g^{-1})	Ni (μg.g^{-1})	Co (μg.g^{-1})	Pb (μg.g^{-1})	Zn (μg.g^{-1})	Cd (μg.g^{-1})
1		0.4–2.84	53–655	15–186	7.0–27	19–76	21–56	83–225	31–260	2.0–18
2				74–1,480	14–937	16–134		19–578	54–2,880	1.1–6.6
3		1.92			7.0	12	7.6	17	33	
4	5.87	3.10	530	61	15	24	12	20	65	0.065
5	4.05	3.77	1,098	77.3	53.47	32.63		50.68	322	0.996
6	5.0	3.3	410	155	190	28	8	140	250	
7	6.75	3.75		231.5	112	34.7		135	176	
8			700	87	25	36	14	21	84	
9	7.8	6.8	1192	103	100.9	52	38.2	16.4	96.2	
10	5.39	1.26	305	177	57	24	15	16	73	0.16

Areas*: *1* Gulf of Aqaba (Red Sea) – Abu-Hilal (1987); *2* Palos Verdes Peninsula, Southern California – Hershelmen and others (1981); *3* HalifaxBay – Knauer (1977); *4* China Shelf Sea – Yiyang and Ming-cai (1992); *5* Tokyo Bay – Fukushima and others (1992); *6* Narragansett Bay – Goldberg and others (1977); *7* Boston Harbour – Bothner and others (1998); *8* Gulf of St. Lawerence – Loring (1978, 1979); *9* Bombay Coast – Dilli (1986); 10 present study – Tuticorin coast, Gulf of Mannar

Co with nondetrital Fe in the Gulf of Mannar sediments suggest that these contributions are derived from iron oxide coatings (Loring 1984).

Comparisons within the Gulf of Mannar samples show some significant difference in composition. On the whole, the southern region sediments contain greater concentrations of Ca, Mg and significantly lower concentrations of Si, Al and Mn than the northern part. These differences reflect the more calcareous nature of the gulf sediments caused by their proximity to carbonate source rocks (Campbell and Loring 1980).

Comparisons of sediment concentration along with various other coastal regions around the world indicate increase in Cr and Co concentration in the study area (Table 5).

Conclusion

The Gulf of Mannar is endowed with a fragile ecosystem and the presence of several coral islands supporting a multitude of fauna warrants its preservation. The area was flourishing as a center for pearl harvesting since medieval times. However, the pearl oyster beds have dwindled and the area has not produced the priced commodity since the 1960s. The anthropogenic activities taking place in the area during the last five decades have had a damaging effect on the marine ecosystem as the effluents from the industries close to the coast are discharged along with domestic sewage from rivers into the Gulf.

The sands with high $CaCO_3$ content dominate the inner shelf area and silt occurs in some parts sheltered from the oceanic currents. The concentration of these metals relative to crustal average shows enrichment in the order of magnitude two to three in the case of Cr, Pb, Cd, Cu and Zn. However, the concentration is less than the levels reported from areas like Boston Harbor (Bothner and others 1998), Tokyo Bay (Fukushima and others 1992), Halifax Bay (Buckley and others 1995) and San Francisco Bay (Van Geen and Luoma 1999a, 1999b). High concentration of acid leachable (non-detrital) Cd, which make up 75.9% of total Cd and moderate enrichment in Co, Mn, and Ni indicate that the metals are scavenged by the uptake by the fauna with calcareous exoskeletons. Statistical analysis reveals that the total metals are related to the mud fraction and organic carbon, while some non-detrital metals are associated with $CaCO_3$.

The metals are principally discharged from industrial waste effluents along the northern side and river discharge in the southern side of the Gulf of Mannar. The area though contaminated is not under severe stress as most of the toxic metals are below the levels to induce toxic effects on marine organisms exposed to the sediments and studies carried out in many contaminated sites have indicated that by proper environmental strategies, the sediment quality can be restored. Although these results are indicative of the direct effect that industrial discharge can have in a coastal zone on area sediment metal concentrations, other direct and indirect effects should be considered in relation to possible long-term perturbations and proper wastewater treatment has to be undertaken by the concerned industries not only to prevent further degradation but also to restore the quality of the marine ecosystem of the Gulf of Mannar.

Acknowledgements This study is partly sponsored by the University Grants Commission—Special Assistance Programme (Phase II), COSIST & DST-FIST awarded to the Department of Geology, University of Madras. M. P. Jonathan thanks the financial assistance from the Council of Scientific and Industrial Research, New Delhi, India. The authors thank Prof. S. P. Mohan, Department of Geology, University of Madras, Chennai for providing laboratory facilities and Dr. N. Rajeshwara Rao for fine tuning the manuscript.

References

Abu-Hilal AH (1987) Distribution of trace elements in near shore surface sediments from the Jordan Gulf of Aqaba (Red Sea). Mar Poll Bull 18(4):190–193

Agemian H, Chau ASY (1976) Evaluation of extraction technique for the determination of metals in aquatic sediments. Analyst 101:761–767

Armstrong Altrin Sam J (1998) Microfabrics and geochemistry of Kudankulam formation, Tamil Nadu, India. PhD Thesis (Unpublished), University of Madras, Chennai, India, 131 pp

Bhosle NB, Dhargalkar VK, Braganca AK (1978) Distribution of some biochemical compounds in sediments of the shelf and slope regions of the West Coast of India. Indian J Mar Sci 7:155–158

Bothner MH, Buchholtzten Brink M, Manheim FT (1998) Metal concentrations in surface sediments of Boston harbor changes with time. Mar Env Res 45:17–155

Brian R, Robert J, Murphy K, Kyle SW (1982) Anthropogenically derived changes in the sediments flux of Mg, Cr, Ni, Cu, Zn, Hg, Pb and P in Lough Neagh, Northern Ireland. Env Sci Tech 16:23–30

Bridgman HA (1992) Evaluating rainwater contamination and sources in southwest Australia using factor analysis. Atmos Env Gen Top 26A:2401–2412

Bryan GW, Langston WJ (1992) Bioavailability, accumulation and effects of heavy metals in sediments with special reference to United Kingdom estuaries: a review. Env Poll 76:89–131

Buckley DE, Cranston RE (1991) The use of grain size information in marine geochemistry In: Syvitski JM (ed) Principles, Methods and Applications of particle size analysis. Cambridge Univ Press, New York, pp 311–331

Buckley DE, Smith JN, Winters GV (1995) Accumulation of contaminant metals in marine sediments of Halifax harbor, Nova Scotia: environmental factors and historical trends. Appl Geochem 10:175–195

Buckley DE, Winters GV (1992) Geochemical characteristics of contaminated surficial sediments in Halifax Harbour: impact of waste discharge. Can J Earth Sci 29(12):2617–1639

Calvert SE (1976) The mineralogy and geochemistry of near shore sediments. In: Riley JP, Chester R (eds) Chemical oceanography. Academic Press, London, pp 187–280

Calvert SE, Pedersen TF, Thunell RC (1993) Geochemistry of the surface sediments of the Sulu and South China Seas. Mar Geol 114:207–231

Calvert SE, Price NB (1983) Geochemistry of Nambian Shelf Sediments. In: Suess E, Thiede J (eds) Coastal upwelling and its sediment record. Plenum Press, New York, pp 337–375

Campbell JA, Loring DH (1980) Baseline levels of heavy metals in the waters and sediments of Baffin Bay. Mar Poll Bull 11:257–261

Canuel EA, Martens CS (1993) Seasonal variations in the sources and alteration of organic matter associated with recently deposited sediments. Org Geochem 20(5):563–577

Dilli K (1986) Geochronology and geochemistry of a sediment core from Bombay coast. Mahasagar Bull Natl Inst Ocean 19(2):87–95

Fitzgerald MG (1980) Anthropogenic influence on the sedimentary regime of an urban estuary-Boston Harbor. PhD Thesis, Woods Hole Oceanographic Institution, AZ, 297 pp

Förstner U, Patchineelam SR (1980) Chemical associations of heavy metals in polluted sediment from the Lower Rhine River. In: Particulates in water "advances in chemistry". Amer Chem Soc 189:177–193

Francois R (1988) A study on the regulation of the concentrations of some trace metals (Rb, Sr, Zn, Pb, Cu, V, Cr, Ni, Mn and Mo) in Saanich inlet sediments, British Columbia, Canada. Mar Geol 83:285–308

Fukushima K, Saino T, Kodama Y (1992) Trace metal contamination in Tokyo Bay, Japan. Sci of the Total Env 125:373–389

Furrer OJ, Gupta SK, Stauffer W (1983) Sewage sludge as a source of phosphorous and consequences of phosphorous accumulation in soils. In: L'Hermite P, Ott H (eds) Processing and use of sewage sludge. Kluwer, Dordrecht, pp 279–294

Gaudette HE, Flight WR, Toner L, Folger DW (1974) An inexpensive titration method for the determination of organic carbon in recent sediments. J Sed Petrol 44:249–253

Gogate SS, Sastry VN, Krishnamurty TM, Viswanathan R (1976) Chemistry of shelf sediments on the west coast of India. Curr Sci 39:171–174

Goldberg ED, Gamble E, Griffin JJ, Koide M (1977) Pollution history of Narragansett Bay as recorded in its sediments. Estu Coastal Shelf Sci 5:549–561

Govindaraju K (1989) 1989 compilation of working values and sample description for 272 geostandards. Geostandard Newslett 13:113

Hart BT (1982) Uptake of trace metals by sediments and suspended particulates: a review. Hydrobiologica 91:299–313

Harris NBW, Santhosh M, Taylor P (1994) Crustal evolution in South India: constraints from Nd isotopes. J Geol 102:139–150

Hashimi NH, Nair RR (1976) Carbonate components in the coarse fraction of western continental Shelf (northern part) of India. Indian J Mar Sci 5:51–57

Henry WM, Knapp KT (1980) Compound forms of fossil fuel fly ash emissions. Env Sci Tech 14(4):450–456

Hershelman GP, Schafer HA, Jan T.-K, Young DR (1981) Metals in marine sediments near a large California municipal outfall. Mar Poll Bull 12(4):131–134

Hirst DM (1962) The geochemistry of modern sediments from the Gulf of Paria-II: the location and distribution of trace elements. Geochim Cosmochim Acta 26:1147–1187

Hornberger MI, Luoma SN, Van Geen A, Fuller C, Anima R (1999) Historical trends in the sediments of San Francisco Bay, California. Mar Chem 64:39–55

Ingram RL (1970) Procedures in sedimentary petrology. Wiley, New York, pp 49–67

Kaiser HF (1958) The varimax criteria for analytic rotation in factor analysis. Psycometrica 23:187–200

Kelin LA, Long M, Nash N, Kirschner S (1974) Sources of metals in New York City waste water. J Water Poll Control 46:2653–2662

Knauer GA (1977) Immediate industrial effects on sediment metals in a clear environment. Mar Poll Bull 8(11):249–254

Krauskopf KB (1956) Factors controlling the concentrations of thirteen rare metals in sea-water. Geochim Cosmochim Acta 9:1–32

Loring DH (1976) The distribution and partition of zinc, copper and lead in the sediments of the Saquenay fjord. Can J Earth Sci 13:960–971

Loring DH (1978) Geochemistry of zinc, copper and lead in the sediments of the estuary and Gulf of St. Lawrence. Can J Earth Sci 15:757–772

Loring DH (1979) Geochemistry of cobalt, nickel, chromium, and vanadium in the sediments of estuary and Gulf of St. Lawrence. J Can Sci 21:1368–1378

Loring DH (1984) Trace metal geochemistry of sediments from Baffin Bay. Can J Earth Sci 21:1368–1378

Loring DH (1991) Normalization of heavy-metal data from estuarine and coastal sediments. ICES J Mar Sci 48:101–115

Loring DH, Nota DJG (1968) Occurrence and significance of iron, manganese and titanium in glacial marine sediments from the estuary of the St. Lawrence River. J Fish Res Board Can 25:2327–2347

Loring DH, Rantala RTT (1988) An intercalibration exercise for trace metals in marine sediments. Mar Chem 24:13–28

Loring DH, Rantala RTT (1992) Manual for the geochemical analyses of marine sediments and suspended particulate matter. Earth Sci Rev 32:235–283

Lowman FG, Phelps DK, McClin R, Roman DeVega V, Oliver De Padovani I, Garcia RJ (1966) Interactions of the environmental and biological factors on the distribution of trace elements in the marine environment. In: Disposal of radioactive wastes into seas, oceans and surface waters. IAEA,Vienna, pp 249–266

Luoma SN, Bryan GW (1981) A statistical assessment of the form of trace metals in oxidized estuarine sediments employing chemical extractants. Sci of the Total Env 17:165–196

Luoma SN, Jenne EA (1976) Estimating bioavailability of sediment-bound trace metals with chemical extractants. In: Hemphill DD (ed) Trace substances in environmental health. Univ Missouri Press, Columbia, MO, pp 343–351

Mac Donald DA (1991) Status and trends in concentrations of selected contaminants in Boston Harbor sediments and biota. NOAA Tech Mem NOS OMA 56

Mohapatra GP, Rao BR, Biswas NR (1992) Morphology and surface sediments of the eastern continental shelf off peninsular India. Geol Surv India Spec Pub 29:229–243

Oakley SM, Williamson KJ, Nelson PO (1980) The geochemical partitioning and bioavailability of trace metals in marine sediments: project completion report, OWRR A-044-ORE-W 73. Corvalis, Oregon State University, pp 1–84

Paropkari AL, Rao CHM, Murty PSN (1978) Geochemical studies on the shelf sediments off Bombay. Indian J Mar Sci 7:8–11

Pragatheeswaran V, Loganathan B, Ramesh A, Venugopalan VK (1986) Distribution of heavy metals and organic carbon in sediments off Madras and Visakhapatnam. Mahasagar-Bull National Inst Oceangr 19(1):39–44

Purnachandra Rao V, Mohan Rao K, Vora KH, Almeida F, Subramaniam MM, Souza CGA (1998) A potential phosphorite deposit on the continental margin off Chennai. Curr Sci 74(7):574–577

Rajamanickam GV, Setty MGAP (1973) Distribution of phosphorus and organic carbon in the nearshore sediments of Goa. Indian J Mar Sci 2:84–89

Raman AV (1995) Pollution effects in Visakhapatnam Harbour, India: an overview of 23 years of investigations and monitoring. Hegolander Meeresunters 49:633–645

Rao CHM (1978) Distribution of $CaCO_3$, Cu^{2+} and Mg^{2+} in sediments of the northern half of western continental shelf of India. Indian J Mar Sci 7:151–154

Rao CHM, Murty PSN (1990) Geochemistry of the continental margin sediments of the Central West Coast of India. J Geol Soc India 35:19–37

Rao UM, Sarma SN (1993) Geochemistry of sediments along the central east coast of India: part 1-major elements. Indian J Mar Sci 22:41–47

Ray SB, Rajagopalan G, Somayajulu BLK (1990) Radiometric studies of sediment cores from Gulf of Mannar. Indian J Mar Sci 19:9–12

Riley JP, Chester R (1971) Introduction to Marine Chemistry. Academic Press, London, 465 pp

Rozanov AG, Volkov II, Yagodinskaya TA (1974) Forms of iron in the surface layer of Black sea sediments. In: Degens ET, Ross DA (eds). The Black sea-geology-chemistry-biology. Amer Assoc Pet Geol Mem 20:532–541

Sahu BK (1973) Factor model applied to a sphericity and roundness data of quartz grains for modern sand. Bull Indian Geol Assoc 6:3–11

Salomons W, Förstner U (1984) Metals in Hydrocycle. Springer, Berlin Heidelberg New York, pp 63–98

Santhosh M, Kagami H, Yoshida M, Nandakumar V (1992) Pan-African charnockite formation in East Gondwana: geochronologic (Sm-Nd and Rb-Sr) and petrogenetic constraints. Bull Indian Geol Assoc 25:1–10

Satyanarayana D, Rao IM, Prasada Reddy BR (1985) Chemical oceanography of harbour and coastal environment of Viskhapatnam (Bay of Bengal): part I-trace metals in water and particulate matter. Indian J Mar Sci 14:139–146

Schropp SJ, Lewis FG, Windom HL, Ryan JD, Calder FD, Burney LC (1990) Interpretation of metal concentrations in estuarine sediments of Florida using aluminum as a reference element. Estuaries 3:227–235

Smith RV (1977) Domestic and agricultural contribution to the inputs of phosphorous and nitrogen to Lough Neagh. Water Res 11:453–459

Spencer DW, Degens TE, Kulbicki G (1968) Factors affecting elements distributions in sediments. In: Ahrens LH (ed) Origin and distribution of the elements. Pergamon Press, New York, 1178 pp

Subramanian V, Mohanachandran G (1990) Heavy metals distribution and enrichment in the sediments of southern east coast of India. Mar Poll Bull 21(7):324–330

Summers JK, Wade TL, Engle VD, Malaeb ZA (1996) Normalization of metal concentration in estuarine sediments from the Gulf of Mexico. Estuaries 19:581–594

Szefer P, Skwarzec B (1988) Distribution and possible sources of some elements in the sediment cores of the southern Baltic. Mar Chem 23:109–129

Taliadouri FV, Varnavas SP (1995) Geochemical and sedimentological patterns in the Thermaikos Gulf, North-west Aegean sea formed from a multicourse of elements. Estu Coastal Shelf Sci 40:295–320

Taylor SR (1964) Abundance of chemical elements in the continental crust: a new table. Geochim Cosmochim Acta 28:1273–1285

Thomson-Becker EA, Luoma SN (1985) Temporal fluctuations in grain size, organic materials and iron concentrations in intertidal surface sediment of San Francisco Bay. Hydrobiologia 129:91–107

Turekian K (1971) Rivers, tributaries and estuaries. In: Hood DW (ed) Impingement of Man on the oceans. Wiley, New York, pp 738

Van Geen A, Luoma SN (1999a) A record of estuarine water contamination from the Cd content of foraminiferal tests in San Francisco Bay, CA. Mar Chem 64:57–69

Van Geen A, Luoma SN (1999b) The impact of human activities on sediments of San Francisco Bay, California: an overview. Mar Chem 64:1–6

Warren LJ (1981) Contamination of sediments by lead, zinc and cadmium: a review. Env Poll Ser B2:401–436

White RJ Jr (1972) The distribution and concentrations of selected metals in Boston Harbor sediments. MSc Thesis (unpublished), Northeastern University,Boston, MA, 82 pp

Yiyang Z, Ming-cai Y (1992) Abundance of chemical elements in sediments from the Huanghe River, the Changjiang River and the continental shelf of China. Chin Sci Bull 37:23

Yiyang Z, Zhaoyang Q, Fengye L, Lijuan H, Jintu W (1988) A study on element-stratigraphy of Okinawa trough. Chin J Oceanol Limnol 6(2):145–156