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Pre-tsunami chemistry of sediments along the inner continental shelf off Ennore, Chennai, southeast coast of India

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The inner continental shelf off Ennore hosts sediment carrying several minor metals of both natural and anthropogenic origin from the Korttalaiyar River through Ennore Creek. The sediments are mostly sandy silt and silty sand. The $CaCO_3$ and organic matter contents in the sediment are very low (~ 2.1% and ~ 0.9%, respectively). The correlation matrix exhibits poor correlation between these components and minor metals indicating an insignificant role of $CaCO_3$ and organic matter in enriching minor metals. The minor metals exhibit strong mutual positive association (R > 0.6 at 95% confidence level). The geographical distribution of the elements shows higher concentration in northern part of the study area when compared with their concentrations in the southern part. In view of the recent M9-tsunami effect on the coastal sediment of this region, the present investigation provides immediate pre-tsunami minor metal distribution levels. This in turn will provide a reference for studying sediment re-distribution due to high energy tsunami tidal waves in the study region.

[**Key words**: East coast of India, surface sediment, geochemistry, minor metals]

Introduction

The sediments deposited in estuarine and coastal environments are becoming increasingly polluted with minor metals due to urban and industrial development in coastal areas. Hence, understanding the sources of pollution in offshore aquatic systems is important to monitor environmental degradation. Metals in sediments occur in the form of adsorbed ions or bound to hydroxides, oxides, phosphates, carbonates, sulphates and organic matter[1,2]. Important anthropogenic sources like discharge of industrial effluents and sewage dumping contribute significantly to pollution and sediments become the ultimate sink[3,4]. The most important parameter influencing minor metal content in sediment is the sediment particle size[3] and the minor metals are adsorbed on to the particles such as clay and silt, due to their relatively larger surface area. It is possible, therefore, to estimate the intensity of pollution by anthropogenic activity by monitoring specific minor metal content of the surface sediment. Knowledge of the natural background levels of those minor metals in the sediment under consideration is essential for such estimation. Further, the recent M9-tsunami that hit the southeast coast of India, (particularly the Chennai coast) on 26th December 2004 appears to have re-distributed the coastal sediment as evident in focusing of heavy minerals in this region. Any further investigations on the redistributed sediment requires pre-tsunami element inventory. The study area is a 16 km stretch along the northern part of Chennai (Madras) coast off Ennore (Fig. 1). Dark coloured sand, rich in organic content, is found closer to the coast in the vicinity of Buckingham Canal, and is indicative of marine sediments of sub recent origin deposited in a lagoonal facies. Dark coloured heavy minerals are also present in minor quantities in the sediments.

Chennai is a metropolitan city with very high population (~7.5 million) and industrialisation. The Ennore-Chennai sector of Tamil Nadu coast hosts major industrial activities such as oil refining, domestic sewage and solid waste treatment disposal, fishing etc. The study area comprises a coastal stretch on either side of an estuary formed by the Korttalaiyar River (Fig. 1). The river is fed mainly by the monsoon

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rains. As far as industrial activities are concerned, the North Chennai thermal power plant, which dumps coal ash on the adjoining river bank, and several small industries located all along the waterways are the potential contributors to minor and heavy metal pollution in the region. The present study has been carried out to understand the distribution of minor metals and their probable source in the coastal sediments off Ennore.

Materials and Methods

Eleven surface sediment samples were collected using Peterson grab from the near shore continental shelf region off Ennore (July 2004) (Fig. 1). Surface sediment samples were collected from a transect parallel to the coast, with water depth varying from 12 to 20 m. Sediment samples were preserved at 4^{o} C in sealed plastic bags prior to processing for further analysis. Acid-cleaned glassware, analytical grade reagents and distilled water were used for chemical processing of the samples. The samples were analysed for grain size distribution, organic matter (OM) and carbonate content following standard methods[5-7]. The concentrations of Fe, Mn, Cr, Cu, Ni, Co, Pb and Zn were analysed utilising acid-digested sediment samples. For the determination of sand-silt-clay, 20 g sediment was washed through a 230 ASTM sieve until clear water passed through[8]. The washings were transferred to a 1000 ml measuring jar. The material retained on the sieve (sand fraction) was dried and weighed. The 230 mm mesh fraction (< 63 µm) was further categorised as silt and clay by pipette method[5,9]. Calcium carbonate ($CaCO_3$) was determined as Ca by EDTA titration using P and R as internal indicator[10]. The OM was estimated as readily oxidisable organic carbon by acid dichromate digestion and subsequent titration[6].

Finely powdered and overnight oven dried sample (1 g) was digested in sealed Teflon vessel in the presence of hydrofluoric acid (48% v/v) and aquaregia at around 100^{o} C. The HF was complexed with H_3BO_3 (boric acid) and the complexed solution was diluted to known volume before analysis. The solution was transferred to pre-cleaned 100 ml polypropylene bottle. The solutions were analysed for major and minor metals on a flame AAS (Varian SpectrAA 200). The international standard reference material BCSS-1 from the National Research Council of Canada (NRCC) was used to estimate the accuracy of analysis. The analytical accuracy for most of the metals is within the acceptable range[11, 12].

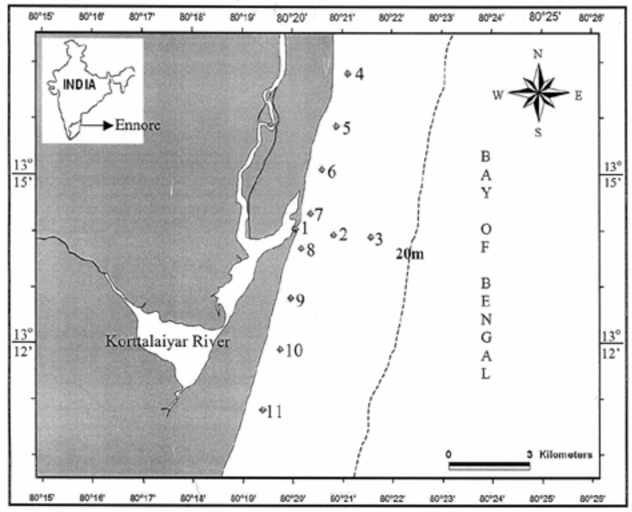

Fig.1—The study area and the sample locations.

Results and Discussion

Sandy-silt and silty-sand dominate in the study region with sand content ranging between 37% and 63% and silt between 33% and 53% (Table 1). Clay content is less than 15%. However, mud (silt + clay) is the dominant fraction (>55%) in most of the sediment samples. The OM content in the sediments is low and ranges from 0.5% to 0.9%. Similar low OM content was also reported from the Krishna Godavari basin[13] and in the Tuticorin shelf region[14] of the Gulf of Mannar indicating that the shelf sediments of east coast of India are generally low in OM. The concentration of $CaCO_3$ in surface sediment is insignificant ranging from 1.2 to 2.1%. Therefore, it is not discussed further. The strong positive correlation between OM and silt and clay (R~0.7) and inverse association with sand (R~-0.8) (Table 2) reflect the greater affinity of OM towards finer fractions[15].

The southern sector of the study area exhibits higher OM content (average of stations 8-11 is around 0.9%) than the northern sector (average of stations 4-7 is around 0.7%). Interestingly, average mud fraction in the southern sector is higher than in the northern sector (Table 1). The distribution of mud content probably explains the strong sympathetic association of OM with fine fraction (Table 2) of the sediment[5].

The spatial distribution of minor metals reveals enrichment form stations 5 to 7 (Fig. 2). The Fe and Mn exhibit strong covariation (R > +0.9: Table 2). Most of the minor metals such as Cr, Co, Ni, Pb and Zn not only exhibit mutual coherency (R > +0.6), but also show strong affinity towards Fe and Mn (R > +0.8: Table 2). Further, these elements show enrichment in the northern sector of the study region as compared to the southern sector (Fig. 2). These observations suggest that most of the minor metals are associated with authigenic Fe-Mn oxyhydroxides particulate fraction in the sediment, and are preferentially enriched in the northern side of the estuary. Station 1, which is located at the centre of the mouth of estuary, appears to mask the boundary of the above separation. The transition metal distribution patterns showing enrichment in the northern sector suggest that most of the metal contaminants entering the estuary are dispersed northward. Assuming the average contents of each metal in the southern sector as natural background, we estimated the percent enrichment of those metals in the northern sector by normalising with the averages obtained for southern sector stations (Fig. 3). The enrichment varies from ~50% to over 200% for different elements, the highest being for Fe and Zn, moderate for Mn, Ni, Co and Cr and lowest for Pb and Cu (Fig. 3). Although the metal distribution and their associations are complex in the present case, the possible scenario is that the local circulation pattern in the study region[16] might be favouring most of the contaminants to migrate northward from the estuarine mouth, leaving the southern part mostly unaffected. However, this needs to be tested vigorously by additional sampling and measurements.

To test the elemental associations, we subjected the compositional data to varimax factor loading. The first factor accounts for 46% of the total variance (Fig. 4) and depicts the strong influence of Fe, Mn, Cr, Ni, Co, Pb and Zn. This explains the general coherence of transition metals probably resulting from a single source. The second factor accounts for 25% of variance incorporating strong positive loading by mud and OM. The third factor accounts for 14% of the total variance and is loaded only by $CaCO_3$ and Cu (Fig. 4). These factor loading results are further supported by the elemental associations obtained by regression analysis.

Table 1—General characteristics of sediments

	Station no.	Depth (m)	Sand (%)	Silt (%)	Clay (%)	OM (%)	$CaCO_3$ (%)	Sediment type Classification[5]
Perpendicular to	1	2	43	50	07	0.9	2.1	Sandy silt
coast	2	15	63	33	04	0.5	1.2	Silty sand
	3	18.5	39	48	13	0.8	2.0	Sandy silt
Northern Sector	4	12	39	53	08	0.7	1.7	Sandy silt
	5	13	56	40	04	0.6	1.8	Silty sand
	6	13	40	45	15	0.9	1.2	Sandy silt
	7	12	50	42	08	0.6	1.8	Silty sand
Southern sector	8	13	42	46	12	0.9	1.9	Sandy silt
	9	13.5	40	47	13	0.9	1.9	Sandy silt
	10	13	37	53	10	0.9	1.5	Sandy silt
	11	13.5	48	50	02	0.7	2.0	Sandy silt
Average values of Northern sector		12.5	46	45	09	0.7	1.6	
Average values of Southern sector		13.25	42	49	09	0.9	1.8	

Table 2—Correlation-matrix exhibiting associations between major components and minor metals in sediments of Ennore Creek (R>0.6 is significant at 95% confidence level; n=11)

	Sand	Silt	Clay	$CaCO_3$	OM	Fe	Mn	Cr	Cu	Ni	Co	Pb	Zn
Sand	1.00												
Silt	**-.89**	1.00											
Clay	-.67	.28	1.00										
$CaCO_3$	-.11	.37	-.28	1.00									
OM	**-.79**	**.70**	**.67**	.09	1.00								
Fe	.17	-.31	.15	-.04	-.21	1.00							
Mn	.30	-.39	-.01	-.20	-.33	**.90**	1.00						
Cr	.20	-.40	.19	-.09	-.29	**.99**	**.87**	1.00					
Cu	.48	-.33	-.30	.10	-.17	.49	.42	.46	1.00				
Ni	.27	-.43	.01	-.23	-.42	**.84**	**.84**	**.83**	.22	1.00			
Co	.18	-.32	.01	-.21	-.38	**.86**	**.84**	**.83**	.22	**.99**	1.00		
Pb	.17	-.34	.02	-.42	-.42	**.57**	**.76**	**.56**	-.10	**.84**	**.83**	1.00	
Zn	.14	-.26	.10	.12	-.24	**.97**	**.85**	**.97**	.49	**.73**	**.75**	.44	1.00

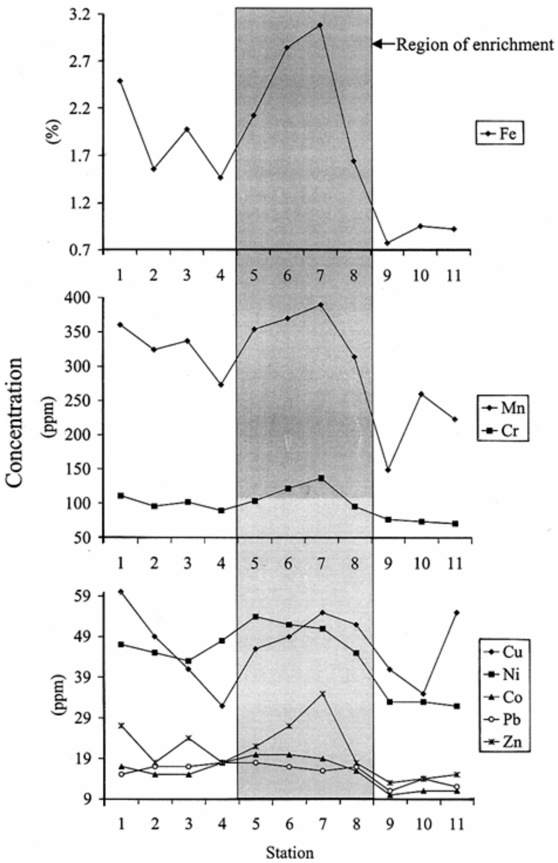

Fig.2—Minor metal concentrations in continental shelf sediments off Ennore.

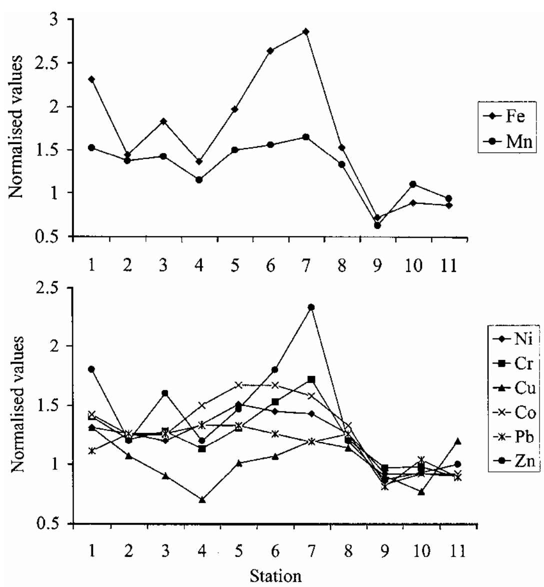

Fig.3—Plots showing enrichment of the minor metals at various sampling locations. The enrichment factor is obtained by normalising each metal concentration by its mean concentration in southern sector sediment

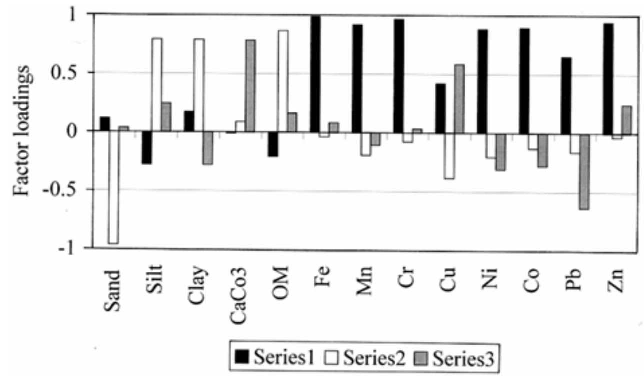

Fig.4—Results of (R-mode) factor analysis exhibiting three primary factors accounting for 85% of the total variance in the studied sediments.

The effluents from the industries and thermal power plant enter the inner shelf off Ennore through Ennore Creek. Northward flowing coastal currents in this region during summer monsoon period[16] may be potential carriers of the contaminants originating from the estuarine region. The coastal currents probably drift the contaminants towards north of the estuary, leading to subsequent incorporation into the sediment as oxyhydroxide particulates. As the sampling for the present study was carried out before the area was hit by M9 tsunami on 26th December 2005, the data presented here may have potential for providing baseline information for post-tsunami sediment redistribution investigations.

Conclusion

The distribution of OM in the surface sediment along the continental shelf off Ennore is controlled by the abundance of mud fraction in sediments. Sediment texture, OM and $CaCO_3$ do not have any influence on the concentration of minor metals. Most of the minor metals are enriched in the northern part of the study area and form a coherent group associated with Fe-Mn hydroxide particulate phase in the sediment. Their enrichment in the northern sector is probably the result of strong summer monsoon currents flowing northward along the coast, and suggests the role of coastal currents in redistributing the contaminants that have been added to the estuary by anthropogenic activity.

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