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Geochemical Assessment of Sediment Quality using Multivariate Statistical Analysis of Ennore Creek, North of Chennai, SE Coast of India

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ABSTRACT

The composite nature of Ennore Creek, receiving polluted waters from Buckingham canal, River Kortalaiyar, and the presence of numerous industries rapidly degrade the coastal environment. In this study, multivariate statistical technique was used to assess the nature of pollution and to identify the factors responsible for the enrichment of trace metals in the creek sediments. Forty samples were collected during pre- and post-monsoon periods to evaluate the seasonal variations on the concentration of trace metals in the sediments. The results indicate that not much seasonal variation exists in the concentration of trace metals in the sediments of Ennore creek. Results of the cluster analysis illustrate that the enrichment of trace metals was mainly from anthropogenic sources. Meanwhile, correlation coefficient among the metals reveals that some of the metals (Fe and Al) derived were of natural origin. The complex data matrix of the sediment were interpreted after reduction to three factors and the results illustrate the extent of the influence of anthropogenic activities. The spatial distribution diagrams demonstrate and demarcate the region of enrichment of metals in the sediments of Ennore creek.

Keywords: Cluster analysis, Factor scores, Ennore creek, heavy metal pollution

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INTRODUCTION

Estuarine environments have traditionally served as recipients of domestic and industrial effluents from the adjacent metropolis (Jayaprakash *et al.,* 2005). The effect of contamination is dependent on the nature and quantum of effluents, and on whether they are discharged directly into the estuary from a point source, or indirectly through river systems. Heavy metal pollution in the estuarine environment is very serious due to their toxicity, persistence and ability to accumulate in biota (Beldi *et al.,* 2006). Heavy metals can remain in the environment unchanged for years and may pose threat to humans and other organisms (Ahmad *et al.,* 2009). Toxicity and bioavailability of heavy metals in an ecosystem depends on the way they are fixed in the sediments. The mobile fraction of the metal adsorbed at the surface of solid bodies is the most labile and known as exchangeable fraction. In this fraction, metals are bound by processes of physical and chemical sorption and they interchange easily with other ions in the environment. Thus, evaluation of heavy metal contamination is vital in order to determine the level of its contamination in the environment. The data obtained from such studies are significant in the decision making of environmental planning strategies.

Hydrodynamic and physico-chemical conditions of the estuary have great influence on the horizontal distribution of metals in creek water and sediments. Physical and chemical partitioning behaviour and speciation of metals, within and between different environmental compartments, are controlled by various physicochemical factors (Padmini *et al.,* 2007). Heavy metal pollution in the water and sediment of Ennore creek is influenced by both point and non-point pollution sources. The high pollution load in Ennore Creek has drastically changed the ecosystem (Azariah, 1997; Jayaprakash *et al.,* 2005; 2008). The study of the geochemistry of sediment requires handling of a large data set, which includes the concentrations of various ions. At the same time, classification, quantification and interpretation of the data are important steps in the assessment of sediment quality. In order to achieve this objective, multivariate statistical techniques have been successfully used by various researchers. Sediment quality data of the area were subjected to factor analysis (FA) to interpret, understand and identify the mechanisms, processes (both natural and anthropogenic) and specific source of water quality deterioration and contamination in the area. In particular, FA explains the correlations between the variables in terms of the underlying factors, which are not apparent otherwise (Yu *et al.,* 2003). In this work, R-mode FA is used to identify and quantify the factors responsible for the enrichment of metals in the sediments of Ennore creek.

STUDY AREA

The study area (Ennore Creek) is located the north of Chennai, where most of the area consist of alluvial tracts and the remaining, in the eastern part, is occupied by beach dunes, tidal flats and creek (Jayaprakash *et al.,* 2008). The Creek is an aperture of the brackish water system into the Bay of Bengal. It is almost 800m wide and elongated in a NE-SW direction. Ennore Creek merges with the backwater bodies and the north-south trending channels connecting it to Pulicat Lake in the north and to the tributaries of Kortalaiyar River in the south (Fig.1). The depth of the creek ranges from 2 to 3m and is shallow near the mouth and on the northwestern part merging with the tidal flats. Mangrove swamps are also noticed in the area. The southern limb of the creek, fringing the northern areas of Chennai city, is well-developed with industries, utilities, suburban residential areas and fishing hamlets. The northern section of the creek or Kosistalaiyar backwater is connected to Pulicat Lake and has two major developmental areas – the North Chennai Thermal Power plant and the recently built Ennore port. Waste water enters the creek through the Buckingham canal, a waterway that was built for navigation. The canal section that traverses between Chennai and Ennore currently serves as an open sewer receiving municipal and industrial wastewaters (Jayaprakash *et al*., 2012). The creek also receives wastewater from the Manali industrial area. It is crucial to note that rapid development of Chennai city in the last three decades has put additional stress on the surrounding aquatic environment.

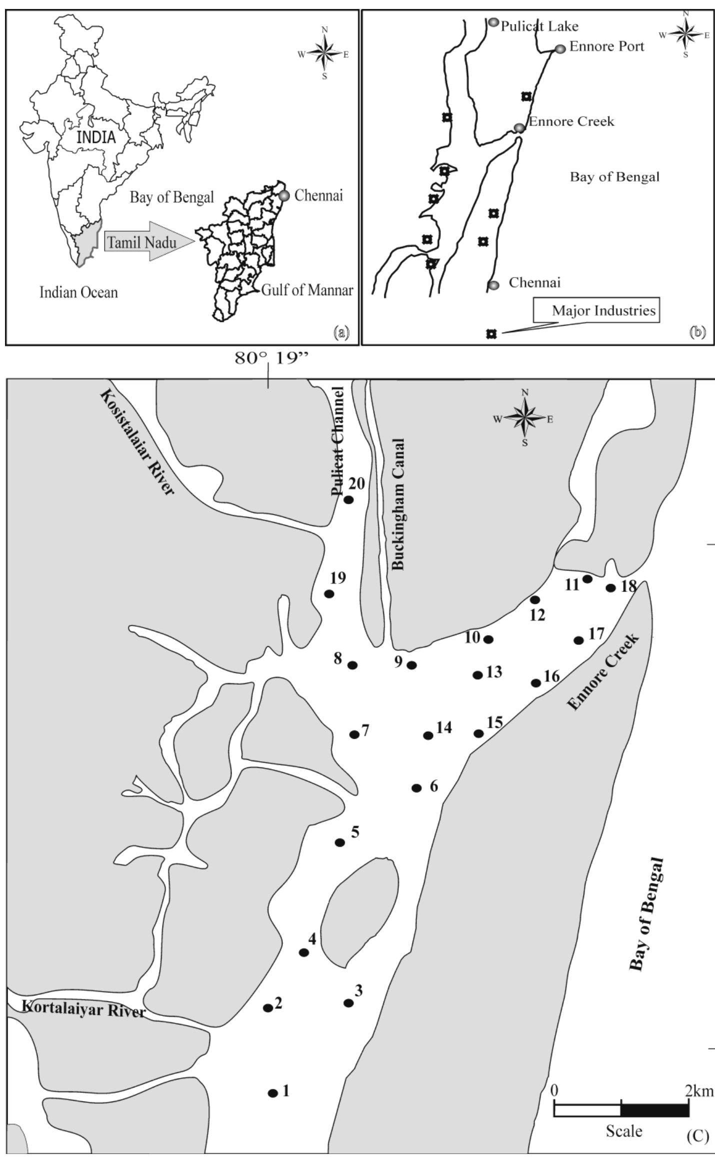

Fig.1: Location map of the study area

MATERIALS AND METHOD

Analytical Methodology

Forty surface sediment samples were collected from a boat using Van Veen grab during the pre- (PRM) and post-monsoon (POM) seasons of 2009 (20 samples in each season). The samples were collected from the entire creek region, which has a variety of branches spread over a wide area, with marshy conditions in many places. The sampling sites were selected on the basis of possible local and point sources. The samples were taken from the central part of the grab sampler to avoid any metallic contamination from the sampler itself and were frozen at -4°C immediately onboard until further analysis. The samples were collected from a depth of 2 m to a maximum depth of 3 m during both seasons. The samples were separated following the cone and quartering method and were powdered in an agate mortar to the 230 um size.

For total metal analysis, a known quantity of sediment was digested with an acid mixture of $HClO_4$ and HF and the final residue was leached with HCl and made up to the required quantity (Tessier *et al.,* 1996). Trace metal concentrations (Fe, Mn, Cr, Cu, Ni, Co, Pb and Zn) were measured using flame atomic absorption spectrophotometer (Perkin-Elmer AA700) that was equipped with a deuterium background corrector. Suitable internal chemical standards (Merck chemicals, Germany) were used to calibrate the instrument. All the reagents used were of analytical grade and high purity. The accuracy of the analytical procedures was assessed using certified reference material MESS-1 (Table 1) from the National Research Council of Canada for the present study.

TABLE 1
Published and obtained analytical results of MESS-1

Elements	MESS-1	Present study	Recovery %
Fe	3.1 ± 0.38	2.95	95.16
Mn	513 ± 25	472	92.00
Cr	71 ± 1.1	69.8	98.30
Cu	25.11 ± 3.88	22.9	91.19
Ni	29.5 ± 2.7	28.3	95.93
Co	10.8 ± 1.9	9.9	91.66
Pb	34 ± 6.1	31.8	93.52
Zn	191 ± 17	173.3	90.73

Statistical Methodology

Cluster analysis (CA) is an effective statistical tool for identifying and evaluating similar groups from the data matrix. In this study, the classification based on the sampling site was performed through CA using Ward's method (Ward, 1963), with Euclidian distance as a similarity measure and synthesis into dendogram plots. Euclidean distance is the geometric distance in multidimensional space. Ward's method is known to be distinct as it uses an analysis of variance approach to evaluate the distances between clusters. This particular method minimizes the sum of squares (SS) of any two (hypothetical) clusters that have been derived at each step (Mcgarial *et al.,* 2000; Vega *et al.,* 1998; Zeng & Rasmussen, 2005).

FA is unique since the patterns of relationship among many dependent variables are studied with the goal of determining the nature of the independent variables that affect them, even though those independent variables are not measured directly. FA was applied to the data matrix in order to reduce the data to an easily interpretable form. Before applying FA, the data were standardized according to the criteria presented by Davis (2002). Computation of the correlation coefficient matrix is the first step in FA between the standardized variables. The Eigen values quantify the contribution of a factor to the total variance. The contribution of a factor is significant when the Eigen value is greater than unity (Kaiser, 1960). Initial factors are extracted and they are subjected to mathematical rotation. Varimax rotation procedure was used to maximize the difference between the variables facilitating easy interpretation of the data. The first factor accounts for as much variance as possible in the data set. The second factor accounts for as much residual variance as possible, and so forth. The factor loading indicates the degree of closeness between the variables and the factor. The highest loading, either positive or negative, suggests the meaning of the dimension, while the positive loading indicates that the contribution of the variables increases with the increasing loading in a dimension, and the negative loading indicates a decrease (Lawrence & Upchurch, 1982). The study of factor scores reveals the extent of influence of each factor on the overall sediment chemistry at all locations of the sampling stations. Extreme negative scores reflect areas that are essentially unaffected by the processes and positive scores reflect the most affected areas. Near-zero scores indicate areas affected to an average degree (Giridharan *et al.,* 2009). In the present study, the variation of factors in each station is indicated by spatial distribution diagrams.

RESULTS AND DISCUSSION

The statistical parameters of the analytical data, such as maximum, minimum, mean and standard deviation, are presented in Table 2.

TABLE 2

Composition of metals and texture study results of Ennore creek sediments

Elements	Pre monsoon				Post monsoon			
	Min	Max	Mean	σ	Min	Max	Mean	σ
Al	48693	119085	86255	21005	39325	110193	81231	18355
Fe	26700	52000	40737	7732	23292	53500	41774	8652
Mn	422.0	949.0	666.3	151.6	391.6	903.0	686.4	153.0
Cr	160.0	700.0	408.6	136.1	211.0	598.0	392.0	110.4
Cu	46.0	222.0	112.9	53.0	42.0	200.0	106.3	48.6
Ni	17.3	52.3	39.0	10.1	23.8	48.0	36.5	8.0
Co	2.8	9.8	7.1	1.9	2.2	6.1	4.6	1.3
Pb	19.5	49.8	36.7	8.3	16.0	42.0	30.3	6.3
Zn	100.0	226.0	163.9	41.8	109.0	214.4	160.2	34.1
Mud	16.0	44.6	29.2	9.2	14.0	48.5	29.8	10.0
OM	2.5	5.0	3.7	0.7	2.0	6.6	4.0	1.3
$CaCO_3$	2.8	5.0	3.8	0.6	2.7	5.1	4.0	0.8

Temporal Similarity and Grouping of Parameters

CA based on linear pairs of coefficient of correlation among the concentrations of geochemical parameters indicates three different clusters during both PRM and POM periods (Fig.2a-b). Cluster 1 includes all trace metals along with mud, $CaCO_3$ and Organic Matter (OM), which clearly indicates that the origin of these metals should have been from anthropogenic activities. Meanwhile, enrichment of these metals in the sediments would have occurred due to the precipitation/coagulation of the pollutants in the water column (e.g., Thangadurai *et al.,* 2005). Inter-elemental association of Cr, Cu, Zn, Pb, and Mn suggests that their origin was mainly from the long-term dumping of solid waste and sewage disposal. Moreover, close linkage distance in these trace metals further suggests that corrosion from heavy transportation vehicles and burning of tires brings in considerable amounts of Cr, Pb, Zn, and Cu which accumulate in the surface sediments (e.g., Turner *et al.,* 2001; Wang *et al.,* 2005).

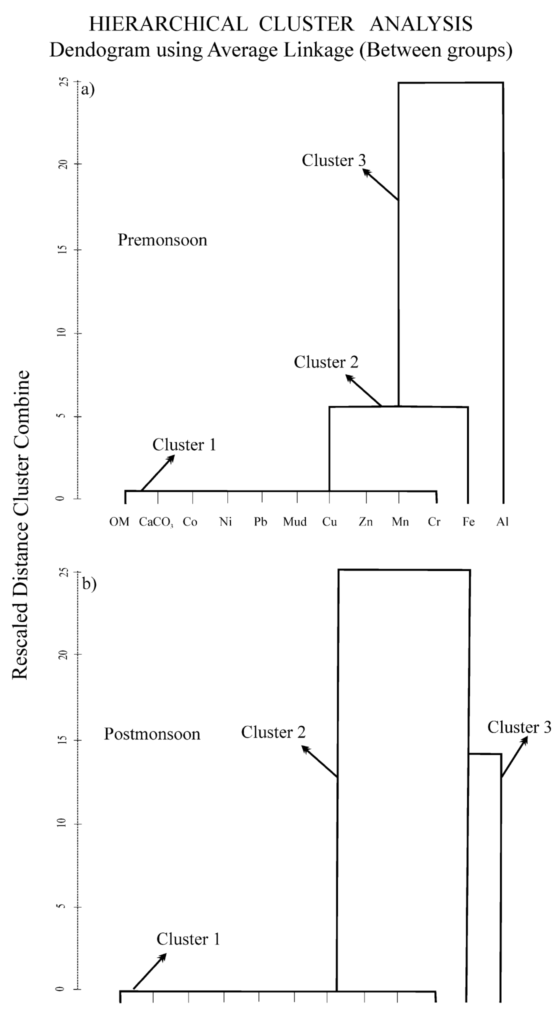

Fig.2: a-b: Dendrogram based on complete linkage method for surface sediments of Ennore creek, SE coast of India

OM has a significant role in the geochemical cycles of trace elements that accumulate in sediments; it may be used as an index of depositional environment and sedimentary processes (Seralathan *et al.,* 1993). The finer particles (mud) get bound to organic carbon and also facilitate the coagulation of trace metals from the water column. Sewage effluents enter the Ennore creek through Buckingham canal and also from the rivers Kortalaiyar and Kosistalaiyar which have increased the OM content in the water and the finer sediments in this region supporting the deposition of organic debris (Rajamanickam & Setty, 1973). Enrichment of the trace metals in the sediment of the study area through anthropogenic activities was clearly demonstrated by the cluster diagram by transporting the trace metals along with mud and OM in one group.

During PRM, Fe and Al fall separately but distinctly from the trace metals. CA shows few relationships between cluster 1 and cluster 2 (Fe); however, cluster 3 (Al) distinguishes discretely. Indeed, these results clearly demonstrate that some quantum of Fe would have originated from anthropogenic activities, whereas, Al content in the sediments may be enriched in the bed sediments by means of lithology of the region or by stream sedimentation process (Jayaprakash *et al.,* 2010). In the case of POM, cluster 1 demonstrates the same parameters as those of PRM, whereas clusters 2 and 3 fall discretely, indicating that their nature and origin may be from the weathering of aluminosilicates (Calvert & Price, 1983).

Correlation Studies

Trace metals and the strong relationships between most of them indicate that they are primarily controlled by Fe-Mn oxyhydroxides (Buckley *et al.,* 1995; Zwolsman *et al.,* 1993). In the present study, majority of the trace metals were observed to be strongly associated with both Fe and Mn, indicating that total trace metals (TTMs) in the region are mainly controlled by Fe and Mn oxyhydroxides, with OM as the functional element (Tessier *et al.,* 1979). The correlation between Co and Cr, Cu, Ni, Pb and Zn during PRM indicates that the chemical cycling of metals has occurred in the study area (e.g., Takematsuuu *et al.,* 1984). In PRM sediments, Fe has strong positive correlation with Mn, Cr, Ni, Co, Pb, OM and mud. The strong correlation of Fe with Ni and Co only indicates that these metals sre not associated with oxide-oxyhydroxides of Fe-Mn phase (Praysers *et al.,* 1991). Ni-Cr-Cu (r=0.8) exhibits a strong positive correlation among them (Table 3a). OM derived from decaying organic remains has a high capability of accumulating Ni, Cu and Cr by adsorption and by the formation of chelating compounds (Wedepohl, 1974). During POM, inter-elemental relationship of TTMs shows that Cr vs Cu (r=0.80); Cr vs Ni (r=0.82); Cu vs Co (r = 0.51), Zn vs Pb (r = 0.82) and Ni vs Co (0.76) in the sediment indicate their nature and origin (Table 3b). The electroplating industries located near the Ennore creek are involved in the processes such as surface preparation and pickling which produce acidic and alkaline wastewater with elevated Zn concentration (Forstner & Wittmann, 1981; Selvaraj *et al.,* 2003). Moreover, effluents from these industries contain significant amounts of Ni, Cr and Cd. Zn shows a strong correlation with Ni, reflecting the association of Ni with the source of Zn from the industrial effluents. Cr, Zn and Cu are known as pollution indicators of paint industries (Lin *et al.,* 2002), and the nature of origin was confirmed from the strong correlation among them.

Factor Analysis

The first three factors accounting for 88% of the variance during PRM and 86% of the variance during POM were extracted from the principal factor matrix after varimax rotation (Table 4). The spatial distribution diagrams of factor scores reveal the extent of influence of each factor on the overall sediment chemistry of the sample stations.

TABLE 3

Correlation matrix (r) of total trace elements in surface sediments of Ennore Creek, SE coast of India (n = 20)

	Al	Fe	Mn	Cr	Cu	Ni	Co	Pb	Mud	OM
Fe	0.84	1								
Mn	0.58	0.78	1					a. PRM		
Cr		0.51	0.78	1						
Cu		0.54	0.78	0.90	1					
Ni	0.56	0.68	0.73	0.83	0.82	1				
Co		0.50	0.67	0.81	0.72	0.76	1			
Pb				0.57	0.58	0.54	0.72	1		
Zn			0.45	0.61	0.68	0.56	0.65	0.79		
Mud	0.90	0.82	0.59			0.50			1	
OM	0.90	0.73	0.53			0.52			0.89	1
$CaCO_3$	-0.77	-0.79	-0.56			-0.58			-0.81	-0.76
Fe	0.86	1								
Mn	0.79	0.81	1					b. POM		
Cr		0.55	0.73	1						
Cu				0.80	1					
Ni		0.58	0.60	0.82	0.78	1				
Co	0.56	0.61	0.61	0.56	0.51	0.76	1			
Pb		0.45						1		
Zn								0.87		
Mud	0.84	0.77	0.82	0.49			0.59		1	
OM	0.83	0.76	0.72				0.57		0.89	1
$CaCO_3$	-0.68	-0.65						-0.47	-0.60	-0.68

TABLE 4

Results of the Principal component analysis - Rotated Component Matrix

PARAMETERS	Factor 1		Factor 2		Factor 3	
	PRM	POM	PRM	POM	PRM	POM
Al	0.932	0.945	0.188	0.126	0.068	0.043
Fe	0.791	0.824	0.513	0.344	-0.004	0.275
Mn	0.474	0.739	0.782	0.537	0.159	0.035
Cr	0.160	0.320	0.847	0.863	0.406	0.061
Cu	0.120	-0.135	0.866	0.965	0.397	-0.045

TABLE 4 (*continue*)

PARAMETERS	Factor 1		Factor 2		Factor 3	
	PRM	POM	PRM	POM	PRM	POM
Ni	0.434	0.249	0.715	0.899	0.394	0.166
Co	0.277	0.543	0.551	0.636	0.670	-0.182
Pb	0.014	0.215	0.211	-0.027	0.954	0.939
Zn	-0.085	0.065	0.459	0.103	0.763	0.958
Mud	0.953	0.889	0.111	0.239	0.146	0.090
OM	0.942	0.924	0.079	0.113	0.110	0.079
$CaCO_3$	-0.850	-0.750	-0.289	0.144	0.148	-0.402
Eigen value	6.910	6.215	2.920	2.491	0.770	1.684
% variance	57.567	51.791	24.363	20.755	6.419	14.032

1. PRM Factors

Factor 1 of PRM explains 57% of the total variance, has high loadings of the ions Al, Fe, mud and OM. The results show that these metals originate from a common source of aluminosilicate weathering of the catchment area. Meanwhile, associations of major metals with mud and OM indicate that the metals incorporated in the mud fractions get bound with OM in the water column and settle onto the sediment in Ennore creek (Lin *et al.,* 2002; Zang *et al.,* 2009). Factor score diagram shows high values in the south eastern part of the study area. In this scrub region, settlements near the creek are denser compared to the other parts of the study area and thus, the anthropogenic activities may have increased the OM content in the creek water which further settle onto sediments (Fig.3a).

Factor 2 of PRM accounts for 24% of the total variance and is characterised by high loadings of Fe, Mn, Cr, Cu, Ni and Co. The areal distribution diagram of factor 2 reveals that major parts of the study area show high values with regard to this particular factor. River Kosistalaiyar and Buckingham canal bring polluted water consisting of both industrial and domestic effluents from the metropolitan city, and the region adjacent to these water sources are shown to contain the highest factor scores (Fig.3c). This illustrates that sediments are enriched with these metals because of the anthropogenic activities in the source region of River Kosistalaiyar and Buckingham canal. The southern part of the study area also shows significant factor scores, where River Kortalaiyar mixes with the creek waters. Since the adjoining industries use this river as an outlet for their effluents, the heavy metal contents in the Ennore creek sediments continuously get augmented by precipitation or coagulation/flocculation from the polluted water column.

Factor 3 of PRM that accounts 6% of the total variance has high loadings of the ions - Co, Pb and Zn. The spatial distribution map of factor 3 illustrates that about 70% of the study area was affected with regard to this factor (Fig.3e). The southern, northern and northeastern parts of the Ennore creek particularly show highly significant factor scores, indicating that the sediments in these regions are highly enriched with these heavy metals. Since these metals are not associated with either Fe-Mn or OM, the origin of these metals can be attributed to the surface run-off of contaminated soil from the adjoining industrial areas.

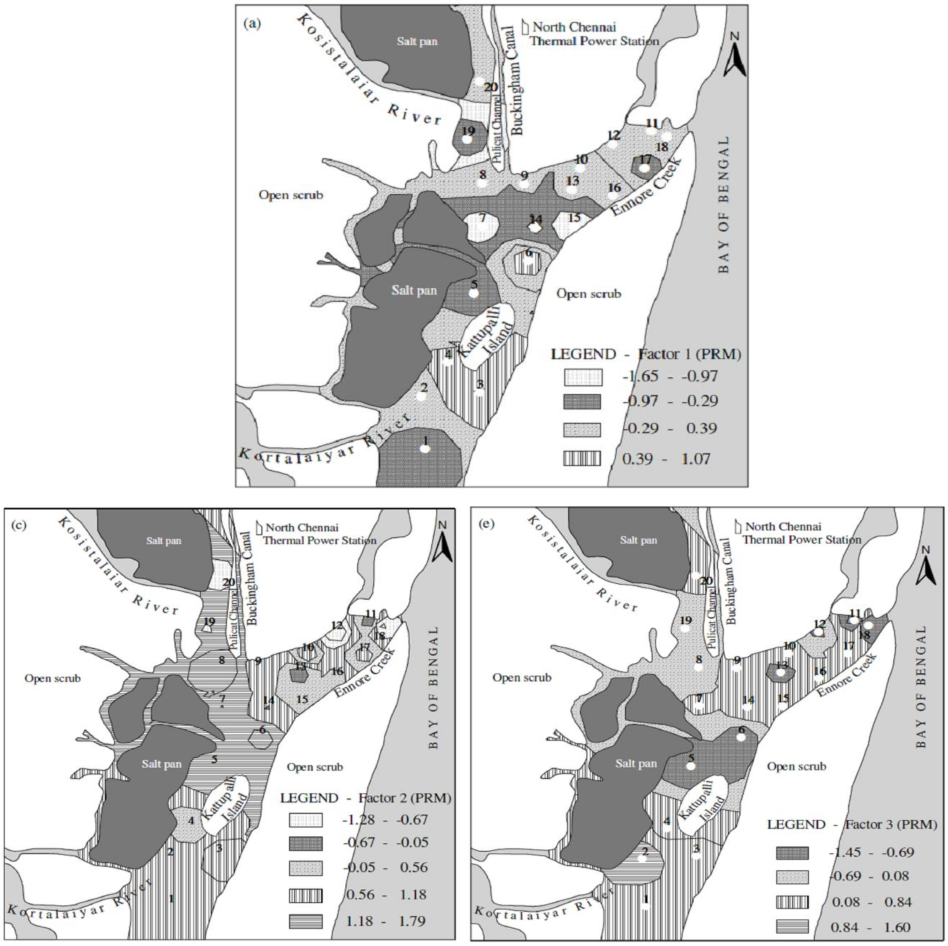

Fig.3(a, c, e): The spatial distribution diagram of factors 1-3 scores for the surface sediments of Ennore creek, SE coast of India during PRM

2. POM Factors

Factor 1 of POM explains 51% of the total variance and has high loadings of Al, Fe, Mn, Co, mud and OM. The high abundance of these metals indicates that their origin must be attributed to anthropogenic and silicate weathering. The factor score diagram shows high values in major parts of the study area (see Fig.3b). Fe-Mn hydroxides and OM act as scavengers and bind to the heavy metals by adsorption/complexation, thereby enriching the heavy metal content in sediments (Tessier *et al.* 1996). Factor 2 of POM accounts for 20% of the total variance and it has high loadings on Mn, Cr, Cu, Ni and Co. The areal distribution diagram of factor 2 reveals that major parts of the study area show high values with regard to this particular factor (Fig.3d). Domestic and industrial effluents are directed into the creek through River Kosistalaiyar, River Kortalaiyar and Buchingham canal, which increase the heavy metal contents in the creek waters. Hence, results of POM fall in line with the PRM with respect to the distribution and concentration of heavy metals. Factor 3 of POM which accounts for 14% of the total variance shows high loadings on Pb and Zn. The spatial distribution map of factor 3 demonstrates that the northern and northeastern parts of the study area show high factor score values, indicating that these regions are affected with regard to this factor (Fig.3f). When compared to PRM, the distribution of these metals during POM was found to be reduced in area and concentrated in the northeastern direction. Seasonal effect was also seen in the distribution and concentration of these metals although the overall effect was minimal.

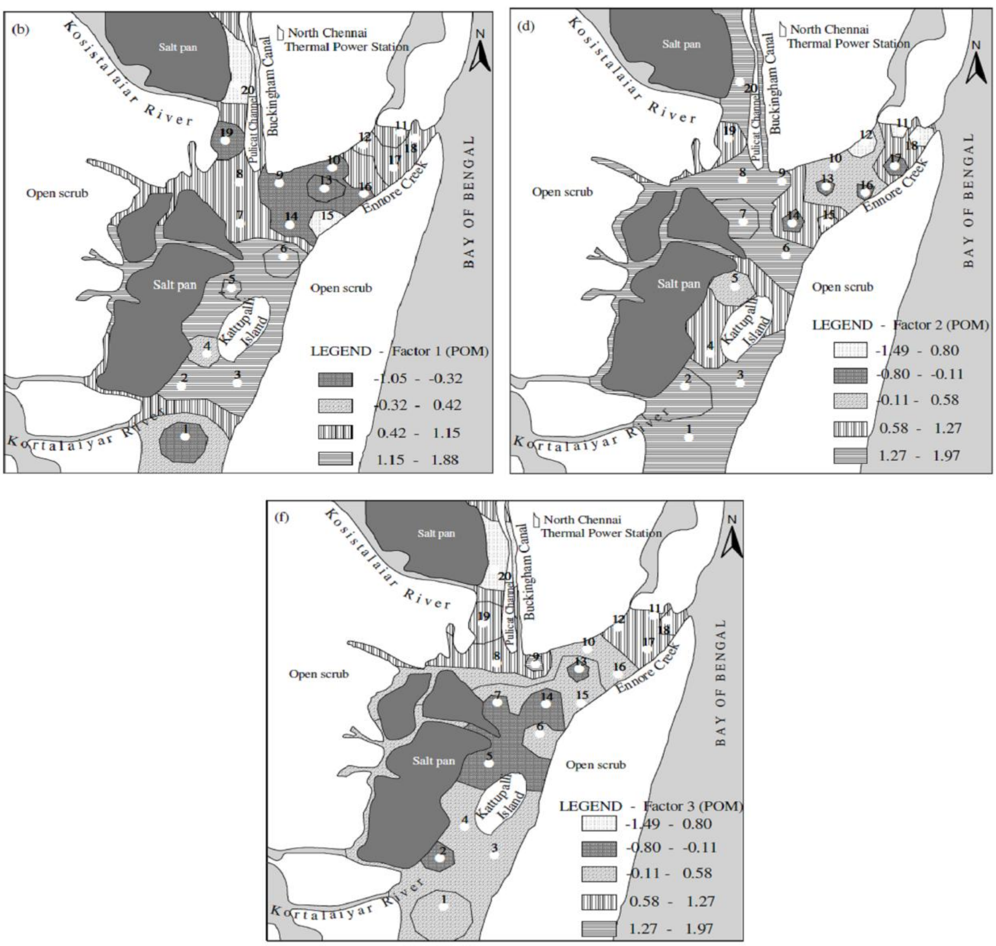

Fig.3(b, d, f): The spatial distribution diagram of factors 1-3 scores for the surface sediments of Ennore creek, SE coast of India during POM

CONCLUSION

The multivariate statistical techniques were applied on the sediment data from Ennore creek and the comprehensive nature of the results from CA and FA clearly demonstrate the effective application of these methods. In addition, the nature and origin of the trace metals were also identified and quantified. The results of CA clearly indicate the associations of all the trace metals with mud and OM, illustrating that the enrichment of metals is mainly from the anthropogenic activities. Meanwhile, the seasonal effects on the trace metal content of the sediments were found to be minimal. The correlation studies have shown that Fe has a strong association with most of the trace metals, along with mud and OM. The industrial activities near Ennore creek are responsible for the enrichment of the trace metals in the sediments. The spatial distribution diagram of the factor scores demonstrates a high concentration of the trace metals near the region, where the highly polluted effluents originate from Buckingham canal. Similarly, the enrichment of metals was observed near the area where the rivers Kosistalaiyar and Kortalaiyar transport both domestic and industrial effluents into the creek waters.

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