

Geochemical and statistical approach for evaluation of heavy metal pollution in core sediments in southeast coast of India

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Received 16 October 2009; revised 6 February 2010; accepted 28 February 2010; available online 1 March 2010

ABSTRACT: Industrialization coupled with urbanization has led to stress in the Buckingham Canal which runs parallel to Bay of Bengal at a distance of around 1 km from the coastline. 4 sediment cores were collected along Ennore – Pulicat stretch to determine acid leachable trace metal concentration. Core samples were collected using gravity corer. The cores were sliced horizontally at 2.5 cm to determine the grain size, sediment composition, pH, organic matter, calcium carbonate, acid leachable trace metals; cadmium, chromium, copper, lead, zinc. The trace metals were extracted using acid mixture containing hydro fluoric acid, nitric acid and sulphuric acid and analysed by atomic emission spectrophotometer. In an attempt to infer anthropogenic input from geogenic input, several approaches including comparison with sediment quality guidelines – ecotoxicological sense of heavy metal contamination and classification by quantitative indexes such as geoaccumulation index, anthropogenic factor, enrichment factor, contamination factor and degree and pollution load index was attempted. Grain size analysis and sediment composition of core samples shows Ennore is sandy in nature having a neutral pH. Organic matter enrichment is observed to a higher extent in core 3. Core 2 at a depth of 5 cm shows organic matter of 9.4 %. calcium carbonate is totally absent at the surface sediments in core 2. Cores collected within the canal showed a higher heavy metal concentration than the cores collected from Pulicat lagoon and 2 km into the Ennore Sea. The trace metal concentration for cadmium, lead and zinc in Ennore does not pose a threat to the sediment dwelling fauna whereas chromium and copper are likely to pose a threat. Quantitative indexes place Ennore under moderately polluted. Ennore is likely to face a serious threat of metal pollution with the present deposition rates unless stringent pollution control norms are adopted.

Keywords: Core; Depth; Ennore; Pollution; Sediment; Trace metals

INTRODUCTION

Heavy metals are one of the serious pollutants in natural environment due to their toxicity, persistence and bioaccumulation problems (Pekey, 2006; Nouri *et al.*, 2006). The impact of anthropogenic perturbation is most strongly felt by estuarine and coastal environments adjacent to urban areas (Nouri *et al.*, 2008). Heavy metals from incoming tidal water and fresh water sources are rapidly removed from the water body and deposited onto the sediments (Tam and Wong, 2000; Samarghandi *et al.*, 2007). Over the last decades, the study of sediment cores has shown to be an excellent tool for establishing the effects of anthropogenic and natural processes on depositional environments. (Vinodhini and Narayanan, 2008; Nadia, 2009). Most of the contaminants can leave their finger prints in sediments. The only condition is the stability within sedimentary column, i.e. no or insignificant post-

depositional mobility is allowed (Tam and Wong, 2000). Sediment analysis offers certain advantages over water analysis for the control and detection of metal pollution in estuaries (Forstner and Wittman, 1983; Luamo, 1990), although its metal concentrations can also fluctuate over time (Araujo *et al.*, 1988) and it was observed the rate of change is well below that of the water (Boyden *et al.*, 1979). On the other hand, surface sediment often exchanges with suspended materials, thereby affecting the release of metals to the overlying water (Zvinowanda *et al.*, 2009). Therefore, the top few centimetres of the sediments reflect the continuously changing present-day degree of contamination, whereas the bottom sediments record its history.

Ennore has now become a major industrial complex. Metals are introduced into Ennore from domestic waste, industrial effluent, urban run-off, atmospheric deposition, as well as upstream run-off accumulate into the sediments. There is little information, however, on

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the impact of these industrial facilities on the environmental loading of heavy metals and particularly the extent to which marine and estuarine sediments have been contaminated by metal-rich waste discharges. The main objective of this study is to examine the metal concentrations in sediment cores along the Buckingham Canal, Ennore. Therefore, the study will attempt to evaluate the extent of heavy metal contamination from the surface to the bottom sediments and the degree to which heavy metals are influenced by other sedimentological parameters such as grain size, pH, sediment composition, and organic matter. The study was carried out for a period of nine months from June 2008 to February 2009. Analysis was carried out in Centre for Environmental Studies, Anna University Chennai. Heavy metals were analysed at Centre for Advanced Studies in Marine Biology, Parangpettai.

MATERIALS AND METHODS

Study area

Ennore Creek (Fig. 1) located in the north eastern part of Chennai City, Tamil Nadu is spread over an area of 4 km along the coast of Bay of Bengal. The creek lies

between Chennai City and Pulicat Lagoon which is 40 km North of Chennai city (Latitude 13° 15'N and Longitude 80° 19'E). Ennore Creek is a fresh/brackish water system, which is nearly 800 m wide and elongated in a NE–SW direction. Ennore Creek is complex, the average depth rarely exceeding 5 m in the non-monsoon period, being fed by Kortalaiyar River and the Buckingham Canal; it is also connected to the Pulicat brackish water lake on the northern side. Ennore is one of the major industrial regions of India, having two thermal power plants – North Chennai Thermal Power Station and Ennore Thermal Power Station both of them drawing coolant water from the creek. Manali industrial complex and the recently built Ennore satellite port are located in the northern section of the creek. The Buckingham Canal stretches as the Ennore creek in the north to Cooum River in the south and further southwards from there on. Several discharges enter this stretch of the Buckingham Canal from industrial sites such as Madras Refineries Ltd., (MRL), Indian Oil Corporation etc. Municipal discharges also enter Ennore through a number of drains from the north Chennai area.

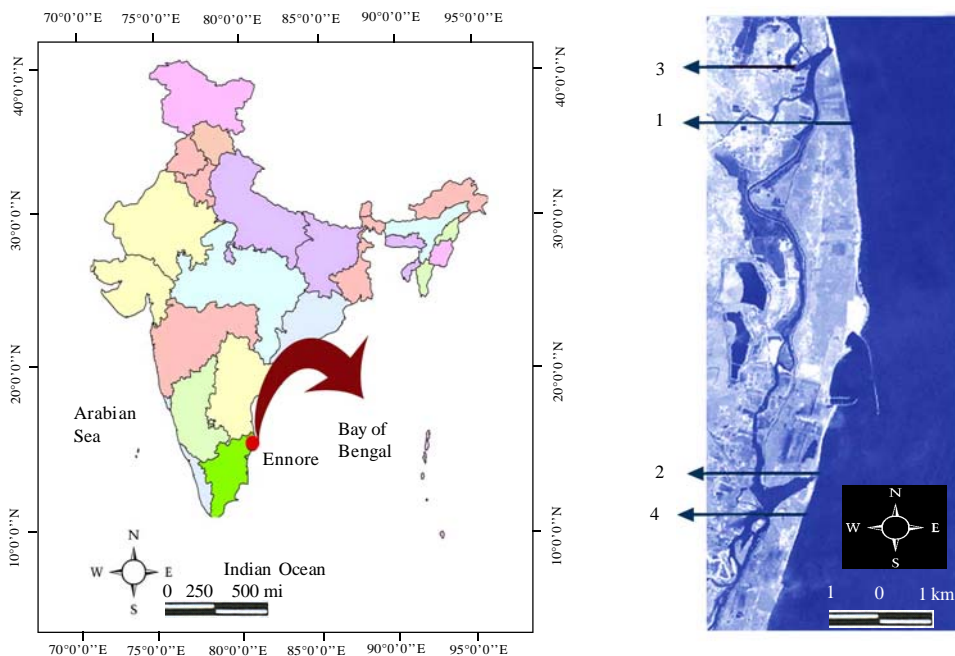


Fig. 1: Location of core sediment sampling station in Ennore, Bay of Bengal

Core collection

Four cores were collected along Ennore to Pulicat stretch (Fig. 1) each depicting an environment which is subjected to a of type anthropogenic stress. Aquafarms are situated along the banks of the canal, near Kattupalli region. There are a large number of aquafarms which run on a small scale basis. All these aquafarms draw water from and discharge their wastewater into the canal. The pollution from aquafarm discharges is less compared to the pollutant contribution from industrial discharges from the surrounding Ennore complex. Core 1 was collected near aquafarm discharge (13°21.419'N and 80°19.923' E). Industrial discharges are seen towards the southern side of the creek. Industrial discharges are loaded with sludge; thereby there is a notable reduction in the free flow of water almost forming a cess pool of stagnant water. Core 2 was collected from the industrial discharge location (13°13.413'N and 80°19.139'E). Two cores were collected from an area apparently unaffected by anthropogenic discharges viz. Pulicat lagoon (13°24.411'N and 80°19.505'E) and Ennore Sea (13°14'5".04N and 80°20'39".33). Core 3 was retrieved from Pulicat area which is located further north from Ennore can be said to relatively pristine as there is only limited or almost no disturbances from human activities, and is considered as a reference point for this study. Core 4 was collected at a distance of 2 km from the coast into Bay of Bengal to determine if the pollutants from the creek have dispersed into the sea and deposited onto the marine sediments.

Sediment cores (Acid washed PVC pipe of 1m length X 10 cm diameter) were collected from a boat on 18.7.2008. The sampling stations determined by GARMIN III global positioning system (GPS). The cores were inserted into the water-sediment interface and pushed to ensure that it reached maximum depth. The cores were slowly retrieved back, closed with its cover immediately and marked as to which is the upward direction. Water depth was measured using a tide pole. Salinity, temperature and dissolved oxygen (DO) of surface water were recorded in the field using a probe

as follows:- DO was measured using WTW Oxi 330i / SET, salinity using Cyberscan Con / TDS with 0.1 mS resolution and temperature was measured using a standard thermometer. Core from Ennore Sea was collected on 05.06.2008 with the help of National Institute of Ocean Technology (NIOT) research vessel Sagar Purvi using a gravity corer. All the cores were transported in a vertical position and frozen for a period of 4 days in vertical position. The cores were sliced at 2.5cm increments and the sediment samples were stored in clean labelled polythene covers. Subsamples obtained from core 1, 2, 3 and 4 were 15, 16, 15 and 8, respectively (Table 1).

Prior to the analysis, all the sediment samples were dried at 70-80 °C for 48 h using hot air oven. The shells in the sediment were handpicked. Raw samples were used to determine grain size and sediment composition. Part of the sample was powdered using agate mortar to estimate calcium carbonate, organic matter and heavy metals. Sediment composition was determined following Krumbein and Pettijohn (1938) method. Grain size analysis was done using a set of 10 sieves ranging from 2000 mm to 45 μ for 15 min using Rotop sieve shaker (Folk and Ward, 1957). GRADSTAT software was used to find out about the nature of the sediments. pH of the sediment samples were determined using pH meter. Calcium carbonate and organic matter were analyzed by adopting the procedure of Loring and Rantala (1992) and Gaudette et al. (1974), respectively. Geoaccumulation index was calculated using an equation given by Müller (1979). $I_{geo} = \log_2 (C_n / 1.5 * B_n)$. Anthropogenic factor (AF) was calculated for the cores collected. $AF = C_s / C_d$ (Szefer et al., 1998). AF is calculated with metal surface concentration and concentration at a depth which enables differentiation between geogenic and anthropogenic input of heavy metals, the results of which would indicate the extent of anthropogenic influence on metal deposition.

For determination of trace metals in sediments, the sediments were sieved using 230 μ and sediment sample was acid digested (Agemian and Chau, 1976; Voutsinou-Taliadouri, 1995). Trace metals were

Table 1: Core details

Core	Latitude (N)	Longitude (E)	Water depth in m	Core retrieval depth in cm	Number of subsamples
1-Aquafarm	13°21.419'	80°19.923'	0.77	40.0	15
2-Industrial discharge	13°13.413'	80°19.139'	0.16	42.5	16
3-Pulicat lagoon	13°24.411'	80°19.505'	0.9	40.0	15
4-Ennore Sea	13°14'5".04	80°20'39".33	6.8	20.0	8



determined by digestion with HF, HNO₃ and H₂SO₄ in a sealed Teflon vessel (Teflon bomb) using a hot plate. The digested samples were filtered with Whatman Grade “A” filter paper and the filtrate was analyzed for Cd, Cr, Cu, Pb and Zn in Optima emission spectrophotometer Optima 2100 Dy. To check the precision of the equipment Merck’s Multielement Standard Solution IV was used. Statistical analysis was carried out using SPSS (1995) to determine inter-element relationship.

RESULTS AND DISCUSSION

Temperature, salinity and DO of surface water were measured using a probe on site at the time of sampling (Table 4). The water column above core 1 recorded maximum DO of 5.4 mg/L was when compared to the other locations. The DO concentration in Ennore ranges from 1 to 6 mg/L (Kalaivani, 2007). This region receives only nutrient rich waters and there is no other source of pollutants capable of reducing the dissolved oxygen content of water. 0.7 mg/L the minimum dissolved oxygen content was observed in core 2. This location is characterized with high sludge content and the nature of sediments itself is blackish and gooey. DOD (2001) report showed that Ennore Creek is contaminated by sewage released from Buckingham Canal with nil to low DO and values of other elements were more or less within limits. This core location also has minimum

salinity value. Maximum salinity value of 30.6 ppt was recorded in core 3. For the sea core no surface water quality no data was obtained.

Grain size

Grain size analysis was carried out only for the surface sediments in each core. GRADSTAT analysis shows that all the core sediments are sandy in nature. Table 3 gives the detailed description of the sediments. The maximum d₅₀ value of 408.3 μm was observed in core 2 and the minimum d₅₀ value of 293.5 μm was observed in core 3. Fig. 2 shows the variations in statistics of grain size. Since trace metal concentrations usually increase with decreasing grain size of sediments, compensation for grain size differences is one of the most important normalization techniques for the detection and quantification of anomalous metal concentrations (Angelidis and Aloupi, 1997). Therefore, the coarser material in the sediments plays the role of the “diluent” affecting the total (bulk) metal concentration. In the present study, this was overcome by sieving the sediments and using only the fine grained sediments for estimation of the trace metals. Ennore sediments fall under the textural group sand. (Jayapraksh, 2002).

Sediment composition

Sediment composition was determined for all subsamples and the results are shown in Fig. 3. Sand was dominating except in core 3 wherein silt is present at slightly higher levels than sand. In core 1, the top 5 cm is composed of 40-45 % sand and silt whereas clay was present only at about 14-15 %. Below 5 cm depth, there was a variation in trend such that sand was present at higher percent ranging from 55 to 90, silt

Table 2: Surface water quality

Core	Temperature (°C)	Salinity (ppt)	DO (mg/L)
1	28.5	28.6	5.4
2	29.0	27.2	0.7
3	30.6	30.6	4.7
4	-	-	-

Table 3: Description of sediments

Core	d ₅₀ μm	Description	Sorting	Skewness	Kurtosis
1	353.3	Medium sand	Poorly sorted	Fine Skewed	Platykurtic
2	408.3	Medium sand	Poorly sorted	Symmetrical	Mesokurtic
3	293.5	Medium sand	Poorly sorted	Coarse Skewed	Mesokurtic
4	315.0	Medium sand	Poorly sorted	Coarse Skewed	Platykurtic

Table 4: I_{geo} classification and AF for core samples of Ennore

Core	I _{geo} Class					AF				
	Cd	Cr	Cu	Pb	Zn	Cd	Cr	Cu	Pb	Zn
Core 1	0	3	5	3	3	0	2.03	1.05	1.33	1.21
Core 2	0	6	3	5	4	0	1.03	0.92	0.55	0.88
Core 3	0	1	1	1	1	0	1.03	0.3	1.25	0.45
Core 4	0	2	1	2	1	0	0.83	1.04	0.45	0.83

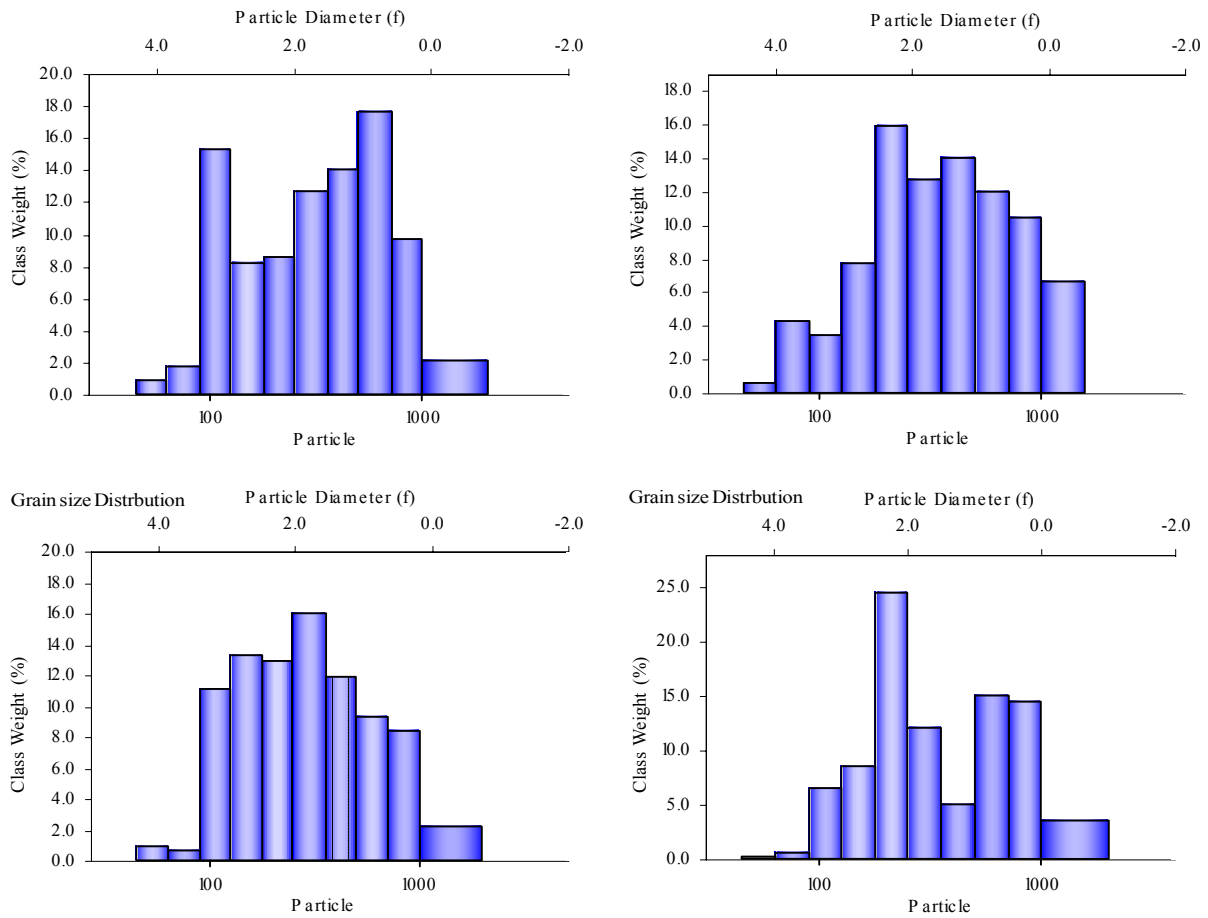


Fig. 2: Grain size variations

content dropped from 40 to 45 % to 5-30 % and clay content also reduced to 1-10 %. This suggested that the recent deposition of sediments is more of a silty sand nature rather than sandy. Core 2 as mentioned earlier shows higher silt content (45-66 %). The clay content was comparatively low and was 14-30 %. Sand content was higher than clay, but lesser than silt. Cores 3 and 4 were similar in their distribution of sediment composition viz. a total sand domination and clay and silt content present at lower fractions. But in core 3 sand was present at much higher fraction (89-94 %) whereas in core 4 sand was present only at 70-80 %. Silt and clay in core 3 was present at very low levels compared to the other cores. Large amounts of trace metals are bound in the fine-grained fraction (<63 mm) of the sediment, mainly because of its high surface area-to-grain size ratio and humic substance content (Horowitz and Elrick, 1987; Moore *et al.*, 1989). Results

from regression analysis (Table 12) showed that the metals correlated positively with clay. The metals in this fine-grained fraction are more likely to be biologically available than those in the bulk sediments (Bryan and Langston, 1992; Everaart and Fischer, 1992). Core 2 had high sand and clay content and it is this core that shows a comparatively higher concentration of trace metals.

pH

The accumulation of certain trace metals in sediments is directly or indirectly controlled by redox conditions through either a change in redox state (e.g., Re and U) and/or speciation (e.g., Mo). Other metals (e.g., Cd) have a single stable valence in aqueous solution but can be precipitated in the presence of dissolved sulfide (McKay, 2007). The down core variations in pH are shown in Fig. 4. The unevenness

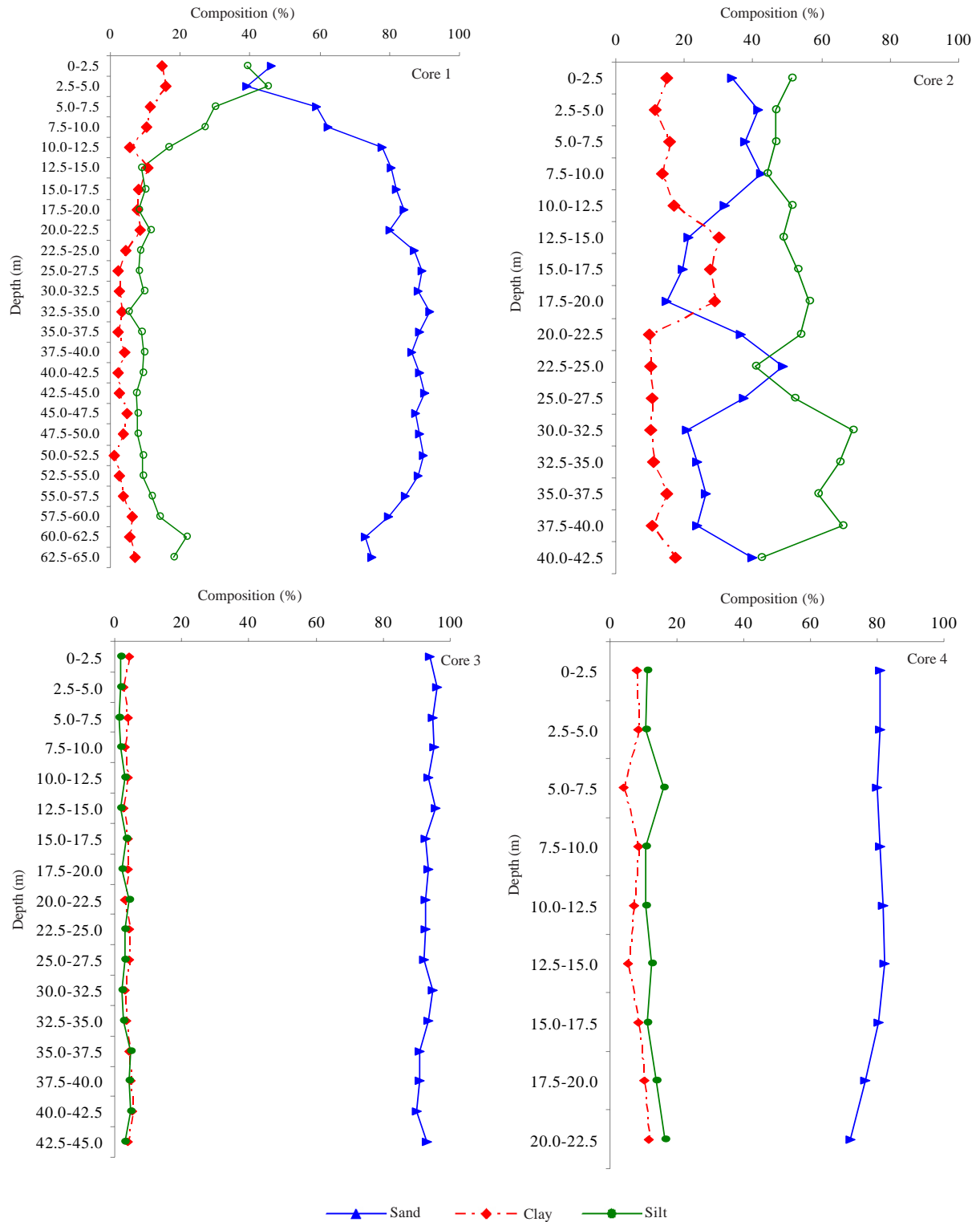


Fig. 3 Sediment composition of Ennore

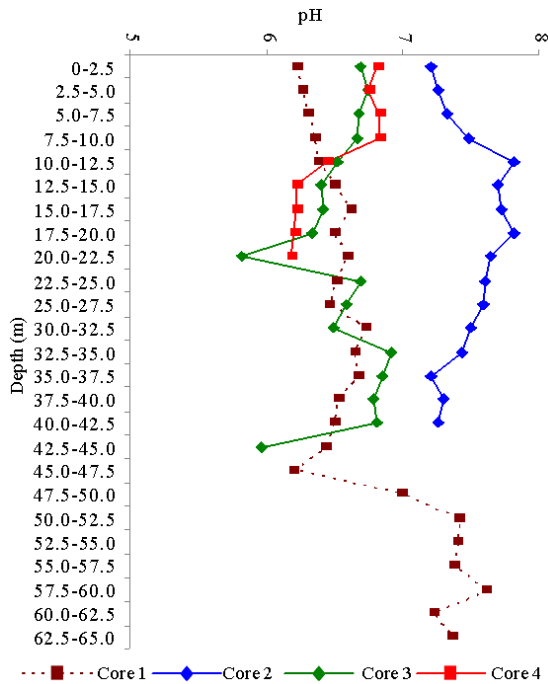


Fig. 4: Down core variations in sediment pH

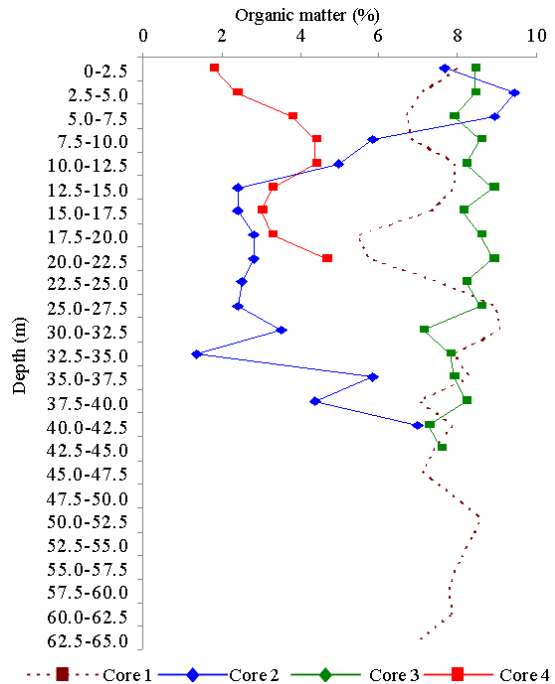


Fig. 5: Vertical profile of organic matter

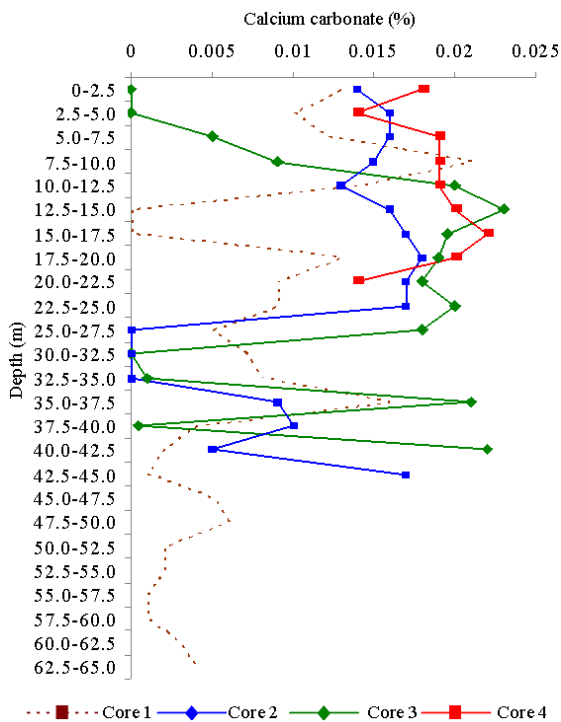


Fig. 6: Variations in calcium carbonate

in the length observed here is due to apparent variations in the core retrieval depth. pH for all the subsamples in the core lie in the range of slightly basic to neutral to slightly acidic. pH in core 1 was around 6.2-6.9 starting from surface subsample till a depth of 50 cm, but from 50 cm till 65 cm there was an increase in the pH (7.2-7.6). Highest pH viz. basic nature was observed in core 2, the reason may be the discharges from the industries are of basic nature. Cores 3 and 4 showed the least viz. a slightly acidic nature and this can be attributed to the natural state of sediments. On a closer observation in core 4 the top 10 cm showed pH values closer to neutral whereas the bottom sediments from a depth of 10 cm till 22.5 cm the pH values was at the range of 6.1-6.4. This indicated that only the recent sediment deposits have a pH value of about 6.7-6.8 and if this trend continues, they will become neutral in nature with time.

Organic matter

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. (Jonathan *et al.*, 2003). Decomposition of organic material produces organic ligands that may extract metals from the sediments which can effectively mobilize metals by increasing their concentration in the water (Fergusson 1990; Taulis 2005). Fig. 5 shows the depth variations in organic matter. Highest percentage of organic matter (9.4 %) was recorded in core 2 at a depth of 5 cm. Clays have high specific surface area and can directly trap heavy metals, but they also may act as a substrate for organic matter flocculation (Keil *et al.*, 1994) that in turn adsorbs metals. It is core 2 that relatively had a higher concentration of trace metals. The source for organic matter within the canal is high sedimentation rates and supply from river runoff (Muthumanickam, 2003). In core 1, the organic matter content varied from 7-9%. Overall higher organic matter was observed in core 3 at 8-9 %, the source being natural organic matter production rather than influence from other terrigenous sources. Organic matter content of about 1-5 % was observed in core 4 with higher concentration in the bottom sediments and lower concentrations at the surface sediments. Tam and Wong, (2000) suggested that the concentrations of organic matter in the fine-grained fraction of the sediment were often higher than that in the sand sized fraction.

Calcium carbonate

Vertical distribution of calcium carbonate is shown in Fig. 6. Calcium carbonate in all the four core samples indicated very low values ranging from 0 – 0.025 %. Surface sediments (top 5cm) of core 2 showed a total absence of calcium carbonate due to heavy sludge loading. In cores 1, 3 and 4 the source for calcium carbonate was related to the shell fragments present in the sediments. Core 1 showed calcium carbonate of 0.001 to 0.021 %. At depths of 12-15 cm, the calcium carbonate content dropped to 0 %. Similarly, in core 3 the calcium carbonate content dropped to 0 % between 25 to 35 cm. In core 2, between 12 to 25 cm calcium carbonate content of 0.02 to 0.018 % was observed. Cores 2 and 3 between 25-35 cm showed a total absence of calcium carbonate. Core 4, calcium carbonate was present at 0.02 to 0.019 %. In all the cores, below a depth of 5 cm the increase in calcium carbonate is due to reprecipitation and increase in

alkalinity generated by sulphate reduction (Gaillard *et al.*, 1989).

Down core profiles of acid leachable trace metals

Sediments represent one of the ultimate sinks for heavy metal discharge into the environment. A variety of processes lead to the association of heavy metals with solid phases, such as direct adsorption by fine-grained inorganic particles of clays, adsorption of hydrous ferric and manganic oxides which may in turn be associated with clays, adsorption on, or complexation with natural organic substances which may also be associated with inorganic particles, and direct precipitation as new solid phases (Gibbs, 1977). Fig. 7 shows the down core variations in the concentrations of acid leachable trace metals. Elemental sequence (ES) of the trace metal is in the order of Zn (0.6-3.7 ppm) > Cu (0.3-7ppm) > Cr (0.2-1.2 ppm) > Pb (0.031-0.1 ppm) > Cd (0-0.04 ppm).

Throughout the vertical profiles of cores 1, 3 and 4 Cd was totally absent. Cd was present in the top 7.5 cm at concentration ranging between 0.004 to 0.023 ppm in core 2. In all the other subsamples Cd is absent. All the cores collected for this study are within the canal and does not extend into the Ennore port area where there is higher possibility of Cd contamination from corrosion resistance paints. Hence the total absence or negligible concentration of Cd in the core samples. Cr behaviour in the core 1 was more or less uniform with its concentration varying at 0.2 to 0.8 ppm. In core 2 till top 10 cm Cu was present at greater concentration beyond a depth of 10 cm Cr dominates. Core 3 being the reference site for this study showed a lower concentration of all the trace metals throughout the core except Cu at depth of 35 cm which occurred at a concentration of 7.7 ppm. Cr again in core 4 showed a uniform trend in the vertical profile. At a depth of 15 cm, Cu concentration shot up to 1 ppm whereas at the same depth Cr and Zn concentration dropped to 0.3 and 0.4 ppm, respectively. Higher concentration of Cu at the surface sediments and bottom sediments (1.3 - 1.7 ppm) and lower concentrations in middle subsamples (0.3-1.0 ppm) was observed for core 1. A detailed study is needed to explain the recent but uniform increase in the concentrations of Cu over the years. In core 2, Cu behaves in a manner similar to that of Cr but a depth of 37.5 to 40.0 cm its concentration raised to about 2.5 ppm the highest concentration of Cu recorded throughout core 2. Core 3, although being

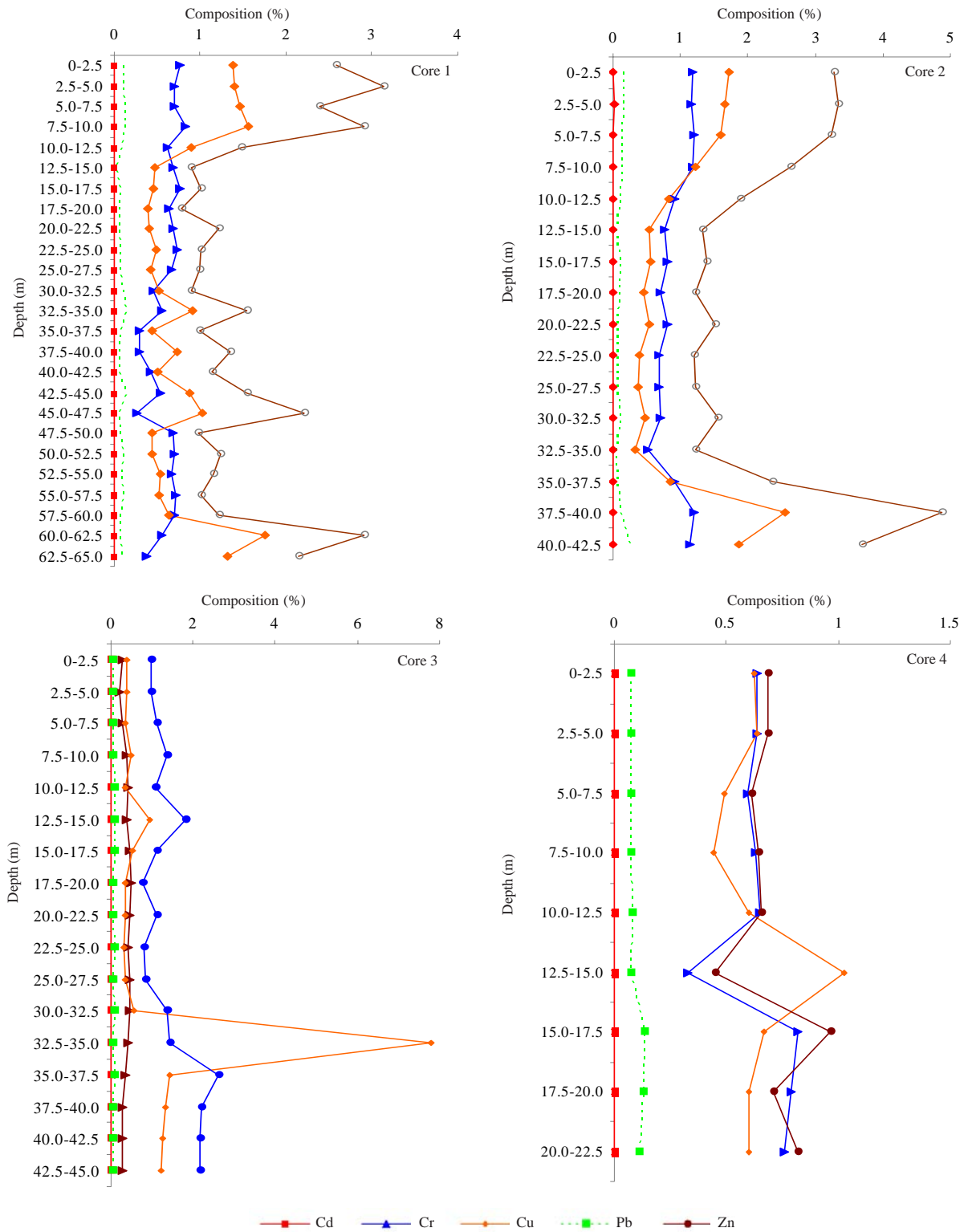


Fig. 7: Down core profile of acid leachable trace metals

reference site, showed a Cu concentration of 7.7 ppm at depth of 35 cm. This is the highest recorded trace metal concentration. Dating of the core would provide a vital indication of the presence of Cu at such a high concentration, but dating was beyond the scope of this study. Pb in core 1 did not show down core variation and was present at very low concentrations (0.04 to 0.1 ppm). In core 2, Pb concentration varies from 0.046 to 0.254 ppm. Core 3 showed a Pb concentration ranging from 0.039 to 0.076 ppm. Pb was present at a concentration of 0.4 to 1 ppm in core 4. Core 4 showed a slightly higher concentration of Pb due to the operation of marine fleet in the Bay of Bengal and greater chances of petrol and oil spillages which contain Pb as additive whereas within Ennore Pb concentration is lower owing to the fact that majority of the fishing activity takes place in tradition catamaran only a few people make use of engine boat for fishing.

The top 12 cm showed a Zn concentration of about 1.5-3 ppm. Below this depth, i.e. from 15-65 cm its concentration varied at about 1 ppm except at a depth of 60 cm where the concentrations shoot up to 2 ppm, dating of the sediments would give a clue for this sudden increase in its concentration. Otherwise it can be said it is the surface sediments that have higher concentration of Zn. Overall Zn is the highest occurring trace metal in cores 1 and 2. Zn has accumulated at higher concentrations at the surface sediments when compared to the bottom sediments. Even in Pulicat it is Zn that is seen to occur at higher concentration although not as high as observed in cores 1 and 2. In Core 3 the Zn concentration is 0.8 to 2 ppm. This is indicative that Zn has a higher background value compared to the other metals within the study area. On a closer observation it can be reported that Zn was present at a higher concentration even in Core 4, proving that Zn is naturally occurring at a higher concentration. Metal absorption capacity is in the order of sand < silt < clay, due to increases in surface area, minerals and organic matter as particle size decreased from sand to clay (Tam and Wong, 2000). Core 2 has higher content of silt and clay compared to sand and this core has higher concentration of heavy metal too. Pulicat being the reference for this study showed that occurrence of trace metal was found to be at very low concentrations which vouched for the fact that Pulicat is pristine and currently not polluted and contaminated from anthropogenic activities. Results of trace metal analysis from core 4 showed that this area is not under

the impact of human activities. Pollutants from Ennore have not dispersed into the sea and this is evident from core 4 that was collected at about 2 km into the Bay of Bengal from the coast.

Results from Regression analysis (Table 12) showed that Cu and Zn correlated positively with Zn in core 1. Cu was found to correlate positively with Zn. Organic matter in core 2 is positively correlated with all the heavy metals. This pointed out that deposition is near source and it has not yet moved to the fine clay fraction. Core 3 not much correlation is observed due to the low clay content and very high sand content (89 – 96 % sand). In core 4, clay correlated positively with Cr, Pb and Zn (R = 0.71, R = 0.65 and R = 0.64, respectively) showing heavy metal adhere to fine grained fraction. Cr and Pb, Cr and Zn, Pb and Zn are positively correlated indicating they are from the same anthropogenic source.

Geoaccumulation index

The geoaccumulation index (I_{geo}) introduced by Muller (1979) was used to assess metal pollution in sediments of Ennore. I_{geo} is expressed as follows:

$$I_{geo} = \log_2 (C_n / 1.5 \times B_n)$$

Where,

C_n - measured concentration of heavy metal in the sediment,

B_n - geochemical background value in average shale (Turekian and Wedepohl 1961) of element n,

1.5 is the background matrix correction in factor due to lithogenic effects.

Geoaccumulation index classes to assess sediment quality

- < 0 Uncontaminated
- 1 Uncontaminated to moderately contaminated
- 2 Moderately contaminated
- 3 Moderately to highly contaminated
- 4 Highly contaminated
- 5 Highly to very highly contaminated
- 6 Very highly contaminated

I_{geo} calculation was carried out only for the surface sediment in each core. The calculated values for Ennore and its surrounding marine environment are given in Table 4.

Ennore is uncontaminated with respect to Cd. Cr in core 2 falls under class 6 indicating very high contamination. Core 3 being reference for this study falls under the category 1. Uncontamination or moderate contamination was observed in Ennore Sea.

Table 5: Heavy metal enrichment factor in core sediments of Ennore

Station	DEPTH (cm)	EF (Cd)	EF (Cr)	EF (Cu)	EF (Pb)	EF (Zn)
Core 1	0 – 2.5	0	1.51	4.77	0.89	4.88
	2.5 – 5.0	0	1.51	5.28	0.93	6.48
	5.0 – 7.5	0	1.41	5.09	0.97	4.56
	7.5 – 10.0	0	1.54	5.07	0.92	5.15
	10.0 – 12.5	0	3.25	8.24	1.95	7.40
	12.5 – 15.0	0	11.67	13.87	1.85	14.60
	15.0 – 17.5	0	2.02	2.10	0.74	2.52
	17.5 – 20.0	0	3.7	3.99	1.19	4.35
	20.0 – 22.5	0	1.44	1.51	0.53	2.45
	22.5 – 25.0	0	1.43	1.67	0.53	1.88
	25.0 – 27.5	0	1.35	1.50	0.56	1.91
	27.5 – 30.0	0	2.58	5.19	2.39	4.86
	30.0 – 32.5	0	1.36	3.88	1.40	3.64
	32.5 – 35.0	0	1.34	3.36	1.15	4.25
	35.0 – 37.5	0	1.37	6.04	1.09	6.06
	37.5 – 40.0	0	1.42	2.92	0.76	3.60
	40.0 – 42.5	0	1.35	3.85	1.39	3.68
	42.5 – 45.0	0	1.35	9.04	1.09	10.61
	45.0 – 47.5	0	1.35	1.52	0.56	1.82
	47.5 – 50.0	0	1.36	1.34	0.75	2.06
	50.0 – 52.5	0	1.23	1.92	0.74	2.23
	52.5 – 55.0	0	1.36	1.78	0.83	1.87
	55.0 – 57.5	0	1.39	2.34	0.61	2.44
	57.5 – 60.0	0	1.46	7.10	0.69	6.43
	60.0 – 62.5	0	1.29	7.83	1.16	7.00
	62.5 – 65.0	0	1.29	7.81	1.10	7.00
Core 2	0 – 2.5	2.90	2.84	7.16	1.52	7.50
	2.5 – 5.0	15.02	2.52	6.28	1.38	6.87
	5.0 – 7.5	5.73	2.57	5.85	1.19	6.52
	7.5 – 10.0	0	3.40	6.12	1.58	7.21
	10.0 – 12.5	0	2.05	3.16	1.10	3.96
	12.5 – 15.0	0	1.71	2.06	0.51	2.79
	15.0 – 17.5	0	1.72	2.04	0.92	2.80
	17.5 – 20.0	0	1.66	1.85	0.78	2.70
	20.0 – 22.5	0	1.82	2.12	0.73	3.24
	22.5 – 25.0	0	1.61	1.57	0.60	2.65
	25.0 – 27.5	0	1.55	1.45	0.57	2.58
	27.5 – 30.0	0	1.54	1.76	0.92	3.15
	30.0 – 32.5	0	0.96	1.03	0.38	2.12
	32.5 – 35.0	0	2.19	3.50	0.75	5.36
	35.0 – 37.5	0	3.22	11.81	1.33	12.36
	37.5 – 40.0	0	2.65	7.49	2.66	8.16
Core 3	0 – 2.5	0	1.83	4.42	1.18	6.26
	2.5 – 5.0	0	1.46	4.40	1.19	6.28
	5.0 – 7.5	0	1.22	2.48	0.87	4.59
	7.5 – 10.0	0	1.31	2.96	0.70	4.45
	10.0 – 12.5	0	1.28	1.97	0.81	3.22
	12.5 – 15.0	0	2.32	10.11	2.17	10.46
	15.0 – 17.5	0	1.23	2.50	0.82	2.87
	17.5 – 20.0	0	1.18	1.45	0.49	1.77
	20.0 – 22.5	0	1.21	1.55	0.48	2.79
	22.5 – 25.0	0	1.16	1.48	0.66	2.04
	25.0 – 27.5	0	1.17	1.56	0.56	2.09
	27.5 – 30.0	0	1.18	2.47	0.87	3.25
	30.0 – 32.5	0	3.10	97.71	1.43	9.82
	32.5 – 35.0	0	1.97	14.30	1.54	14.51
	35.0 – 37.5	0	3.18	27.33	1.81	24.53
	37.5 – 40.0	0	3.13	25.95	1.70	24.42
40.0 – 42.5	0	3.12	24.99	1.68	24.27	
42.5 – 45.0	0	3.11	25.29	1.65	24.41	
Core 4	0 – 2.5	0	1.49	2.55	0.79	1.53
	2.5 – 5.0	0	1.51	2.62	0.79	1.54
	5.0 – 7.5	0	1.50	2.14	0.80	1.46
	7.5 – 10.0	0	1.49	1.82	0.76	1.44
	10.0 – 12.5	0	1.51	2.43	0.82	1.45
	12.5 – 15.0	0	1.51	8.15	1.44	1.95
	15.0 – 17.5	0	2.01	2.83	1.50	2.24
	17.5 – 20.0	0	2.05	2.71	1.50	1.75
	20.0 – 22.5	0	1.98	2.70	1.31	2.02

At all, it is core 2 that showed high contamination for all the heavy metals.

Anthropogenic factor (AF)

In order to evaluate the data in detail, the anthropogenic factors of elements in the cores were calculated according to the following formula,

$$AF = C_s / C_d \text{ (Szefer et al., 1998)}$$

Where, C_s and C_d refer to the concentrations of the elements in the surface sediments and at depth in sediment column. According to Ruiz-Fernández et al., (2001), if AF is >1 for a particular metal, it means contamination exists; otherwise, if AF is ≤ 1, there is no metal enrichment of anthropogenic origin. AF for the cores collected in Ennore is tabulated in Table 4.

Cd had no anthropogenic enrichment since Cd was absent. Cr has metal enrichment in all cores except in core 4 proving that pollutants have not got dispersed and deposited onto the marine sediment. Cu in cores 2 and 3 have no anthropogenic origin. Zn showed anthropogenic input in core 1. On the whole, it was core 1 that showed higher anthropogenic input compared to the other cores.

Enrichment factor (EF)

EF was calculated to determine if levels of metals in sediments of Ennore and its surrounding marine environment were of anthropogenic origins (e.g., contamination). To identify anomalous metal

concentration, geochemical normalization of the heavy metals data to a conservative element, such as Al, Fe, and Si was employed. Several authors have successfully used iron to normalize heavy metals contaminants (Schiff and Weisberg, 1999; Baptista Neto et al., 2000; Mucha et al., 2003). In this study, iron was also used as a conservative tracer to differentiate natural from anthropogenic components. According to Ergin et al., (1991), the metal EF is defined as follows:

$$EF = \frac{(M / Fe)_{sample}}{(M / Fe)_{Background}}$$

EF values were interpreted as suggested by Birch (2003) where EF < 1 indicates no enrichment, < 3 is minor; 3-5 is moderate; 5-10 is moderately severe; 10-25 is severe; 25-50 is very severe; and > 50 is extremely severe. Table 5 gives Heavy metal Enrichment Factor in core sediments of Ennore. Cd in all the cores showed no enrichment except in core 2. The surface sediments showed minor, severe and moderately severe enrichment in the top 7.5 cm, respectively indicating increase in Cd concentration in the recent few years due to the close proximity of this site to industrial discharges. Cr in cores 1 and 4 showed minor enrichment throughout the vertical profile except at a depth of 15 cm in core 1 which shows severe enrichment. Cores 2 and 3 have minor to moderate Cr enrichment. Cu enrichment down the cores 1, 2 and 4 is highly variable with minor, moderate and moderately severe enrichment. The same holds good for 3 as well but the enrichment factor shoots upto 97.71. The raise in value is due to the higher concentration of the heavy metal recorded at a depth of about 35 cm. Pb shows no enrichment in all the four cores. Moderate to moderately severe enrichment is observed for Zn in the cores collected from Ennore.

Contamination factor (CF) and degree of contamination

Hakanson (1980) had suggested a contamination factor (C_p^i) and the degree of contamination (C_d) to

Table 6: Classification of contamination factor and contamination degree

C_f^i	C_d	Status
$C_f^i < 1$	$C_d < 7$	Low degree of contamination
$1 < C_f^i < 3$	$7 < C_d < 14$	Moderate degree of contamination
$3 < C_f^i < 6$	$7 < C_d < 28$	Considerable degree of contamination
$C_f^i > 6$	$C_d > 28$	Very degree of contamination

Table 7: Contamination factor and contamination degree

	C_f^i Core 1	C_f^i Core 2	C_f^i Core 3	C_f^i Core 4
Cd	0.00	0.00	0.00	0.00
Cr	1.63	2.49	1.00	1.77
Cu	0.74	0.92	1.00	0.59
Pb	1.54	2.06	1.00	1.85
Zn	1.10	1.59	1.00	0.49
Contamination degree C_d				
	Core 1	Core 2	Core 3	Core 4
	5.01	7.06	4.00	4.69

Table 8: Pollution load index

Metal	Pollution load	Index
Cd	0.00	Not polluted
Cr	1.48	Polluted
Cu	1.25	Polluted
Pb	0.98	Not polluted
Zn	0.97	Not polluted

Table 9: Concentration of heavy metal in Ennore and its comparison with SQGs

Element mg/kg	Sampling stations				SQG non- polluted (mg/kg)	SQG moderately polluted (mg/kg)	SQG Heavily Polluted (mg/kg)
	Core 1	Core 2	Core 3	Core 4			
Cd	0.00	0.00	0.00	0.00	-	-	-
Cr	60	91	37	65	<25	25-75	>75
Cu	80	100	108	63	<25	25-50	>50
Pb	9	10	5	9	<40	40-60	>60
Zn	155	225	141	69	<90	90-200	>200

Table 10: Sediment quality guideline and definitions used

Sediment guideline	Description
Effect range low (ERL)/ Effect range median (ERM)	Adverse effect infrequent
Threshold effect level (TEL)/ Probable effect level (PEL)	Adverse effect likely to occur

Table 11: Ecotoxicological sense according to SQGs for Ennore

Element mg/kg	Sampling stations				TEL mg/kg	PEL mg/kg	ERL mg/kg	ERM mg/kg
	Core 1	Core 2	Core 3	Core 4				
Cd	0.00	0.00	0.00	0.00	0.68	4.20	1.20	9.60
Cr	60	91	37	65	52.30	160.00	81.00	370.00
Cu	80	100	108	63	18.70	110.00	34.00	270.00
Pb	9	10	5	9	30.20	110.00	46.70	218.00
Zn	155	225	141	69	124.00	270.00	150.00	410.00

describe the contamination (Table 6) of given toxic substance given by:

$$C_f^i = C_{0-1}^i / C_n^i \text{ and } C_d = \sum_{i=1}^7 C_f^i$$

Where, C_{0-1}^i is the mean content of the substance;

C_n^i is the reference value for the substance.

Core samples collected from Ennore fall under the category of low to moderate contamination. Degree of contamination was low except for core 2 which showed C_d 7.06 marginally falls under moderate contamination (Table 7).

Pollution load index (PLI)

Tomlinson *et al.* (1980) had employed a simple method based on pollution load index to assess the extent of pollution by metals in estuarine sediments. Sediment pollution load index was calculated using the equation:

$$CF = C_{\text{metal}} / C_{\text{background}}$$

$$PLI = \sqrt[n]{(CF_1 \times CF_2 \times CF_3 \times \dots \times CF_n)}$$

Where, CF is the contamination factor,

C_{metal} is the concentration of pollutant in sediment

$C_{\text{background}}$ is the background value for the metal

n is the number of metals.

The PLI value > 1 is polluted whereas < 1 indicates no pollution.

Table 8 gives PLI calculation. Results showed that Ennore is not polluted as far as Cd, Zn and Pb is considered but polluted for Cr and Cu.

Assessment of sediment pollution based on sediment quality guidelines

The primary purpose of sediment quality guidelines (SQGs) are to protect aquatic biota from the harmful and toxic effects related with sediment bound contaminants and is a useful tool for evaluating potential for contaminants within sediment to induce biological effects (Spencer and Macleod, 2002). Sediments were classified as non-polluted, moderately polluted, based on SQGs of USEPA (Perin *et al.*, 1997). According to SQGs, Cr was under the category heavily polluted in core 2 whereas in other cores it was Moderately Polluted. Ennore was seen to be heavily polluted with Cu whilst not polluted in case of Pb and Zn (Table 9).

Ecotoxicological sense of heavy metal contamination

The ecotoxicological sense of heavy metal contamination in sediments was determined using SQGs developed for marine and estuarine ecosystem (Bakan and Ozkoc, 2007). Table 11



Table 12: Correlation coefficient matrix of sedimentological parameters and heavy metals from Ennore, Southeast coast of India (P < 0.05)

Core 1									
	Sand	Clay	Silt	CaCO ₃	OM	Cr	Cu	Pb	Zn
Sand	1.00								
Clay	-0.91	1.00							
Silt	-0.99	0.82	1.00						
CaCO ₃	-0.44	0.38	0.44	1.00					
OM	0.27	-0.48	-0.18	-0.30	1.00				
Cr	-0.38	0.43	0.33	0.12	-0.05	1.00			
Cu	-0.72	0.54	0.76	0.34	-0.19	0.03	1.00		
Pb	-0.30	0.08	0.37	0.24	0.15	0.26	0.45	1.00	
Zn	-0.79	0.61	0.82	0.36	-0.23	0.07	0.96	0.42	1.00

Core 2									
	Sand	Clay	Silt	CaCO ₃	OM	Cr	Cu	Pb	Zn
Sand	1.00								
Clay	-0.55	1.00							
Silt	-0.73	-0.17	1.00						
CaCO ₃	0.00	0.51	-0.42	1.00					
OM	0.45	-0.18	-0.38	-0.37	1.00				
Cr	0.38	-0.12	-0.35	-0.33	0.87	1.00			
Cu	0.24	-0.21	-0.11	-0.45	0.73	0.39	1.00		
Pb	0.34	-0.03	-0.38	-0.12	0.69	0.28	0.72	1.00	
Zn	0.23	-0.26	-0.06	-0.46	0.73	0.37	0.90	0.99	1.00

Core 3									
	Sand	Clay	Silt	CaCO ₃	OM	Cr	Cu	Pb	Zn
Sand	1.00								
Clay	-0.85	1.00							
Silt	-0.93	0.60	1.00						
CaCO ₃	0.29	-0.25	-0.26	1.00					
OM	0.33	-0.39	-0.23	0.50	1.00				
Cr	0.03	-0.22	0.05	-0.15	0.19	1.00			
Cu	-0.08	0.02	0.09	-0.49	-0.27	0.07	1.00		
Pb	0.28	-0.40	-0.20	-0.08	0.03	0.55	-0.12	1.00	
Zn	-0.50	0.33	0.52	-0.20	-0.43	-0.45	0.23	-0.09	1.00

Core 4									
	Sand	Clay	Silt	CaCO ₃	OM	Cr	Cu	Pb	Zn
Sand	1.00								
Clay	-0.72	1.00							
Silt	-0.73	0.05	1.00						
CaCO ₃	0.43	-0.38	-0.24	1.00					
OM	-0.38	0.12	0.43	-0.04	1.00				
Cr	-0.54	0.71	0.08	-0.05	0.08	1.00			
Cu	0.23	-0.24	-0.09	0.18	-0.28	-0.62	1.00		
Pb	-0.58	0.65	0.20	0.25	0.06	0.77	-0.05	1.00	
Zn	-0.44	0.64	0.01	0.00	-0.01	0.90	-0.39	0.79	1.00

outlines sediment quality guideline and definitions used. Impacts would be observed on all sediment dwelling fauna.

Cr and Cu in cores 1, 2 and 4 exceed TEL values which can lead to adverse impact on the sediment dwelling fauna (Table 11). Core 3 does not exceed the guideline thereby proving that Pulicat is uncontaminated. Pb and Zn again do not exceed the guideline concentrations.

CONCLUSION

Ennore’s sandy environment (80-90 %) had pH

values ranging between 5.97-7.81. High percentage of organic matter was found in core 3 (7.8 to 8.2 % as compared to 1.3 to 8 %). Calcium carbonate was present at very low percentage (0-0.025). Results of trace metals concentration in the cores collected from Buckingham Canal, Ennore show considerable amount of trace metal accumulation. Zn is found to be the highest occurring trace metal and Cd was the least occurring trace metal. The distribution patterns of Cd, Cr, Cu, Pb and Zn were controlled by the distribution of the fine-grained fraction in the sediments. Cd was absent in all cores and Pb was almost absent except in core 4. Core 4 results

showed that pollutants present in Ennore had not dispersed into the Bay of Bengal. Among the studied trace metals only Cr and Cu was of concern, which occasionally may be associated with adverse biological effects based on the comparison SQGs technique. This requires biological and ecological studies to elucidate the impact of Cr and Cu on the organisms of Ennore. Furthermore, with respect to the quantitative indexes, the sediments of Ennore are considered to be moderately polluted.

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How to cite this article: (Harvard style)

Seshan, B. R. R.; Natesan, U.; Deepthi, K., (2010). Geochemical and statistical approach for evaluation of heavy metal pollution in core sediments in southeast coast of India. Int. J. Environ. Sci. Tech., 7 (2), 291-306.