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ORIGINAL ARTICLE

Metal pollution in coarse sediments of Tuticorin coast, Southeast coast of India

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Abstract Indian coastal waters are subjected to considerable pressure from sewage and industrial wastes, which are responsible for the contamination of the coastal sediments with consequent loss in biosphere. The present investigation attempts to study the significance of coarse material (Sand fraction) in the distribution of metals in polluted marine sediments. The study revealed that coarse Sand component contains a relatively significant proportion of the anthropogenic metals (Cd, Cu, Pb and Zn) and therefore it cannot be neglected in metal pollution studies of coastal sediments. Further, the distribution of anthropogenic metals in both Silt + Clay and Sand fraction follow the same suit indicating similar pollution sources. From the total sediment type (Silt + Clay and Sand fraction) all anthropogenic metals had a noticeable amount (>50%) in the acid extractable (and potentially bio-available) fraction. This article stresses the importance of coarse fraction in metal pollution studies in Indian coastal system.

Keywords Metal pollution · Sand fraction · Coastal zone · Significance · Sediment · Bay of Bengal

Introduction

Many pollution impacts on coastal zones can be traced back directly to the industrialized centers and urban sewage, which release an array of chemical contaminates to effluent system. Others are more difficult to delineate because they are largely derived from contaminants supplied by diffused sources such as run-off from land and atmospheric fallout. One of the significant factors that affect, the metal fractions in coastal sediments is the type of sediment fraction. Higher concentrations are found in the finer particles (Gibbs 1977; Horowitz and Ebrick 1987; Aloupi and Angelidis 2002), due to a synergetic action of physical (surface area) and chemical (mineralogy) characteristics of the particles in each size fraction. Firstly the smaller particulars have a greater specific surface area than the larger ones. Secondly finer particles consist mainly clay minerals, which have more metal binding sites than the silicate or carbonate minerals, which are the major components of carbonate minerals, which are the major components of coarser material in the marine sediments (Campbell et al. 1988; Sarkar et al. 2002). As a result finer particles offer much more sites than the coarser ones for chemical reactions. Therefore, although high metal concentrations can be occasionally found in coarse sediment material (Filipek et al. 1981; Robinson 1982), the Silt and Clay fractions usually contain higher metal concentrations than the sand fraction (Aloupi and Angelidis 2002). That is why metal pollution studies are often carried on the finer fraction (<63 μm), suggesting that the coarser material is significant with regard to metal contribution.

Nevertheless, in the coast front, the coarse material is an important constituent of the sediment and may represent more than 50% of the bulk sediment mass. Therefore it can't be neglected when assessing the pollution. In addition, the vicinity of land based pollution sources which may dispose off large particles, with relatively high metal content (Urban and industrial effluents and deposits) may

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lead to enhanced metal concentrations in coarse sediment material (Aloupi and Angelidis 2002).

The present study attempts to investigate the relative importance of coarse sediments as metal carries in a coastal area affected by land—based pollution sources, compared to fine grained. As total concentrations in sediments are the results of both geological and anthropogenic inputs in the marine environment, we used the extraction with 0.5 N HCl to isolate the anthropogenic effect. This technique removes the non-residual, i.e., non-lattice held metals from sediment grains (Soylak et al. 2002; Tuzen et al. 2004; Soylak and Yýlmaz 2006). These metals are not of the silicate matrix and have been incorporated in to the sediments from aqueous solution by process such as adsorption and originating from anthropogenic sources (Aloupi and Angelidis 2002; Mahmoud et al. 2003; Hoang et al. 2007). The non-residual metals are considered to represent the bio-available part of metal content of marine sediments (Loring 1992). In order to compare the amounts accumulated to both granulometric fractions, we examined separately the sand (63 μm to 1 mm) and Silt + Clay (i.e., <63 μm).

The study area Tuticorin is the harbor city and the coastal area of Tuticorin (population 10,80,000) receives untreated urban effluents through over 20 sewage outfalls, located along the cities coastal line (Fig. 1). In general, the urban effluents of Tuticorin, through including significant industrial (SPIC-Southern Petro Chemical Industries) effluents contained important loads of organic matter and anthropogenic metals (Jayaraju and Reddy 1996). Earlier works on the contamination of surface sediments in the vicinity of the city revealed high-enriched concentration of Cd, Cr, Cu, Pd and Zn in the inner and outer harbor. Some enrichment was also recorded in a part of the sediments of harbor located at the northern part of the city. Further signs of metal contamination were also detected in the wider coastal zone (Jayaraju and Reddy 1996). The coastal area is characterized by fine grain sediments in the inner and outer harbor turning in to coarser texture seawards. The sediments of the harbor are sandy with very small amounts of fine grained material.

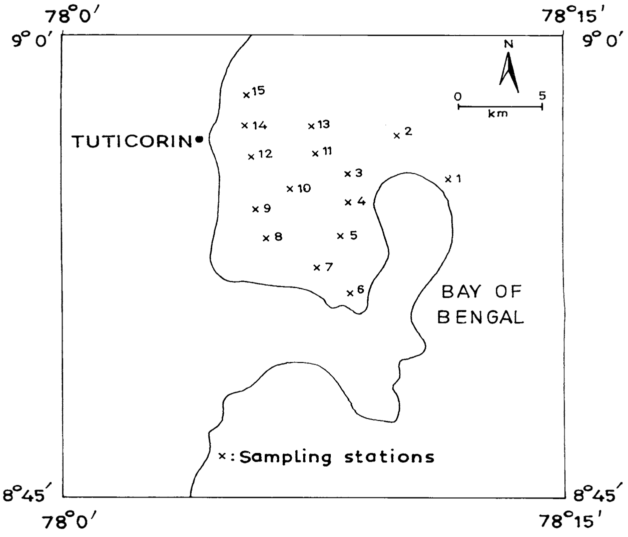

Fig. 1 Study area map with sampling locations

Materials and methods

Surface sediment samples were collected from 15 stations in the harbor and the coastal area of Tuticorin (Fig. 1). Grain size was measured by wet sieving and the following fractions were measured: Gravel (>1) Sand (63 μm < X < 1 mm) and Silt + Clay (<63 μm). The total metal (Cd, Cr, Cu, Fe, Mn, Pb and Zn) content of the samples was measured after total decomposition of 200 mg of dried ground sediment [combined Clay + Silt + Sand (<mm) sample] with 1 ml of *Aqua regia* and 6 ml of Hydrofluoric acid (Loring and Rantala 1992). The most available metal content of the sediments was determined separately in the Silt + Clay fraction and the sand fraction of the sediment was determined separately (Agernion and Chain 1976). Metal determinations were performed using Atomic Absorption Spectrophotometer (Aloupi 1999). In the determinations of the total and extractable metal concentrations the 20% of the samples were analyzed in duplicates.

Table 1 Total metal concentrations and Silt + Clay content in surface sediments from Tuticorin coast area

Stations	Silt + Clay	Fe (%)	Cd	Cr	Cu	Mn	Pb	Zn
			μg g^{-1}					
1	84.63	2.58	0.296	148	65.6	249	82.1	169
2	70.59	2.49	0.310	143	64.2	252	80.3	172
3	89.67	2.78	0.395	151	79.5	250	91.3	213
4	74.73	2.43	0.214	128	50.2	236	65.2	196
5	92.57	2.58	0.364	139	61.4	249	76.5	141
6	86.54	2.41	0.312	132	52.2	258	61.5	149
7	91.04	2.36	0.281	105	48.6	248	62.2	162
8	15.10	1.64	0.162	94.1	28.4	328	42.4	81.4
9	65.36	1.98	0.146	104.2	31.3	310	34.5	76.3
10	64.13	2.41	0.121	124	40.1	268	39.4	104.5
11	65.15	2.49	0.156	113	41.8	272	51.6	118.2
12	67.21	2.15	0.162	92.3	36.4	256	54.3	94.7
13	63.51	2.36	0.142	114	29.5	272	48.4	72.4
14	86.40	2.68	0.101	126	25.6	293	39.2	75.4
15	74.31	2.78	0.092	118	32.3	305	40.4	73.6

Table 2 A measure of 0.5 N HCl extractable metal concentrations (in μg g^{-1} except for Fe in %) in the Silt + Clay and Sand fractions of surface sediments from Tuticorin coastal zone

Station	Cd		Cr		Cu		Fe		Mn		Pb		Zn	
	Silt + Clay	Sand	Silt + Clay	Sand	Silt + Clay	Sand	Silt + Clay	Sand	Silt + Clay	Sand	Silt + Clay	Sand	Silt + Clay	Sand
1	0.364	0.179	17.8	9.14	41.4	20.2	0.421	0.193	103	112	52.4	42.6	116	72.3
2	0.521	0.413	13.9	10.6	43.5	24.2	0.410	0.243	109	117	56.5	48.1	121	84.7
3	0.496	0.214	15.6	7.51	54.9	15.6	0.392	0.162	98.6	121	75.4	37.6	146	59.5
4	0.243	0.179	12.6	4.51	36.5	5.4	0.312	0.110	104.5	103	58.6	28.4	79	35.4
5	0.352	0.212	16.4	6.91	41.5	18.9	0.412	0.214	115	104	59.8	39.5	126	45.9
6	0.242	0.169	14.6	6.52	38.4	15.3	0.345	0.196	105	114	46.9	27.9	86.2	42.3
7	0.200	0.146	14.2	4.15	26.8	10.3	0.365	0.060	121	105	51.6	40.3	82.1	24.3
8	0.268	0.145	12.9	6.42	25.9	8.48	0.251	0.242	118	262	46.5	25.4	98.6	30.4
9	0.210	0.136	13.5	4.52	20.6	5.48	0.532	0.068	105	163	34.9	20.6	46.2	10.5
10	0.191	0.113	14.2	5.12	18.4	6.43	0.358	0.321	101	106	36.2	10.5	6.2	20.2
11	0.171	0.102	14.6	3.12	20.2	10.51	0.254	0.210	103	102	60.5	25.6	39.5	38.6
12	0.172	0.149	13.5	4.12	16.5	4.36	0.201	0.085	110	120	49.6	2.5	58.5	36.2
13	0.160	0.108	13.0	5.32	18.4	6.71	0.263	0.215	93.6	107	36.3	15.2	38.9	18.2
14	0.110	0.091	15.2	3.58	15.3	3.51	0.163	0.012	103	65.3	31.5	10.3	23.5	10.52
15	0.096	0.084	13.2	6.50	14.3	6.51	0.321	0.153	215	74.6	30.2	14.2	16.5	4.56

Results and discussion

The total metal concentrations and the Silt + Clay content in the bulk sediments (Clay + Silt + Sand fraction) of the study area are presented in Table 1. Acidic extractible of the metals in the Sand + Silt + Clay fractions of the sediments is also done (Table 2). With regard to the total concentrations, acidic extractible concentrations of the anthropogenic metals (Cd, Cr, Pb and Zn) were higher in the sediments of the harbor of the city (Stations 3,4) compared to the sediments of the wider coastal area, for both the fine (Silt + Clay) and coarse (Sand) fractions. For all metals (with the excepting of Mn) concentrations in the Silt + Clay fractions were higher than in the sand as anticipated (Fig. 2).

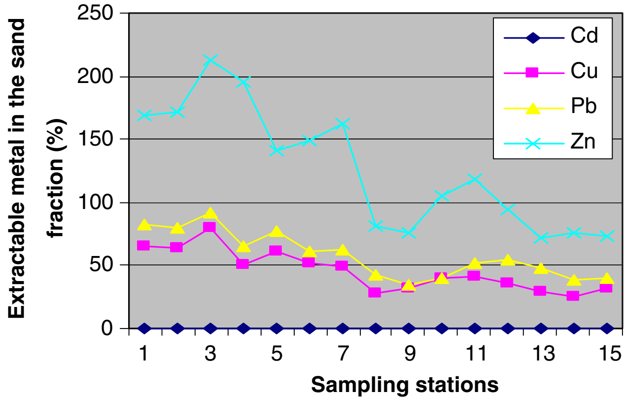

Fig. 2 Percentage of Extractable Cd, Cu, Pb and Zn from the Sand fraction

Table 3 Correlation co-efficient of 0.5 N HCl extractable metal concentrations in each of the Silt + Clay and the Sand Fractions of the sediment

		Cd	Cr	Cu	Fe	Mn	Pb
Cr	Silt + Clay	0.46^{a}					
	Sand	0.43^{a}					
Cu	Silt + Clay	0.89^{b}	0.42^{a}				
	Sand	0.76^{b}	0.72^{a}				
Fe	Silt + Clay	0.48^{a}	0.69^{b}	NS			
	Sand	NS	0.72^{b}	0.63^{b}			
Mn	Silt + Clay	NS	NS	NS	NS		
	Sand	NS	NS	NS	NS		
Pb	Silt + Clay	0.49^{a}	0.03	0.68^{b}	NS	NS	
	Sand	0.68^{a}	0.63	0.72^{b}	NS	NS	
Zn	Silt + Clay	0.86^{b}	0.46	0.91^{b}	NS	NS	0.65^{b}
	Sand	0.81^{b}	0.78^{b}	0.78^{b}	NS	NS	0.86^{b}

NS non significant

[a] Correlation significant at 0.05 level (two-tailed test)

[b] Correlation significant at 0.05 level (two-tailed test)

Nevertheless, the sand fractions had also important metal concentrations, especially in the stations from the Harbor of Tuticorin (Table 2). Metal enrichments in coarse sediments have already been recorded in polluted areas (Aloupi and Angelidis 2002; Mostafa et al. 2004) and may be explained in the formation of coatings on the surface of the particles. High correlation co-efficients were calculated for the human related metals Cd, Cr, Cu, Pb and Zn in each grain—size fraction separately (Table 3) indicating similar distribution processes. Also, the concentrations of each of the anthropogenic metals in the Silt + Clay and Sand fractions were highly correlated (Table 3). Such correlations suggest that the metal enhancement in the sediments of a polluted area is simultaneously recorded in both Silt + Clay and sand fractions (Table 3).

The acid extractable concentrations in the bulk sediment (Silt + Clay + Sand) were calculated by summing the partial concentrations weighed to the percentage of the relative granulometric fraction in the sediment. Afterwards the same were compared to the total metal concentrations to estimate the percentage of the acid extractable, i.e., non-residual metal.

The non- residual character of the metals follows the order: Cd > Pb > Zn > Cu > Mn > Fe. Cadmium appears to be totally extractible and bioavailable (104 ± 17%) in

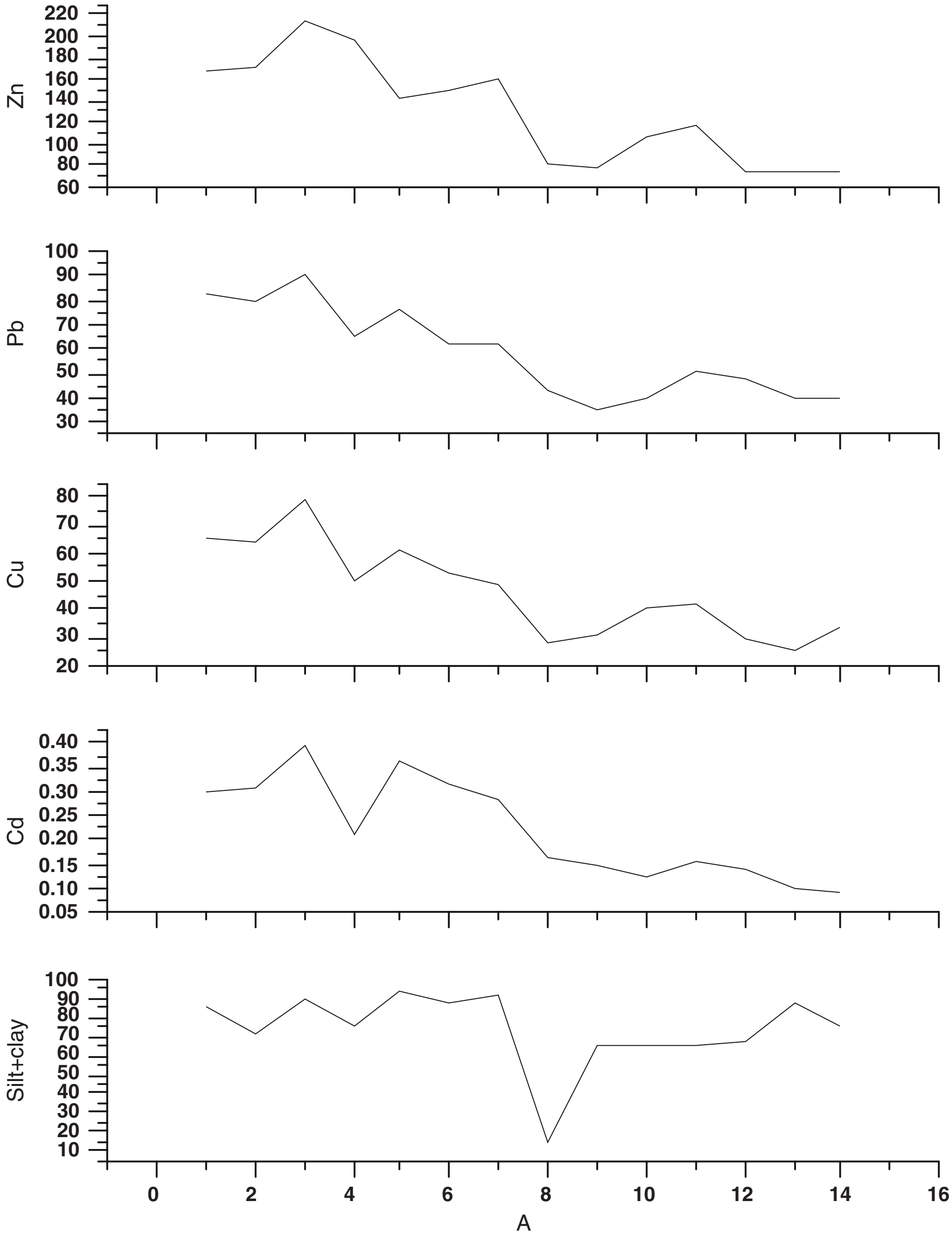

Fig. 3 The concentrations of Heavy metal in the sampling stations

accordance to the literature (Campbell et al. 1988). The other anthropogenic metals had also high extractable percentages (48 ± 12% for Cu, 69 ± 20% for Pb and 59 ± 13% for Zn) were placed in the first positions of the sequence. On the other hand Fe and Cr were the less acid-extractable metals (12 ± 3 and 117 ± 27%), respectively, indicating their association mostly to the lattice of minerals of the sediments. These results indicate that an important part of the metals accumulated in fine, as well as in coarser sediments of the marine coastal environment of Tuticorin are potentially bio-available and may be released to the marine tropic chain.

The percentage of total metal concentrations (Cd, Cu, Pb and Zn) extracted by 0.5 N HCl (Sigma, St Loius, MO, USA) four of the sand fraction of the study area were calculated and are presented (Fig. 3). For all metals examined, the percentage of total concentrations extracted from the sand fraction increases with the sand content of sediments, reflecting the increasing relative importance of the coarser fraction in the sediment, as expected. Therefore, since contamination is restricted to the harbor area, the real importance of sand as anthropogenic metal carrier seems negligible. Nevertheless, this is not the case in the sediments of the earlier harbor which are considered contaminated by anthropogenic metals. Although, the fine material is efficiently dispersed from the study area by the hydrological regime of the area, contamination is still recorded in the sandy sediments.

Conclusions

The study of the acid extractable metals in the surface sediments of the coastal area of Tuticorin revealed the contamination of the harbor sediments by Cd, Cu, Pb and Zn. Although concentrations were higher in the Silt + Clay fraction than in the sand fraction, percentages of total concentrations extracted from the coarse fraction, especially in the sandy harbor area showed that sand is also an important carrier of extractable metals. The high correlation co-efficients found between the acid-extractable concentrations of the metals Cd, Cu, Pb and Zn in both grain size fractions as well as for each metal in the granulometric fractions, indicate their common anthropogenic source. Also, it seems that the metal contamination is recorded in Silt + Clay and Sand fraction of the polluted sediments. It is therefore suggested that coarse sediments should not be disregarded in pollution studies of the coastal zone, especially in areas where an important part of the sediment material may have a texture characterized as sand. The concentrations of these heavy metals, which fluctuate from one station to another with high correlation coefficient suggest anthropogenic sources.

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