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HEAVY METALS AND ECOLOGICAL RISK ASSESSMENT IN MARINE SEDIMENTS OF CHENNAI, INDIA

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Abstract: Enrichment of surface sediment with heavy metals (Cu, Cr, Ni, Pb and Zn) poses potential ecological risks off Chennai in the Bay of Bengal, India. The geo-accumulation index (I_{geo}) revealed that the value of Cr was typically high for all the sampling locations. Enrichment factor (EF) and Pollution Load Index (PLI) values showed that the northern part of the study area was more contaminated by heavy metals than the southern part. The silt content showed strong positive correlation with most of the metals as revealed by correlation matrix values. Multivariate statistical analyses indicated that Fe oxides, which usually concentrated in the fine particles, controlled the distribution of heavy metals. This study suggested that heavy metal input to the Chennai coast should be regulated in the future, particularly with regard to Cu, Cr and Ni, on the basis of Threshold Effect Level (TEL) and Effects Range-Low (ER-L) benchmarks. The results presented in this paper could be helpful in monitoring the further increase of heavy metal levels in the marine sediments along the coastal region.

Keywords: Marine Sediment, Heavy metals, Enrichment factor, Geo-accumulation index, Pollution load index, Bay of Bengal

1. INTRODUCTION

Heavy metals are introduced to the marine environment by domestic and industrial activities as anthropogenic pollutants. Much of this input ultimately accumulates in the estuarine zone and continental shelf, which are important sinks for suspended matter and associated land-derived contaminants (Leong &Tanner, 1997). The analysis of heavy metals in marine sediment is widely used to assess longer term anthropogenic inputs into the marine environment. In many places, it started more than decades ago and the contamination level is increasing day-by day without any major process to control the level of pollution (Fukushima et al., 1992; Zhao & Yan, 1992; Ravichandran et al., 1995; Dassenakis et al., 1996; Li et al., 2010). This type of contamination disturbs the aquatic environment severely and also affects the adjacent coastal zone area with major ecological degradation (Jonathan & Rammohan, 2003; Selvaraj et al., 2004; Jonathan et al., 2004; Janaki Raman et al., 2007; Stephen-Pichaimani et al., 2008). Metal contamination of surface sediments could directly affect the seawater quality, resulting in potential consequences to the sensitive lowest levels of the food chain and ultimately to human health (Christophoridis et al., 2009).

Sediments act as sinks and sometimes potential sources of various contaminants in aquatic systems. The accumulation and distribution of metals within the aquatic environment is governed by complex processes of material exchange affected by various anthropogenic activities and/or natural processes, including riverine or atmospheric inputs, coastal and seafloor erosion, biological activities, water drainage, and discharge of urban and industrial wastewaters (Christophoridis et al., 2009).

Sediments are heterogeneous mixtures that include mineral phases (Fe and Mn oxides) and detrital organic matter (Förstner, 1990).

Contaminants may bind to these phases by adsorption, precipitation, and co-precipitation (Allen, 1994) and element mobility is controlled by both the properties of the binding phase and binding mechanisms. In assessing the impact of heavy metal pollution on estuarine, coastal, and marine environment, various reference methods and quantification methods have been used (Zhou et al., 2007; Idris, 2008; Christophoridis et al., 2009; Li et al., 2010; Qi et al., 2010).

India has a long coastline of 8,129 km and of this 6,000 km is rich in estuaries, creeks, brackish water and lagoons. The southeast coast of India is an important stretch of coastline with many significant landmark features, where many major rivers drain into the Bay of Bengal and also richer in marine fauna than the western coast of India (Jonathan et al., 2008). The present study focuses on the level of heavy metals concentration and their ecological risk assessment in coastal environment off Chennai, southeast coast of India.

2. MATERIALS AND METHODS

2.1. Study area and sampling

Chennai is the fourth largest city in India and the capital of the Indian state of Tamilnadu located on the southeast coast of the Bay of Bengal (Fig. 1).

The average wind speed along the Chennai coast is 14.82 km/h year round. The deepwater significant wave height varies predominantly between 0.5 and 1m during February to April, 1 and 2.5m during May to September, and 1 and 2m during October to January. Tides in this region are predominantly semi-diurnal, with an average spring tidal range of about 1m and an average neap tidal range of about 0.41m. The average surface and bottom current speed along the Chennai coast is 0.16 m/s. Two rivers meander through Chennai, the Cooum River (or Kuvam) through the centre and the Adayar River to the south. The Cooum river originates from the surplus waters from the Cooum tank in Thiruvallur taluk. The catchment of the river is about 290 Km^2.

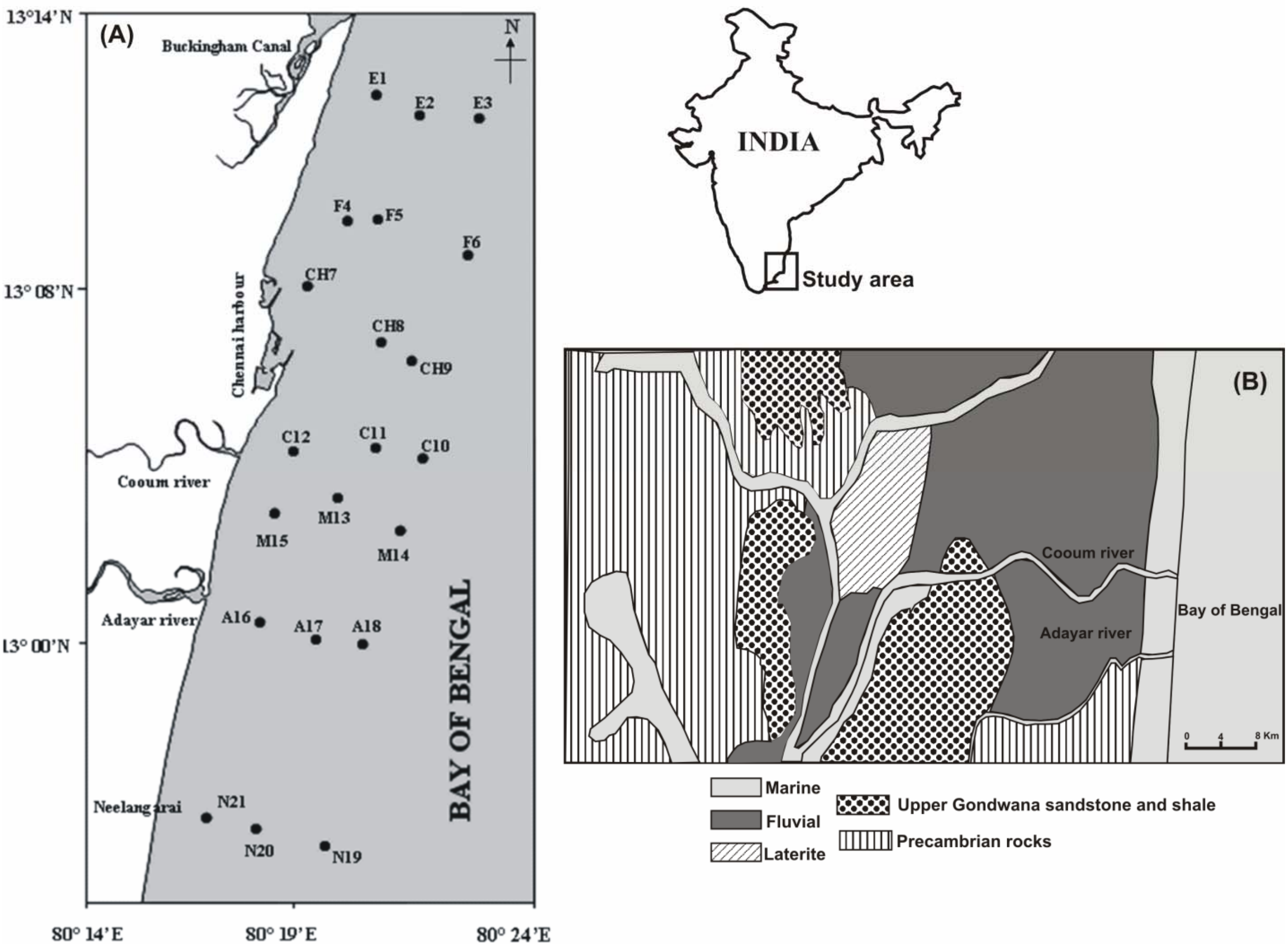

Figure 1. The study area map (A) The sediment sampling sites in the Chennai coast (Note: E – Ennore; F – Fishing harbour; CH – Chennai harbour; C – Cooum river; M – Marina; A – Adyar river; N – Neelangarai), (B) The geological background of Cooum and Adayar rivers.

The length of the river is about 65 km of which 18 km fall within the city limits. Cooum River runs towards east direction in Chennai city. The major part of Chennai city's treated and untreated sewages are channelized through Cooum river to the sea. This river also serves as a conveyor of storm water from the city's sewage drain network. The bed slope of the river is very mild. This, together with the formation of sand bar at the river mouth and a tidal range below 1.2m prevent the effective flushing of the river during the ebb tide. As a result, for periods other than monsoon, the stagnant river is anoxic and very rich in organic matter. There is periodic reversal of this trend only at the river mouth due to weak tidal effect. Adayar River is located south of the Cooum River. The length of the Adayar river is 42 km with the catchment area of 860 km^2. The surplus of Chemparabakkam tank causes flood in this river. It also flows towards the east direction. A total of 58 drain outlets discharge into Adayar between the stretch of Jafferkhanpet and Thiru Vivekannanda Nagar Bridge. According to Gowri & Ramachandran (2001), about 0.775 mld of industrial effluents carrying heavy metals and about 8.1 mld of domestic sewage are allowed to flow into Adayar river. The sand bar nearby Adayar river mouth also prevents tidal flushing (Shanmugam et al., 2007). The northern part of the study area has high alluvium and red soils. The most conspicuous relief of the area is the ferricrete surfaces (Achyuthan and Thirunavukarasu, 2009). Almost the entire area is covered by Pleistocene/ Recent alluvium, deposited by the two rivers, namely, Cooum and Adayar. Nearly 40,000 hut dwelling families are living along Cooum and Adayar riverbanks at several locations. The thickness of this formation ranges from a few meters in the southern parts to as much as 50m in the central and northern parts, with an average of 20 to 25m. This alluvium is made up of mainly clays, sands, sandy clays and occasional boulder/ gravel zones. Sandy areas are found along the river banks and coasts. Igneous/ metamorphic rocks are found in the southern area. The marine sediments containing clay-silt sands and charnockite rocks are found in the eastern and northern parts. The western parts are composed of alluvium and sedimentary rocks. A thin layer of laterites is also found at some places. Well rounded pebbles and small boulders have been encountered at several locations at varying depths. It is seen that in general, the eastern coastal zone is predominantly sandy, while the northwestern region is mostly clayey in nature (Boominathan et al., 2008). The city is served by two major ports, Chennai Port, one of the largest artificial ports, and Ennore Port. Chennai port is the largest ports in the Bay of Bengal and is India's second busiest container hub, handling automobiles, motorcycles and general industrial cargo. A smaller harbour at Rayapuram is used for local fishing boats and trawlers.

Twenty-one surface sediment samples were collected from southern Ennore to Neelangarai at 10m, 15m and 20m water depths in July 2008 during a Cruise onboard the Research Vessel "Sagar Paschimi", using a Van Veen grab sampler. Differential Global Positioning System (DGPS - Trimble) was used to determine the geo-coordinate points of the sampling locations. The water depth at each sampling point was determined using Multi-beam Echo-sounder. Samples were taken from the central part of the grab sampler to avoid contamination from the metallic sampler. The samples were packed by self-packing polythene bags and frozen at -4°C immediately until further analysis.

2.2. Textural and Geochemical Analyses

Textural studies on the sediments were performed for sand, silt and clay distributions (Ingram, 1970). Extraction of acid leachable metals was done by taking 0.5g of dry sediment sample in a high quality plastic bottle. The samples were mixed with 4:1 ratio HNO_3:$HClO_4$ and allowed to stand overnight. The mixture was then heated to near dryness and allowed to cool before 20ml of 5M HNO_3 solution was added. The samples were allowed to stand overnight and then filtered through Whatman Grade 'A' filter paper. The filtrates are transferred to a 100ml volumetric flask and made up to mark with 0.5M HNO_3. Metal concentrations (Fe, Al, Mg, Cu, Cr, Ni, Pb, Zn, and Mn) were measured using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES, Perkin-Elmer, Optima 2100 DV). Suitable internal chemical standards (Merck, Germany) were used to calibrate the instrument. Precision and accuracy of the metal analysis were checked against the marine sediment Standard Reference material from National Institute of Standards and Technology. The analytical precision expressed as coefficients of variance is <10% for all the metals, based on replicate analysis.

2.3. Metal enrichment assessment

The anthropogenic contribution of the selected heavy metals in marine sediments can be estimated from the metal enrichment relative to background levels. Various methods have been suggested for quantifying metal enrichment in surface sediments. The central notion is to produce a numerical result comparing the metal content of each sample with a background level, such as the average continental shale (Turekian & Wedepohl, 1961) or average continental crust abundances (Taylor & McLennan, 1995). An alternative approach is to use the metal content found in deeper sediment samples as reference backgrounds (Abrahim & Parker, 2008). For the purpose of pollution assessment the following methods have been suggested.

2.3.1. Enrichment factor (EF)

Enrichment factor can be used to evaluate the metal contamination in the studied sediment in more comprehensive way. This method normalizes the measured heavy metal concentration with respect to a reference metal such as Fe or Al (Ravichandran et al., 1995). Fe and Al usually have relatively high natural concentrations, and are therefore not expected to be substantially enriched from anthropogenic sources in estuarine sediments (Niencheski et al., 1994). Currently, Al is the most frequently used geochemical normalizer in estuarine and coastal sediments (Kersten and Smedes, 2002).The EF is calculated using the following equation:

$$EF = (C_{HM}/Al)_{sample} / (C_{HM}/Al)_{crustal\ average}$$

Where, $(C_{HM}/Al)_{sample}$ and $(C_{HM}/Al)_{crustal\ average}$ are, the metal concentration (µg g^{-1}) in relation to Al (%) in sediment samples and crustal average values (Al – 8.04%, Cu – 25 µg g^{-1}, Cr – 35 µg g^{-1}, Ni – 20 µg g^{-1}, Pb – 20 µg g^{-1}, Zn – 71 µg g^{-1}) (Taylor & McLennan, 1995).

2.3.2. Geo-accumulation Index (Igeo)

The geo-accumulation index (I_{geo}), originally defined by Muller (1979) is a quantitative measure of the metal pollution in aquatic sediments (Ranjan et al., 2008). To characterize the level of pollution in each sampling point, Igeo values were calculated using the following mathematical formula (Abrahim & Parker, 2008)

$$I_{geo} = \log_2\left(\frac{C_{HM}}{1.5 \times B_{HM}}\right)$$

Where, C_{HM} is the measured concentration of heavy metal in the sediment, B_{HM} is the geochemical background value for the heavy metal taken from the literature (Taylor &McLennan, 1995). It is distinct from EF because of the factor 1.5 is introduced to include possible variations of the background values that are due to lithogenic variations (Mohinddin et al., 2010). In addition, EF does not take into account the nature and genesis of the matrix, which play a crucial role in metal contamination (Sahu & Bhosale, 1991).

2.3.3. Pollution load index (PLI)

The Pollution load index (PLI) is a result of the contribution of several heavy metals and it is defined as the n^{th} root of the multiplication of the concentration factors (CF_{HMk}) (Tomlinson et al., 1980).

$$PLI = \sqrt[n]{\prod_{k=1}^{n} CF_{HM_k}}$$

Where, CF_{HMk} is the ratio between the concentrations of each heavy metal (C_{HM}) to the background values (Taylor & McLennan, 1995). The PLI gives an assessment of the overall toxicity status for a sample, and it is a result of the contribution of five heavy metals (Lu et al., 2009).

2.4. Threshold Effective Level (TEL) and Effects Range-Low (ER-L)

A potential level of ecological risk associated with the concentrations of heavy metals was determined applying the Threshold Effective Level (TEL) (MacDonald, 1994) and Effects Range – Low (ER-L) (Long et al., 1995) benchmarks. The Threshold Effective Level (TEL) is the geometric mean of the 15^{th} percentile in the effects data set and the 50^{th} percentile in the no effects data set. Effects Range - Low (ER-L) is the 10^{th} percentile in the effects data set. Although ER-L is indicative of concentrations below which adverse effects rarely occur, the TEL also includes chemical concentrations observed or predicted to be associated with no adverse biological effects (no effects data) (Jones et al., 1997).

2.5. Statistical analysis

Multivariate statistical analyses including Pearson correlation analysis, Factor Analysis (FA), and Cluster Analysis (CA) were conducted using the statistical software SPSS for Windows Ver. 16 to identify the association of metals and geochemical parameters (Chork & Govett, 1985; Aitchison, 1986). A correlation matrix was used to understand the relationship among the metals. R-mode factor analysis was applied to transform the correlation matrix, with an aim of explaining the relationships between different factors. The resulting factors were then rotated using varimax method, for deriving more significant information on the distribution of the weights of the variables on the factors (Davis, 1986).

The factors are presented as factor 1 (F1), factor 2 (F2) and factor 3 (F3) for 21 sediment samples. Hierarchical Cluster Analysis (HCA) was performed on the normalized data set by means of Ward's method.

3. RESULTS AND DISCUSSION

3.1. Spatial distribution of abundant and heavy metals

The concentration ranges of abundant metals Fe, Al, Mg and Mn are 3.37 – 4.32 %, 8.13 – 9.27 %, 0.68 – 1.97 % and 254.94 – 426.34 μg g^{-1} respectively. The concentration of heavy metals Cu, Cr, Ni, Pb and Zn are 24.66 – 49.66, 71.18 – 134.70, 22.10 – 37.42, 20.74 – 35.22, and 77.38 – 137.46 μg g^{-1} respectively. The spatial distribution of abundant metals (Fe, Al, Mg and Mn) and heavy metals (Cu, Cr, Ni, Pb and Zn) are shown in figures 2 and 3 respectively. Heavy metal accumulations showed a decreasing trend from the northern part to southern part of the study area and also towards the sea from shore. The distribution reflects the presence of major pollution sources such as Chennai harbour, sewage input from Cooum and Adayar rivers, industrial and urban effluent input along the coast.

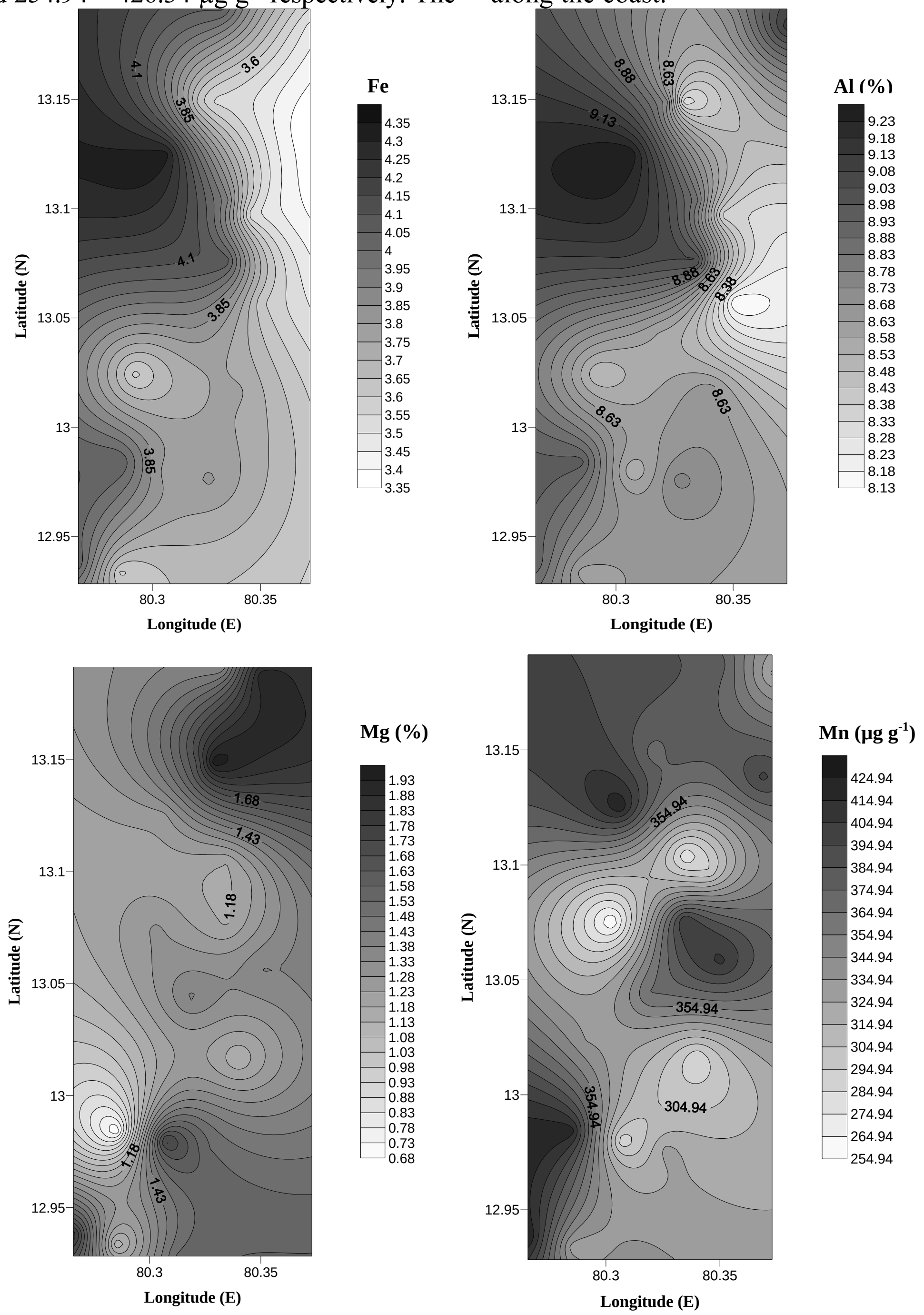

Figure 2. Spatial distribution of Fe, Al, Mg and Mn along the Chennai coast (n = 21)

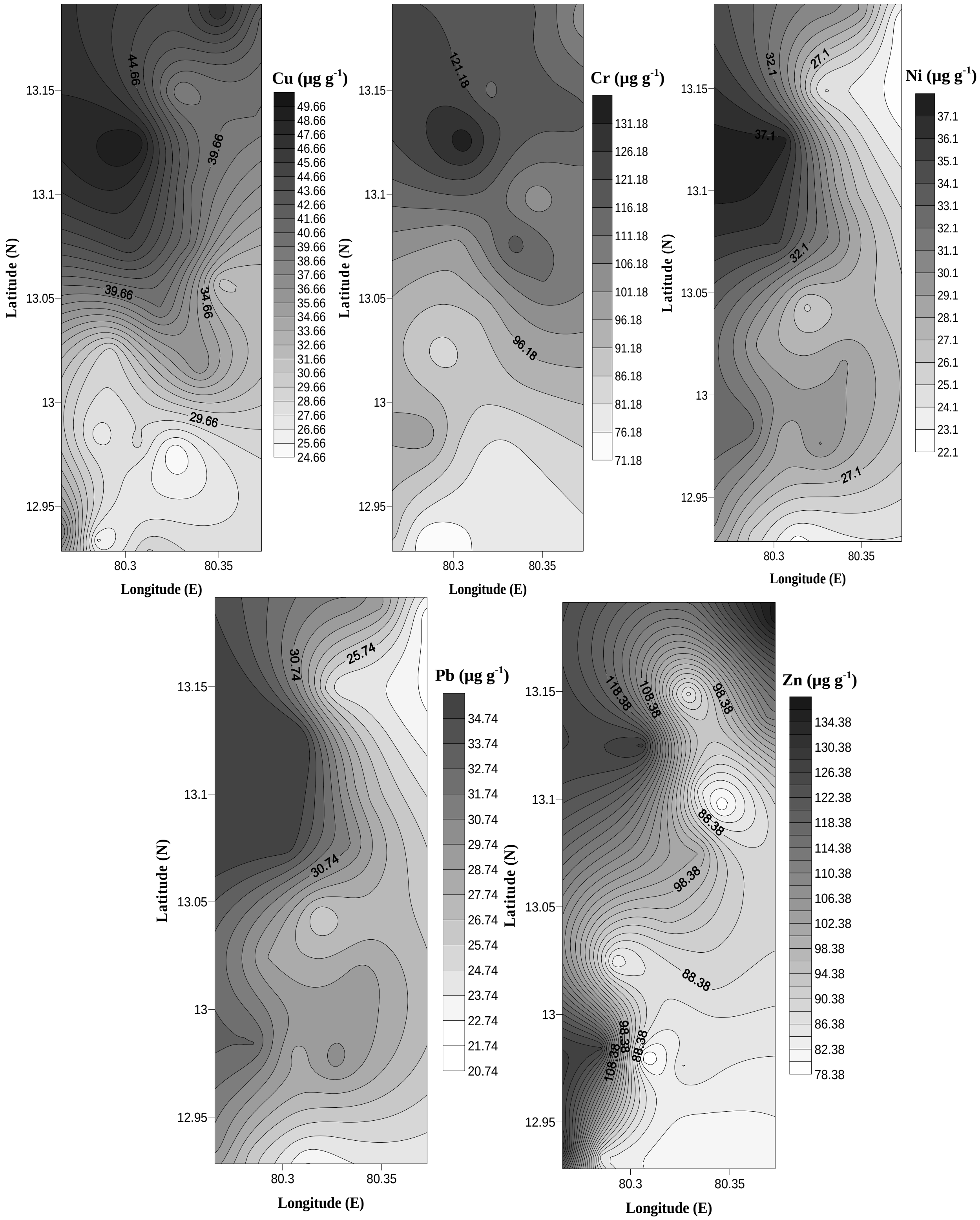

Figure 3. Spatial distribution of Cu, Cr, Ni, Pb and Zn along the Chennai coast (n=21).

The point sources of pollution are mainly the Ennore thermal power plant (production capacity of 200 MW), North Chennai thermal power plant (production capacity of 600 MW), Chennai harbour and Fishing harbour activities, petrochemical industries, other nearby industries and untreated urban wastes from metropolitan Chennai. There are 14 major industries located in the northern part of the study area. These are mostly chemical based, manufacturing petro-chemicals, fertilizers, pharmaceuticals, and paints. The difference in the distribution of metals in E1, E2, C11, C12, A16 stations can be attributed to the anthropogenic wastes and the brackish water from the Buckingham canal, inflow of sewage water from the rivers (Cooum and Adayar), which were the point sources for heavy metals in these areas. Even though the Cooum and Adayar River have an almost similar geological setup, there was a wide variation in their metal distribution, indicating the possible addition of metals by anthropogenic input.

The high concentration of heavy metals in CH7 is due to the shipping and fishing activities from Chennai harbor and fishing harbors respectively. Maximum heavy metal values are obtained at CH7, C11, C12 and N21. Sand is predominant along the coast and high mud (silt + clay) percentages are observed at CH7, C11, C12 and N21 (Fig. 4). Clay and silt particles generally contain the highest concentrations of pollutants and are more readily transported in suspension in natural waters (Fytianos & Lourantou, 2004). Fine-grained sediments tend to have relatively high metal concentrations, due in part to the high specific surface area of the smaller particles. This enrichment is mainly due to surface adsorption and ionic attraction (McCave, 1984; Horowitz & Elrick, 1987; Veerasingam et al., 2010a, Veerasingam et al., 2011). Moreover, the northern part of the study area has high percentages of iron oxides derived from ferricretes are reflecting mobilization of iron, litho dependency on parent material (Achyuthan and Thirunavukarasu, 2009).

Venkatachalapathy et al., (2010a, 2010b, 2011a, & 2011b) have proved that northern part of the study area has high concentration of petroleum hydrocarbons and iron oxides. Hydrodynamic conditions and landform can affect the physical properties of sediments, further affecting heavy metal concentrations and spatial distribution (Mitchell el al. 1998). The high mud content of the Cooum and Adayar estuaries indicate that fresh water inputs contain fine particles that settle when current and wind speed are reduced (Thomson-Becker & Luoma, 1985). The results of heavy metals are compared with other coastal regions around the world (Table 1).

3.2. Enrichment of heavy metals

To evaluate the heavy metal enrichment in marine sediment, an enrichment factor was calculated and shown in figure 5.

As indicated by their respective enrichment factor (EF) values, the enrichment of heavy metals in Chennai coastal sediments decreases in the order Cr > Cu > Ni > Zn > Pb. Enrichment factor values less than 1.5 suggest that the heavy metals may entirely be from natural weathering processes and the values greater than 1.5 suggest an anthropogenic source (Veerasingam et al., 2010b).

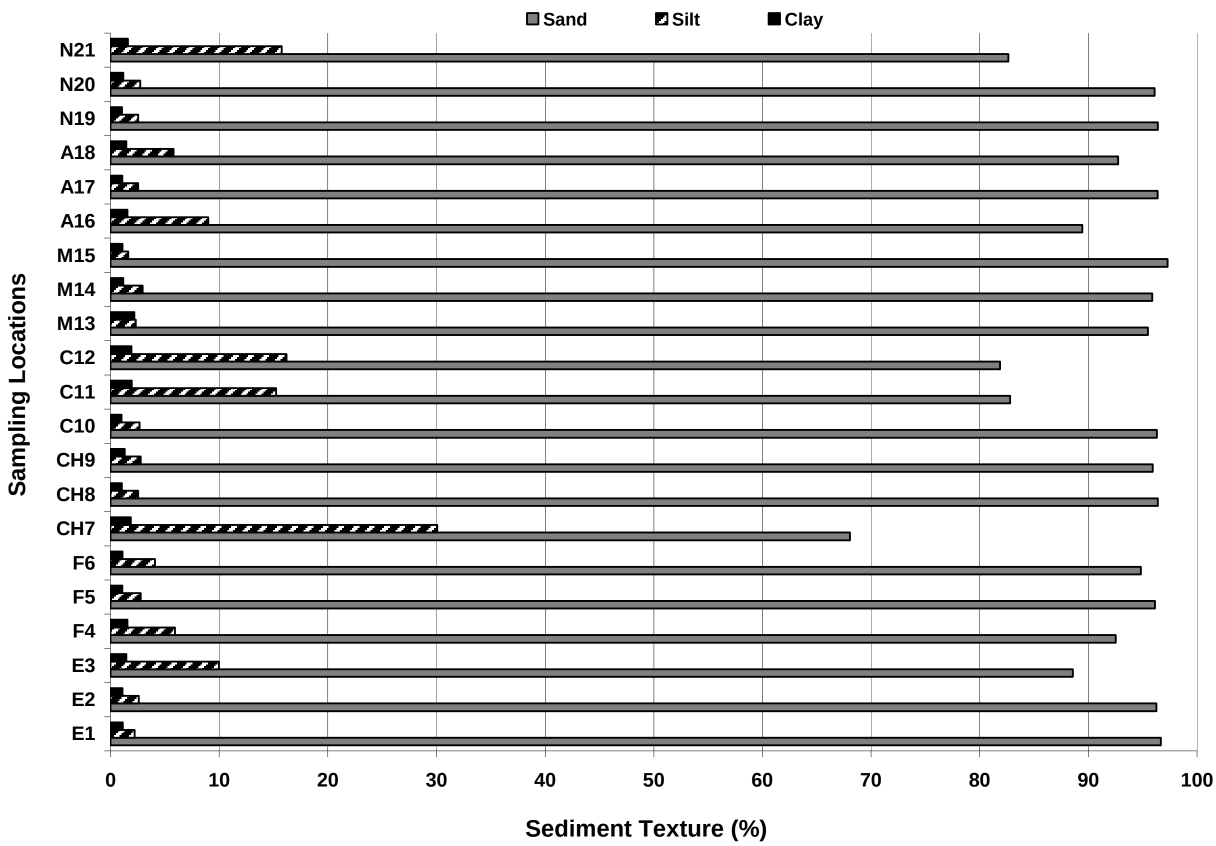

Figure 4. Distribution map for texture size of surface sediments along the Chennai coast (n=21)

Table 1. Cu, Cr, Ni, Pb and Zn pollution levels in marine surface sediments of different areas around the world (values in μg g^{-1}).

Study area	Cu	Cr	Ni	Pb	Zn	Reference
Ennore creek, India	22	49.5	17.7	31.75	96.7	Jayaprakash et al., 2008
Cuddalore coast, India	3.77	6.79	3.77	7.2	8.88	Ayyamperumal et al., 2006
Point Calimere coast, India	24.81	75	34.27	18.72	58.53	Stephen-Pichaimani et al., 2008
Muthupettai coast, India	11.35	21.76	21.14	30	15.89	Janaki Raman et al., 2007
Kalpakkam coast, India	–	2.6	2.49	9.96	5.92	Selvaraj et al., 2004
Gulf of Mannar, India	–	4.25	5.91	3.06	3.60	Jonathan & Rammohan, 2003
Tuticorin coast, India	57	177	24	16	73	Jonathan et al., 2004
China shelf sea	15	61	24	20	65	Zhao & Yan, 1992
Tokyo Bay, Japan	53.47	77.3	32.63	50.68	322	Fukushima et al. ,1992
Hong kong coast, China	118.68	48.93	24.72	53.56	147.73	Zhou et al., 2007
Taranto Gulf, Ionian sea, Italy	47.4	85.9	53.3	57.8	102.3	Buccolieri et al., 2006
Thermaikos Gulf, Greece	80	47	–	77	184	Christophoridis et al., 2009
Chennai coast, India	37.12	101.69	28.40	24.93	100.85	Present study

The high proportions of Cr, Cu and Zn imply that the sediments are contaminated by harbour activities, industrial and domestic effluent discharges through Cooum and Adayar rivers, atmospheric deposition of finer particle from thermal power plants and petrochemical industries. Chromium is a toxic heavy metal and it produces health hazards (Hawa Bibi et al., 2007). Chromium and its compounds are primarily used in the manufacture of steel and other alloys, chrome plating and pigment production (Krishna & Govil, 2005 and 2008). The source of Cr appears anthropogenic, from industries producing steel and textiles in this area. Large Cr concentrations at all locations indicate a primarily anthropogenic origin, likely controlled by sediment characteristics (particle size).

Larger Cu concentrations in the northern part of the study area can be attributed to the land based sources such as the chemical and metallurgical industries and also sewage and industrial effluents (Dauby et al., 1994). Zinc is one of the potentially hazardous metals in the sediments (Romic & Romic, 2003). Elevated Zn concentrations at the E1, E2 and E3 locations are mainly due to the coal powered thermal power plant and atmospheric deposition of fly ash in the region.

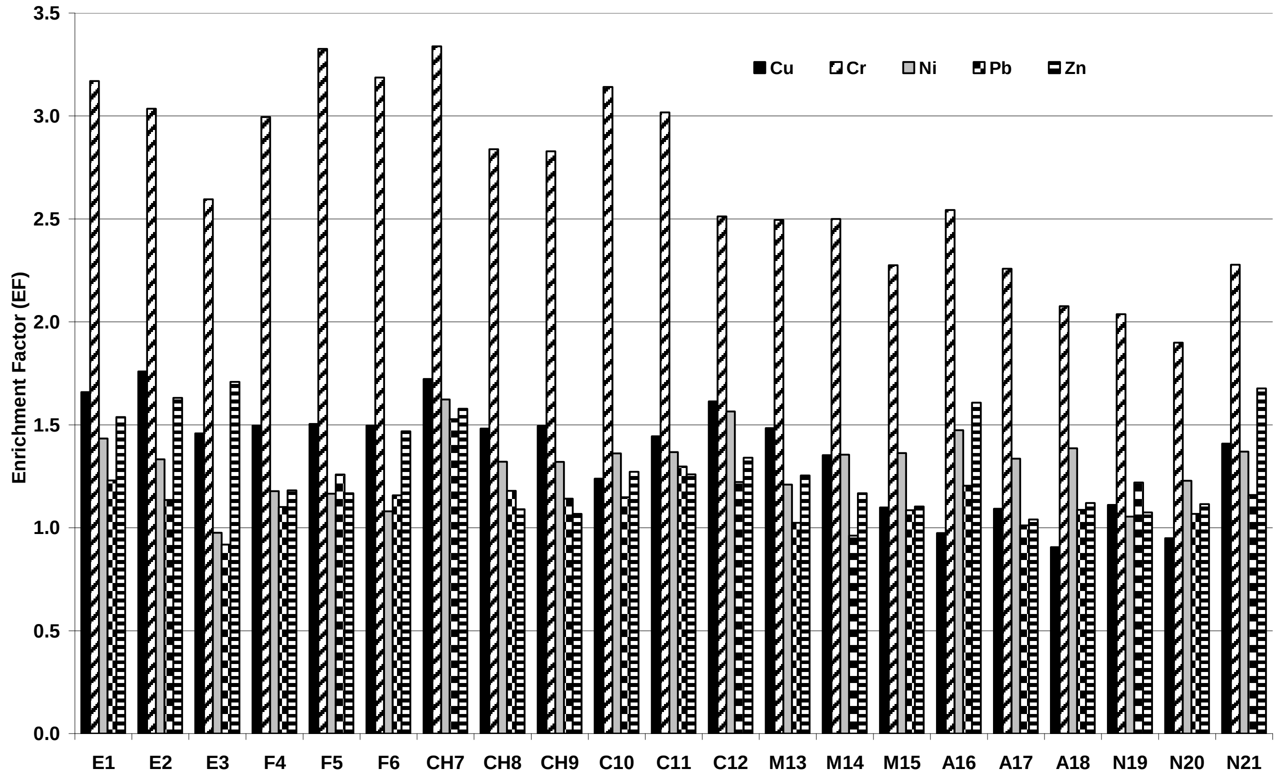

Figure 5. Enrichment factor of Cu, Cr, Ni, Pb and Zn along the Chennai coast

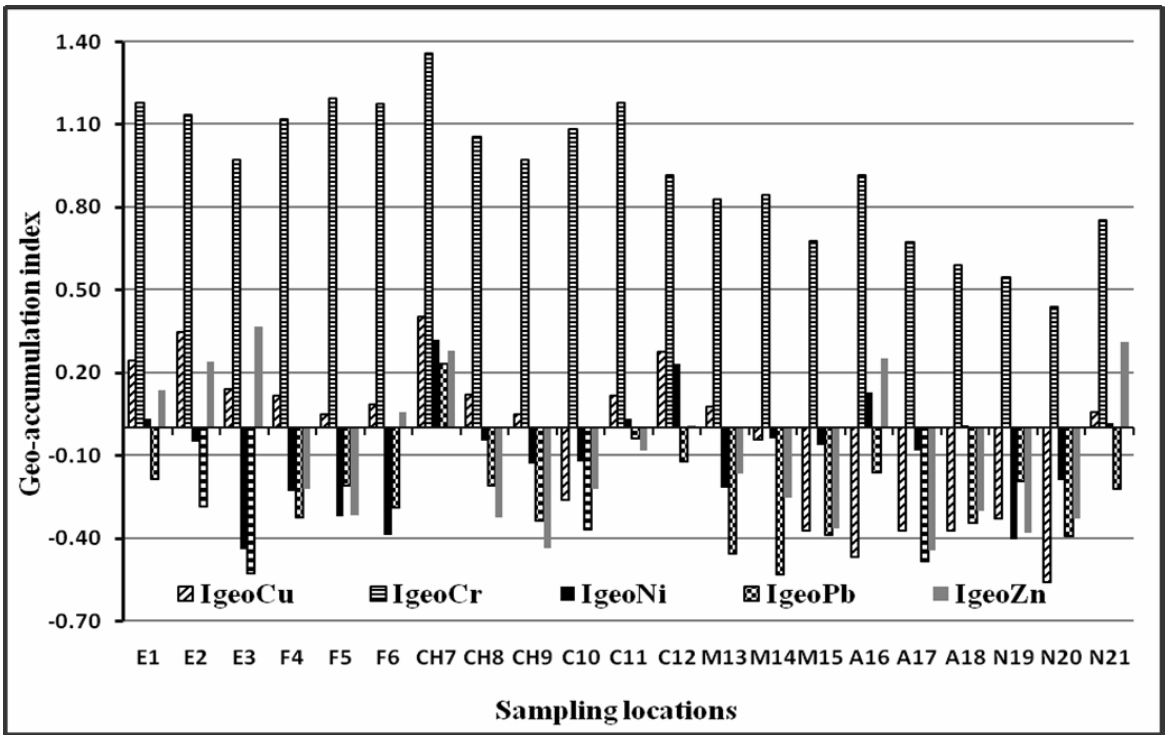

Figure 6. Geo-accumulation index of Cu, Cr, Ni, Pb and Zn along the Chennai coast

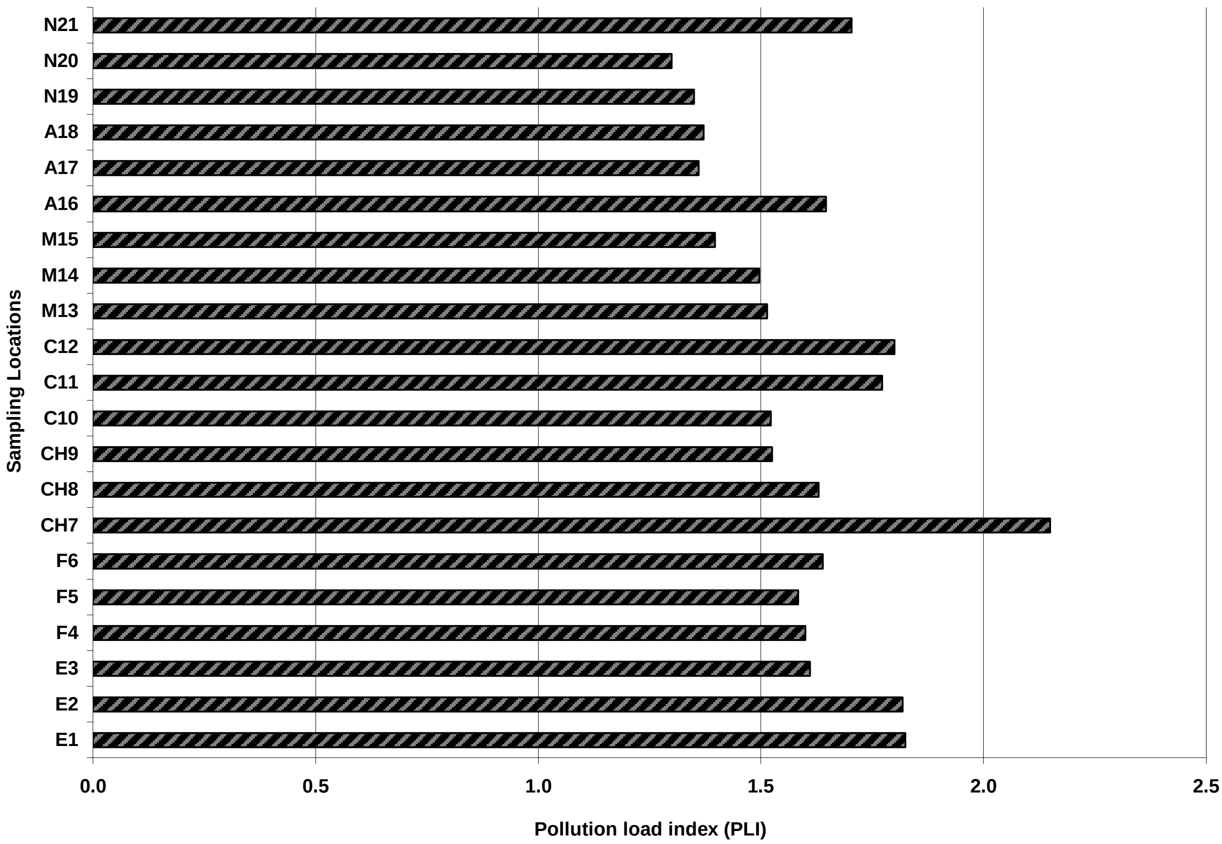

Figure 7. Pollution load index of Chennai coastal sediments

The Geo-accumulation index is calculated for the selected metals (Fig. 6).The Geo-accumulation index of heavy metals in Chennai coastal sediments decreases in the order Cr > Cu > Ni > Zn > Pb. According to Igeo values, the sediments can be classified as uncontaminated or contaminated. Igeo values greater than one suggest that the heavy metals are derived from anthropogenic activities, while values less than 1 indicate the heavy metals may be entirely derived from natural weathering processes. The Igeo reveals that sediments of the Chennai are contaminated by Cr and all metals are more enriched in northern areas.

The integrated pollution load index (PLI) of the five metals (Cu, Cr, Ni, Pb, and Zn) is shown in figure 7. The PLI is used to determine the synthetic pollution effect at different stations by the metals. Values of PLI = 1 indicate heavy metal loads close to background, and values above 1 indicate progressive pollution (Tomlinson et al., 1980). PLI values for the entire northern part of the study are were never less than 1 (Fig.7), so no site could be classified as "unpolluted" with respect to the five heavy metals included in this study. PLI values showed that the northern part of the study area is more contaminated than the southern part.

3.3. Ecological risk assessment

The heavy metals data from Chennai coast were compared to Sediment Quality Guidelines (SQG), including the Effect Range Low (ER-L) (Cu – 34 µg g^{-1}, Cr – 81 µg g^{-1}, Ni – 20.9 µg g^{-1}, Pb – 46.7 µg g^{-1}, Zn – 150 µg g^{-1}) (Long et al., 1995), and Threshold Effect Level (TEL) (Cu – 18.7µg g^{-1}, Cr – 52.3 µg g^{-1}, Ni – 15.9 µg g^{-1}, Pb – 30.2 µg g^{-1}, Zn – 124 µg g^{-1}) (MacDonald, 1994). The ecological risk assessment of the study area is shown in table 2.

Table 2. Ecological risk assessment of Cu, Cr, Ni, Pb and Zn on the basis of Threshold Effect Level and Effects Range-Low benchmarks (P – Potentially toxic, R – Rarely toxic, N – Nontoxic; n=21)

Site	Cu	Cr	Ni	Pb	Zn
E1	P	P	P	N	N
E2	P	P	P	N	R
E3	P	P	P	N	R
F4	P	P	P	N	N
F5	P	P	P	N	N
F6	P	P	P	N	N
CH7	P	P	P	R	R
CH8	P	P	P	N	N
CH9	P	P	P	N	N
C10	R	P	P	N	N
C11	P	P	P	N	N
C12	P	P	P	N	N
M13	P	P	P	N	N
M14	P	P	P	N	N
M15	R	P	P	N	N
A16	R	P	P	N	R
A17	R	P	P	N	N
A18	R	R	P	N	N
N19	R	R	P	N	N
N20	R	R	P	N	N
N21	R	P	P	N	R

Samples were considered "nontoxic" when concentrations were lower than ER-L and TEL values, as "rarely toxic" when concentrations were lower than ER-L but higher than TEL values, and as "potentially toxic" when concentrations were higher than ER-L and TEL. Potentially toxic levels of Cu, Cr and Ni characterize most samples, whereas the concentrations of Pb and Zn in the sediments are unlikely to pose risks to biota (Prundeanu & Buzgar, 2011). The northern part of the study area has greater potential level of ecological risk than the southern part.

3.4. Statistical results

The correlation coefficient matrix of sediment texture, Fe, Al, Mg, Mn, Cu, Cr, Ni, Pb, and Zn in Chennai coastal sediments is presented in Table 3. A correlation matrix can indicate relationships among metals and sediment texture. High correlation coefficients between different metals mean their common sources, mutual dependence and identical behavior during transport. The absence of strong correlations among other metals suggests that the concentrations of these metals are not controlled by a single factor, but are a combination of geochemical support phases and their mixed association (Jain et al., 2005). The good correlation of Fe versus Cu, Cr, Ni, Pb and Zn indicates that these metals are contributed by the Fe oxides (Sipos, 2010; Sipos et al., 2011). The positive relationship of Cu, Cr, Ni, Pb and Zn with silt and the negative relation with sand suggest that the sampling locations with high heavy metal contents are dominated by the fine fractions, while, the sites with coarse fractions lacked heavy metals (Stumm & Morgan, 1981; Calvert et al., 1993). Finally, the correlation matrix revealed that Fe oxides, which usually concentrated in the fine particles, controlled the distribution of heavy metals.

Factor analysis was carried out on the data set (12 variables) to compare the compositional patterns between heavy metal samples and to identify the sources of variation. Factor loadings were based on the eigenvalues and factor scores were computed from the original raw data to create an entirely new set of smaller composite variables to replace the original set of variables and are presented as factor 1 (F1), factor 2 (F2), and factor 3 (F3) respectively (Fig. 8).

F1 accounts for 50.318% of the total variance with an eigen value 6.04, F2 accounts for 16.9% of the total variance with an eigen value 2.03, and F3 accounts for 9.09% of the total variance with an eigen value 1.09 respectively. F1 showed high positive factor loading (> 0.5) of six variables (Fe, Al, Ni, Zn, silt and clay) but negative with sand. F2 includes four variables (Cu, Cr, Pb and Mn) with high positive factor loading.

Table 3. Correlation coefficient matrix of Fe, Al, Mg, Mn, Cu, Cr, Ni, Pb, Zn and sediment texture (n=21) in Chennai coastal sediments

	Fe	Al	Mg	Cu	Cr	Ni	Pb	Zn	Mn	Sand	Silt	Clay
Fe	1.00											
Al	0.65	1.00										
Mg	-0.38	-0.15	1.00									
Cu	0.34	0.40	0.29	1.00								
Cr	0.23	0.17	0.15	0.76	1.00							
Ni	0.87	0.51	-0.49	0.25	0.22	1.00						
Pb	0.70	0.53	-0.20	0.46	0.55	0.63	1.00					
Zn	0.41	0.64	0.15	0.51	0.41	0.30	0.37	1.00				
Mn	0.21	0.07	0.11	0.14	0.45	0.08	0.44	0.52	1.00			
Sand	-0.69	-0.79	0.11	-0.45	-0.37	-0.65	-0.76	-0.58	-0.32	1.00		
Silt	0.68	0.78	-0.10	0.45	0.37	0.65	0.77	0.58	0.33	-1.00	1.00	
Clay	0.57	0.61	-0.20	0.34	0.14	0.43	0.37	0.35	0.18	-0.68	0.65	1.00

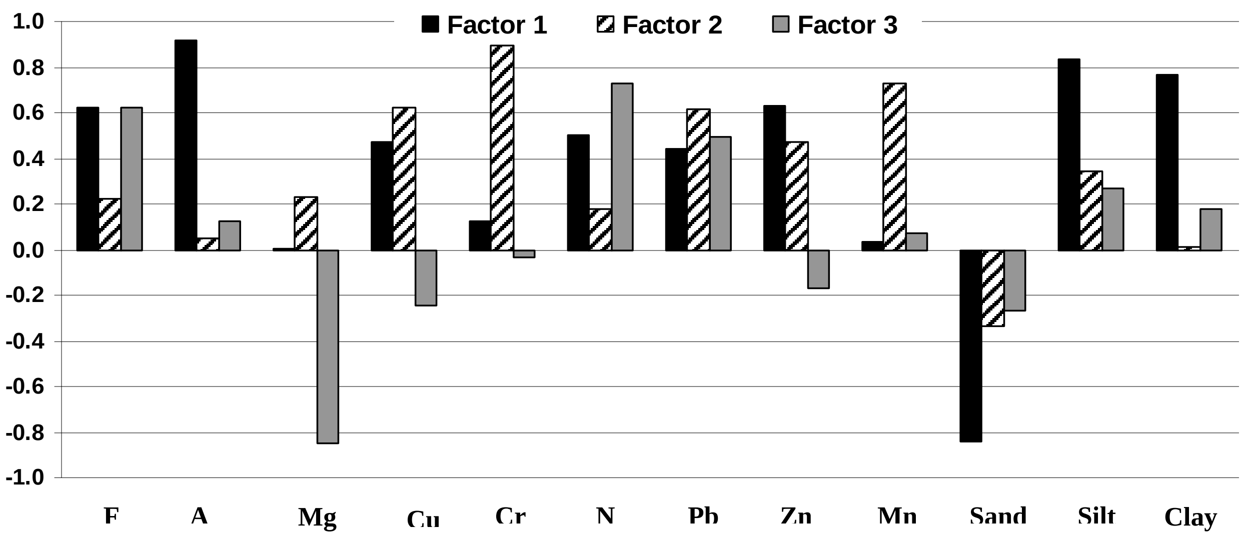

Figure 8. Results of factor analysis (R-mode) showing the association of the three primary factors F1, F2 and F3 accounting for 76.31% of the total variance in the Chennai coastal sediments.

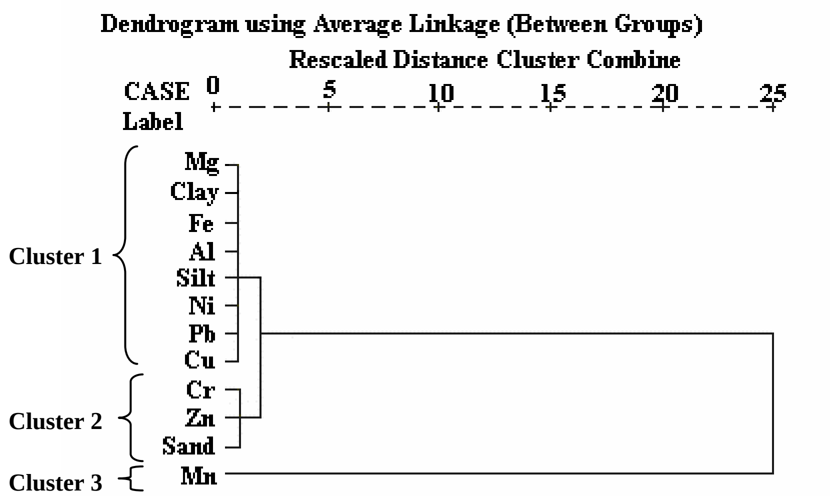

Figure 9. Dendrogram based on complete linkage method for Chennai coastal sediments

F3 showed high positive factor loading with Fe and Ni. The association of Fe with Ni, Zn, silt and clay in F1, and the association of Mn with Cu, Cr, and Pb in F2 indicate that Fe oxides play an important role in adsorbing the heavy metals especially in the fine grained sediments (Pruysers et al., 1991)

Hierarchical Cluster Analysis (HCA), as the most cluster analysis method most commonly used for environmental analysis, identifies groups of samples according to their similarities. The results obtained could be presented in a two-dimensional plot called dendrogram. The dendrogram based on the linear pair coefficient of correlation between the variables indicate different clusters for Chennai coastal sediments (Fig.9). Three groups were distinguished in the dendrogram, performed using the Ward method, which used the squared Euclidean distance as a similarity measure. The domination of clay, silt, Cu, Ni and Pb with Fe indicates their association with the Fe oxides and fine particles.

4. CONCLUSIONS

The spatial distribution of heavy metals in Chennai coastal sediments are controlled by various physical and chemical processes. The enrichment of heavy metals over background concentrations suggests that the region is moderately contaminated and in certain region the presence of excess amount of Cr, Cu, Ni, Pb and Zn, which are mainly due to the harbour activities, Cooum, Adayar river inputs, industrial and urban sewage wastes. Enrichment factor (EF) and Pollution load index (PLI) revealed the northern part of the study area is more contaminated than the southern part but the Geo-accumulation index (Igeo) for Cr was typically high for all the sampling locations. Multivariate statistical analyses indicated that Fe oxides, which usually concentrated in the fine particles, controlled the distribution of heavy metals. This study suggested that heavy metal input to the Chennai coast should be regulated in near future, particularly with regard to Cu, Cr and Ni, on the basis of Threshold Effect Level (TEL) and Effects Range-Low (ER-L) benchmarks. These results will be helpful future monitoring of further increase of heavy metal concentrations in marine sediments along the coastal region.

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