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Assessment of metal enrichments in tsunamigenic sediments of Pichavaram mangroves, southeast coast of India

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Abstract The 26 December 2004-Tsunami has deposited sediments in the Pichavaram mangrove ecosystem, east coast of India. Ten surface and three core sediment samples were collected within thirty days of the event. High concentrations of Cd, Cu, Cr, Pb, and Ni were observed in the tsunamigenic sediments. With respect to Fe, Zn, and Mn, there was little variation as compared to pre-tsunami values. The geo-accumulation index was calculated in order to assess the contamination of heavy metals in the sediments. The sediments were extremely contaminated with respect to Cd and they showed moderate to strong contamination with respect to Cr, Pb and Ni. The study highlighted the future risk of enhanced metal pollution in near future in this mangrove ecosystem.

Keywords Tsunami · Sediments · Heavy metals · Pichavaram · Mangroves · Geo-accumulation index

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Introduction

Mangroves are among the most productive coastal ecosystems in the world. They are confined to the tropics and subtropics, which dominate approximately 75% of the world's coastline between 25° N and 25° S and are estimated to cover an area of 1.7 to 2.0× 10^5 km^2 (Borges et al. 2003). Through out welling of leaf litter and dissolved organic matter, mangroves act as detritus sources to the adjacent oligotrophic marine food webs, supporting valuable estuarine and coastal fisheries (Singh et al. 2005). They are regarded not only as sinks of sediment and nutrients, but also as sources of organic matter of low nutrient quality (Boto 1982, 1992). Despite being of low nutrient quality, the mangrove sediments are characterized by high organic matter and ammonia contents but low oxygen content (Morell and Corredor 1993), contributions of nutrients, organic matter and detritus to the nearby coastal ecosystem are high (Singh et al. 2005). These productive, tropical wetlands are exposed to anthropogenic contamination from tidal water, river water and land-based sources (Klekowski et al. 1994) as well as to the natural calamities like tsunamis (Seralathan et al. 2006).

A tsunami is an extremely large ocean wave triggered by an underwater earthquake, volcanic activities or landslides. Tsunami waves have unusually long-wavelengths in excess of 100 km, are generated in the open ocean and transformed into a train of catastrophic oscillations on the sea surface close to coastal zones. These waves can produce extensive changes in coastline topography due to considerable erosion and subsequent deposition of a substantial quantity of sediments in a relatively short time span (Dawson 1994; Bryant et al. 1996; Bryant 2001; Scheffers and Kelletat 2003 and Szczucinski et al. 2005). Translation of large amounts of seawater on land by tsunami waves introduces large amounts of salt into surface and ground water, substantially impacting the coastal ecosystem. In spite of the number of studies focused on contemporary tsunami sediments (Nishimura and Miyaji 1995; Shi et al. 1995; Dawson et al. 1996, Dawson and Shi 2000; Nanayama et al. 2000; Gelfenbaum and Jaffe 2003 and Szczucinski et al. 2005), the impact of metal contamination and possible sources has never been addressed.

The 2004-tsunami reached the coasts of most landmasses bordering the Indian Ocean, killing large numbers of people and inundating coastal communities across South and Southeast Asia, including parts of Indonesia, Sri Lanka, India, and Thailand. In India resulted in the death of approximately 12,405 people and the displacement of 647,599 others, eventually resulting into a socioeconomic crisis in the area (Situation Report, No. 32-/2004-NDM-Government of India, Ministry of Home Affairs Ministry of Home Affairs; retrieved June 20, 2007 from http://www.tsunamispecialenvoy.org/country/india.asp). The mangrove vegetation, along the southeast coast of India, acted as a shield, protecting the human settlements in the vicinity from the killer tsunami waves. As a result, there was reduced destruction in the areas with mangrove vegetation (Danielsen et al. 2005; Kathiresan and Rajendran 2005).

Mangrove sediments are anaerobic and are rich in sulphides and rich in organic matter (Silva et al. 1990). They, therefore, favor the retention of water-borne heavy metals and the subsequent oxidation of sulphides between tidal events, allowing metal mobilization and bioavailability (Silva et al. 1990 and Tam and Wong 2000). Concentrations of heavy metals in sediments usually exceed those of the overlying water by three to five orders of magnitude. With such high concentrations, the bioavailability of even a minute fraction of the total sediment metal content assumes considerable importance with respect to bioaccumulation within both animal and plant species living in the mangrove environment. Since heavy metals cannot be degraded biologically, they are slowly transferred to and become concentrated in plant tissues and pose long-term damaging effects on vegetation. After decomposition of mangrove leaves, heavy metals ultimately reach to mangrove sediment (Zabetoglou et al. 2002). Tam and Wong (1993) suggested that the mangrove soil component has a large capacity to retain heavy metals, and the role of mangrove plants in retaining metals will depend on plant age and their biomass production. Tsunami waves are considered to be a transporter of offshore sediments rich in heavy minerals, which become deposits at the coast (Szczucinski et al. 2005). Further the retreating water carries the anthropogenic load with itself which in turn may get deposited at the coastal sediments. The tsunami waves are therefore believed to serve as one of the major contaminating agents of costal sediments (Kathiresan 2005).

Present study was undertaken with the aim of assessing heavy metal contamination in the sediments of the Pichavaram mangrove resulting from the 26 December 2004 tsunami.

Study area

The Pichavaram mangroves are located between the Vellar and the Coleroon estuaries (latitude 11°23–11°30 N and longitude 79°45–79°50′ E) in the southeast coast of India (Fig. 1). It serves as a good example of the degradation of a mangrove ecosystem due to aquaculture practices. During 1970s, there were no aquaculture ponds in the area, whereas in 1984 it increased to 3.99 km^2 and in 1996 to 6.99 km^2 (Hong Yeon et al. 2004; Kathiresan 2004, 2005). Furthermore the anthropogenic (domestic and industrial) discharges from the nearby densely populated area contribute significantly to the ecological vulnerability of this ecosystem (Prasad 2005; Ranjan et al. 2007).

The 11 km^2 of Pichavaram, consisting of 51 islets, is 50% covered by forest, 40% by waterways and the rest filled by mud and sand flats (Fig. 1; Krishnamurthy and Jayaseelan 1983). The ecosystem faces two monsoons seasons; southwest monsoon from June to July and northeast Monsoon from October to January. The annual temperature variation is 18.2–36°C. The biogeochemical processes in this ecosystem are governed by the heavy input of sediments and

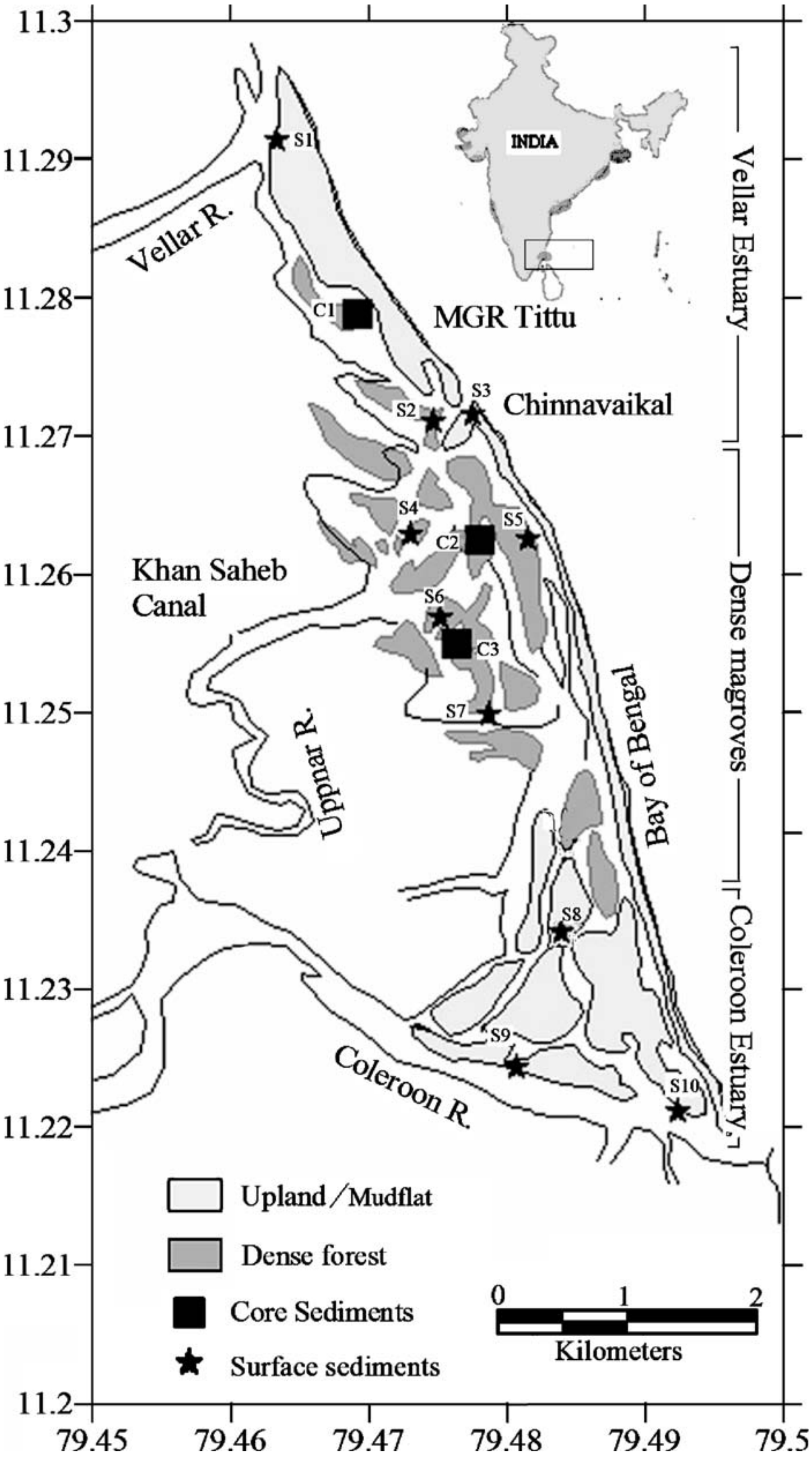


Fig. 1 Map of study area—Pichavaram mangrove

anthropogenic discharges from the Vellar and Coleroon River (Figs. 1 and 2). Uppnar River and Khan Saheb Canal contributes significantly discharge during monsoon season. The anthropogenic input from the nearby agricultural, domestic and industrial processes through Khan Sahab canal has made this pristine ecosystem vulnerable for the heavy metal contamination (Yeon CHO et al. 2004; Prasad 2005). The Pichavaram forest is tide dominated with amplitude ranging from 0.5 to 1 m. Geomorphically, the area is mostly covered by floodplain, sedimentary plain and beach sand. Alluvium is dominant in the western part whereas fluvial marine and beach sand covers the eastern part of the mangrove. Thirteen species of true mangrove flora species are present in the area with Avicennia and Rhizophora as the most common and dominant (Kathiresan and Ramanathan 1997). The Tsunami of 2004 has caused the deposition of offshore sediments containing heavy minerals and heavy metals to the mangroves (Babu et al. 2007; Seralathan et al. 2006).

Despite the fact, that this pristine ecosystem has been continuously exposed to anthropogenic pressure, there exist very few recent studies about the impact of heavy metals and other contaminants for the past few years (Ramanathan et al. 1999; Periakali et al. 2000).

Materials and methods

Sampling locations

Surface sediment samples were collected from ten different locations covering the entire Pichavaram mangrove (Fig. 1) and adjoining estuarine complex in January, 2005. The sampling locations were divided in three parts namely Vellar estuary region {S1 and S2 (MGR Tittu), S3 (Chinnavaiklal)}, dense mangrove forest region (S4, S5, S6, and S7) and Coleroon estuary region (S8, S9 and S10). Sediment cores were collected from the three sites to understand the interaction of various components (Tsunami, Anthropogenic input, natural impact etc). Core 1 was collected from Vellar estuary region, whereas Core 2 and Core 3 were collected from dense mangrove forest region. A comparison with previous study (Ramanathan et al. 1999) was made for the identical sampling locations.

Sample collection and preservation

Sediment samples (1 kg each) were collected in polyethylene bags using a stainless steel scooper. Stainless steel corer with an internal diameter 7 cm was used for the collection of three cores. The locations were chosen carefully in order to reflect the tsunami impact through sedimentary records as reported by Seralathan et al. (2006), which were observed up to 38cm using textural and heavy mineral analysis. Two cores of 40 cm (at site 1 and 3) and one core of 50 cm (at site 2) were collected which were sliced at 5 cm intervals. The segments were immediately transferred into polyethylene zip bags. All samples were stored on ice chest in the field and were transferred to laboratory where they were stored at 4°C.

Analysis of sediments

Grain size analysis

The sediment size fraction greater than 63 μm was separated using sieving techniques. Further separation of <63 μm size fractions was carried out using Atternburg sedimentation cylinders methods based on Stokes' law (Griffiths 1967). Grain size analysis was completed following methods outlined by Shapiro (1975). It was performed with seven samples (S1, S2, S5, S6, S7, S8 and S9) due to limitation of sample quantity.

Preparation of digest for heavy metal analysis

Analysis of heavy metals in the surface and core sediments was carried out as per Shapiro (1975). Approximately 0.1 g of finely ground sample was digested using three acids (2 ml of HNO_3: HCl in 1:3 ratio and 5 ml HF) at 100°C for 1.5 h. 5.6 g of Boric acid crystal (H_3BO_3) was added and the final sample volume was made 100 ml by adding double distilled water. The gelatinous precipitate of borosilicate was separated by centrifugation followed by filtration with Whattman 0.45 μm cellulose nitrate filter paper.

Standardization of AAS

Canadian soil standards, as reference standards, were digested as per the methods described in "Preparation of digest for heavy metal analysis" section above. Heavy metals in the sediment extracts were analyzed

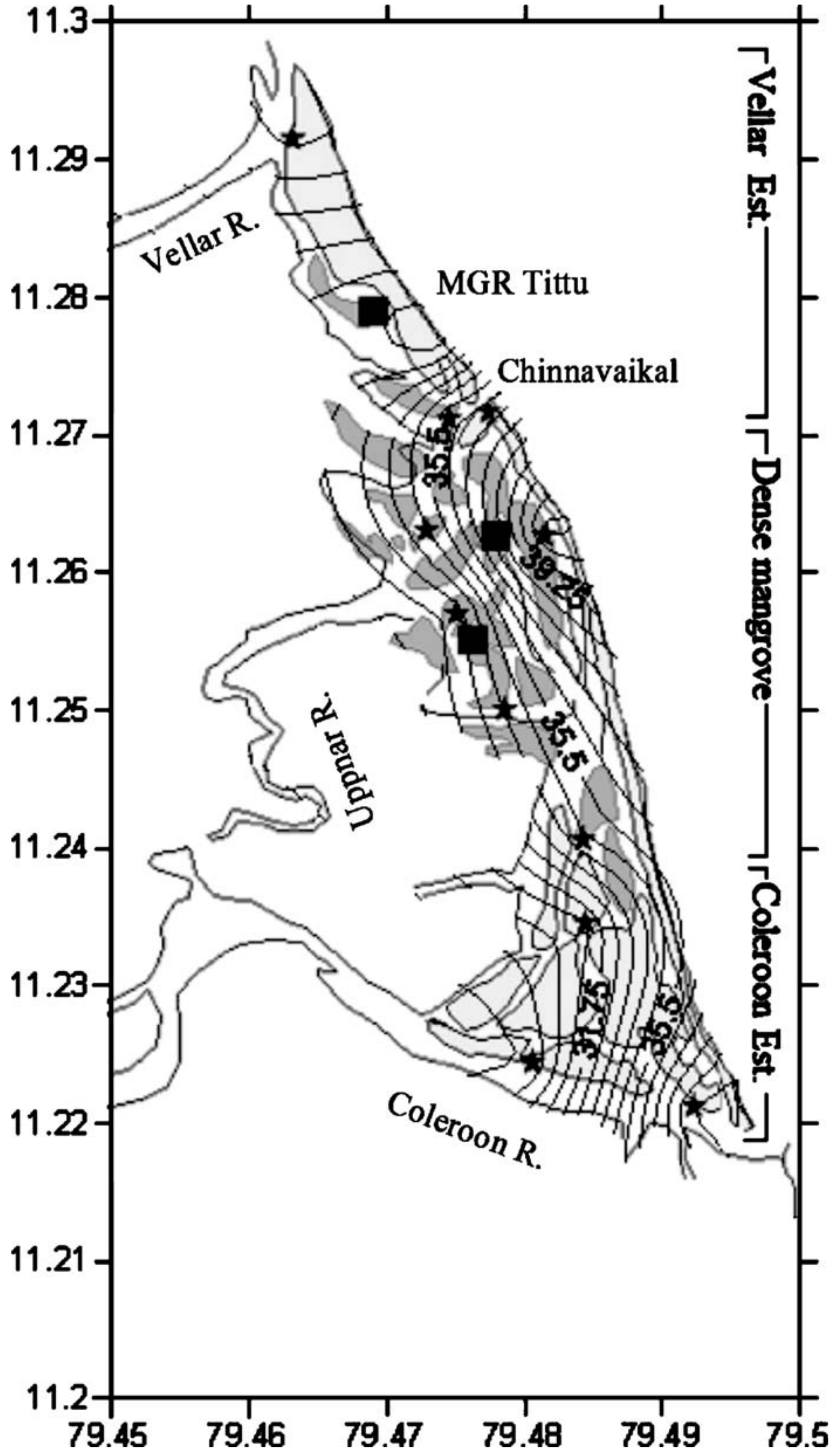


Fig. 2 Spatial distribution of Cadmium (in μg/g) in post-tsunami sediments of Pichavaram

by using an (Shimadzu-AA-6800) Atomic Absorption Spectroscope. The instrument was standardized using multi-elemental standard MESS 2 (Merck). When the reported values for the Canadian soil standards were compared to the observed value a variation of 5–11% was observed.

Statistical analysis

The observed results were statistically analyzed using computer aided packages EXCEL (Microsoft Office version 2003), SPSS version 10.5, and SIGMAPLOT version 2001. Digitization of the map was done using GEOMATICA and contours were drawn using SURFER Version 8.0. The values expressed in the Table 1 are the mean of ten sampling locations.

Geoaccumulation index (I_{geo})

The geoaccumulation index (I_{geo}) was originally defined by Muller (1979) as a quantitative measure of the metal pollution in aquatic sediments (Ridgway and Shimmield 2002). I_{geo} was used as a part of this study to understand trace metals contamination in the sediments. The world average concentration of these elements reported for shale (Turekian and Wedepohl 1961) was taken as the background values.

The formula used for the calculation of the geoaccumulation index is as follow:

$$I_{geo} = \log_2 \frac{C_N}{1.5 B_N} \qquad (1)$$

Where C_N is the measured content of element, and B_N is the content of 'average shale' (Turekian and Wedepohl 1961).

Results

Heavy metals were categorized into two groups based on the basis of change in concentrations in the mangrove sediments due to the tsunami (Table 1). The first group included Cadmium (Cd), Cupper (Cu), Chromium (Cr), Lead (Pb), and Nickel (Ni), whose concentrations were higher in tsunamigenic sediments as compared to previous studies (Ramanathan et al. 1999). In the second group, Iron (Fe), Zinc (Zn), and Manganese (Mn), showed little variation or decrease as compared to the sediments studied before the tsunami.

Variation of heavy metals in the surface sediments

The cadmium concentration in surface sediments near Khan Saheb Canal was highest which may be a result of the synergistic effect of anthropogenic inputs e.g. fertilizers driven by Vellar, Uppnar and Coleroon river as well as from the tsunami driven sediments derived from the deep ocean (Li et al. 2006; Seralathan et al. 2006). The mean value of cadmium concentration in pre-tsunami sediments was reported to 6.96 μg/g (Table 1; Ramanathan et al. 1999). It is reported that the phosphate fertilizers may contain from 10 to 200 ppm cadmium (Cook and Morrow 1995) and over a longer time scale, it tends to accumulate in the agricultural soil (Mench 1998; Ghrefat and Yusuf 2006). The average Cd concentration in the earth's crust varies between 0.1 and 0.5 μg/g. High levels of Cd accumulate in sedimentary rocks, and marine phosphates and phosphorites have been reported to contain levels as high as 500 μg/g (WHO 1992; Cook and Morrow 1995). Therefore, the increase in Cd concentration may also be attributed to fact that marine sediments from deep oceans, rich in Cd, might have been trapped in mangrove sediments after the tsunami. This may have resulted in such an enormous increase in its concentration. Similar observation were made in Thailand where the mean concentration of Cd showed was observed as 1.2 μg/g (range 0.6–1.7 μg/g) after the tsunami (Szczucinski et al. 2005).

A high concentration of Chromium was observed at all locations (Fig. 3). Seralathan et al. (2006) reported that considerable amounts of heavy minerals

Table 1 Comparison of heavy metals (mean values in μg/g) in (pre-tsunami and post-tsunami sediment from Pichavaram

Pichavaram	Cd	Cr	Cu	Ni	Pb	Fe	Mn	Zn	
Post tsunami	34.74	617	132.3	252.1	143.8	24,998	801	106	Present study
Pre tsunami	6.96	141.2	32	62	11.2	32,482	701	89	Ramanathan et al. 1999

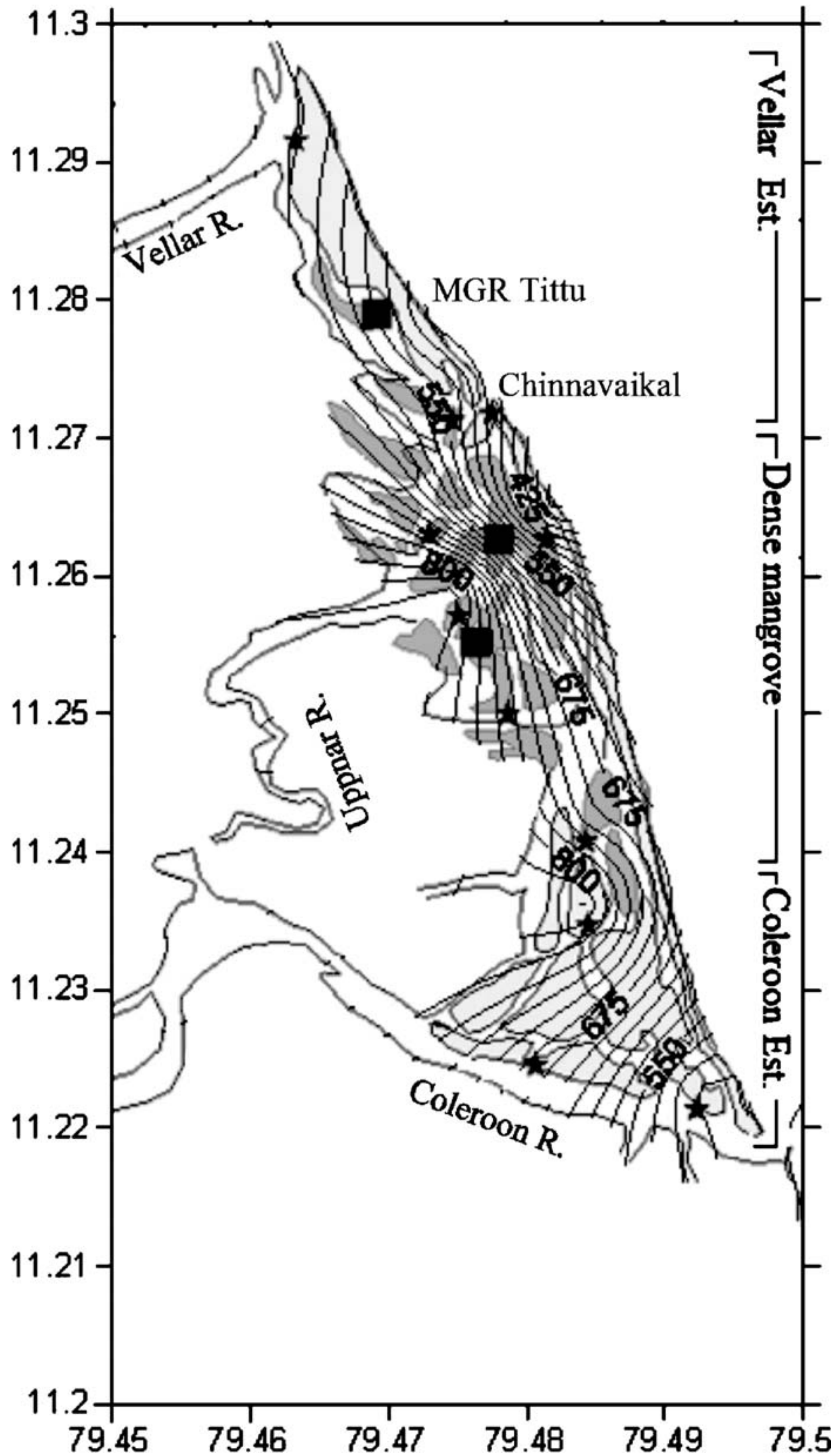
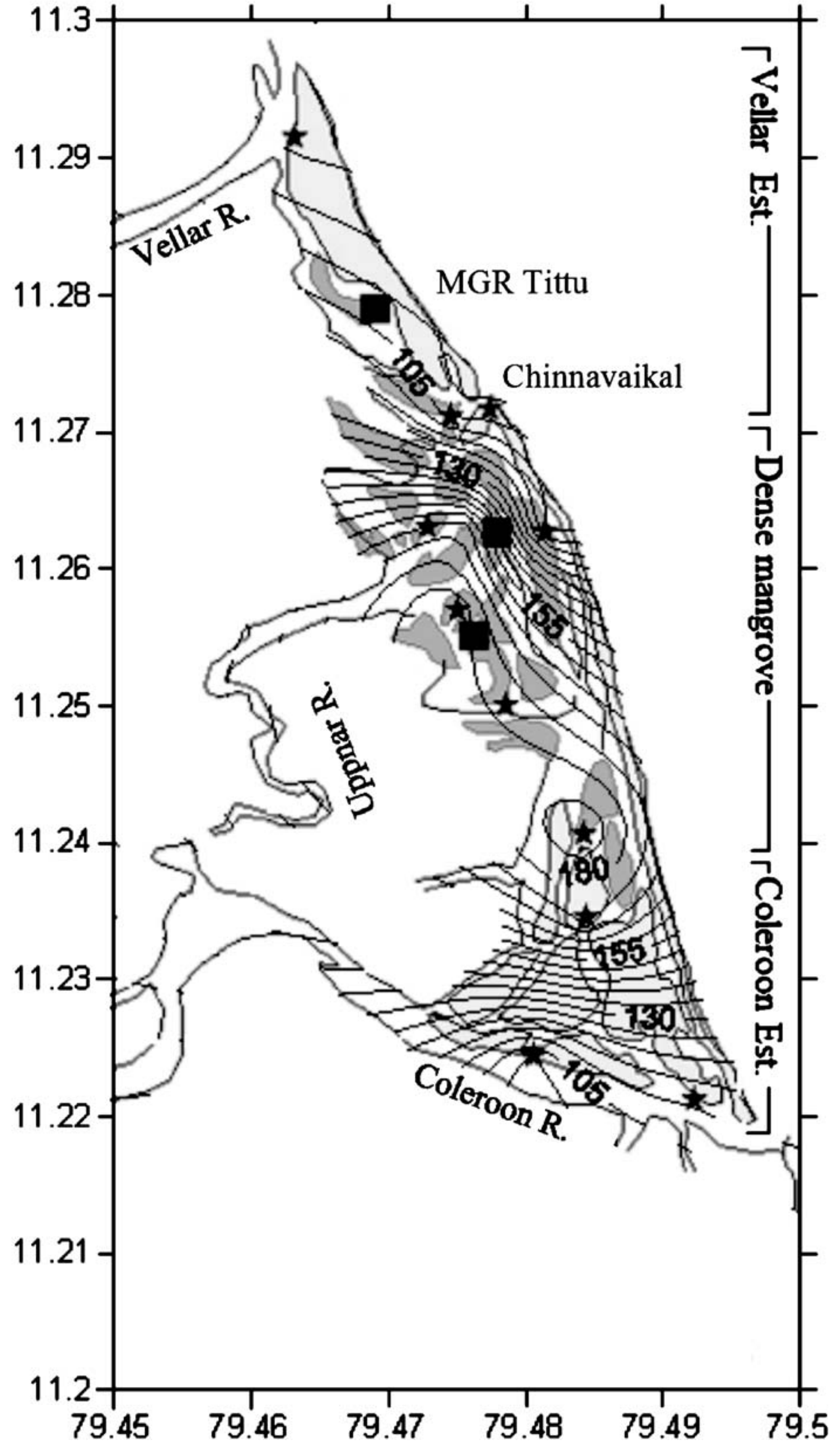


Fig. 3 Spatial distribution of Chromium (in μg/g) in post-tsunami sediments of Pichavaram

Fig. 4 Spatial distribution of Cupper (in μg/g) in post-tsunami sediments of Pichavaram



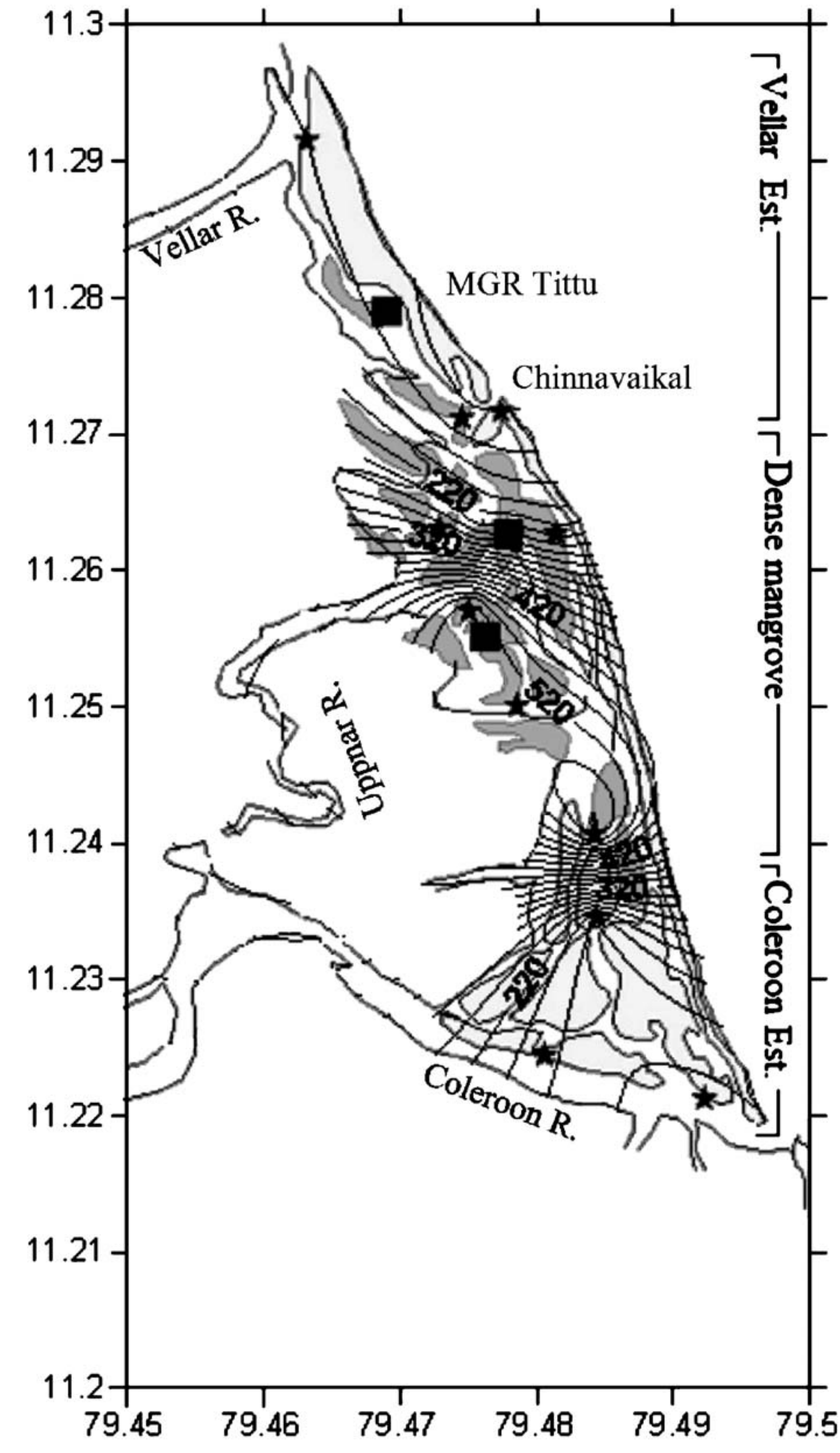


Fig. 5 Spatial distribution of Nickel (in μg/g) in post-tsunami sediments of Pichavaram

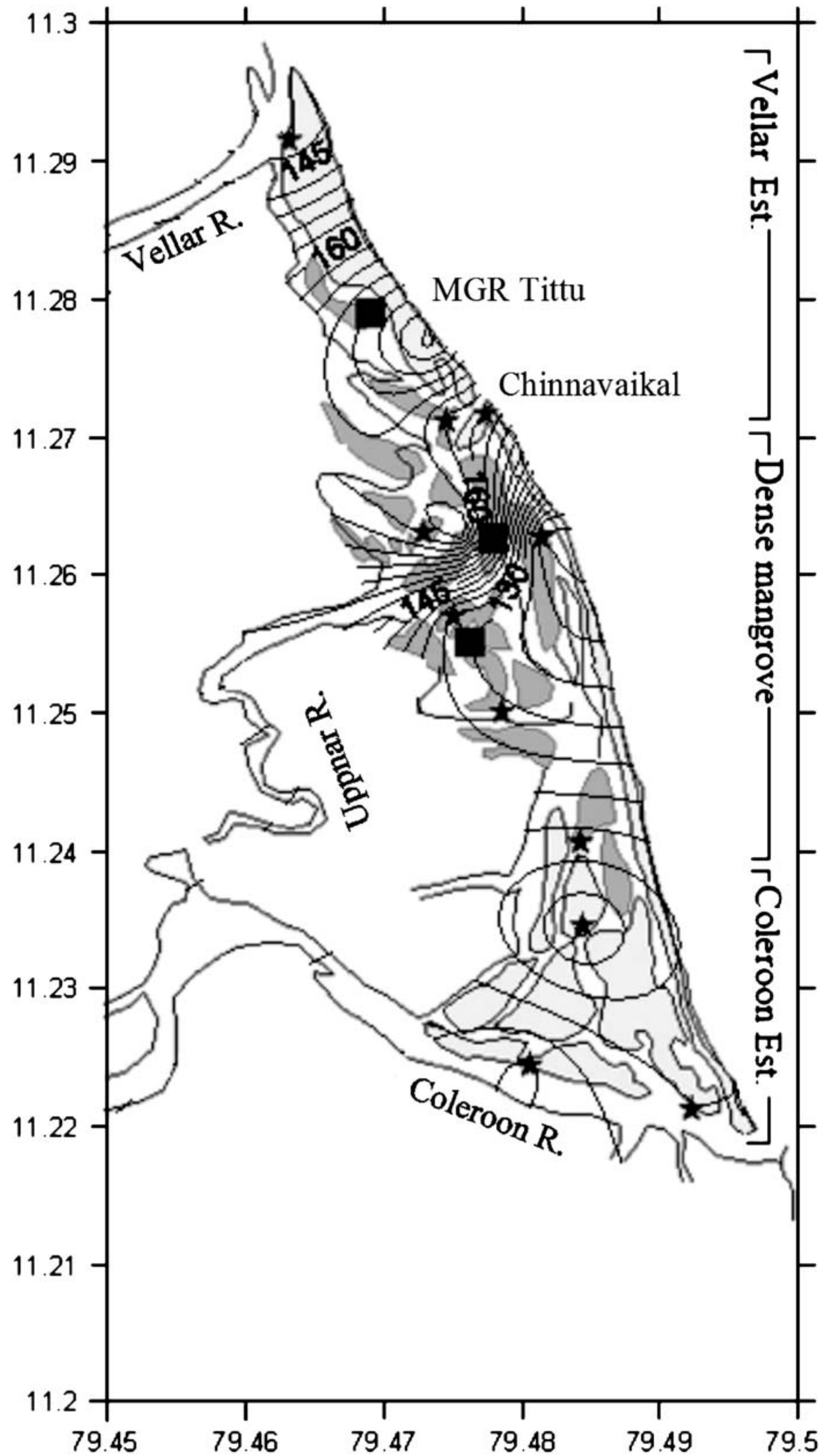


Fig. 6 Spatial distribution of Lead (in μg/g) in post-tsunami sediments of Pichavaram

Table 2 Correlation matrix of total heavy metal in sediments of Pichavaram: post tsunami (n=10)

	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn	OC
Cd	1.00								
Cr	−0.67	1.00							
Cu	−0.38	0.73	1.00						
Fe	0.04	0.66	0.62	1.00					
Mn	−0.43	0.74	0.29	0.53	1.00				
Ni	−0.15	0.55	0.75	0.43	0.32	1.00			
Pb	−0.50	−0.13	−0.09	−0.57	−0.53	−0.38	1.00		
Zn	0.08	0.29	0.19	0.45	0.25	0.43	−0.39	1.00	
OC	0.70	−0.07	0.29	0.60	−0.14	0.38	−0.60	0.54	1.00

which surfaced after tsunami waves in the southeast coast of India and attributed their presence due to the abundance of garnet mineral family. Uvarovite [Ca_3Cr_2 $(SiO_4)_3$] being the dominant among the garnet minerals in the tsunamigenic sediments may be the major contributor of Cr during Tsunami. In addition, the untreated effluent discharges of the industries situated in the vicinity of Uppnar estuary might have also caused higher Cr concentration in the sediments during and after tsunami (Schumacher et al. 2001; Khan et al. 2004).

The mean concentration of copper was observed as 132.3 μg/g with a minimum value of 88 μg/g and maximum value of 188.7 μg/g. Contouring (Fig. 4) indicates that the concentration of Cu in the Vellar Estuary area is less than that of the Coleroon River estuary. The Cu concentration in pre-tsunami sediments was 32 μg/g (Ramanathan et al. 1999) and the significant increase in the Cu concentration is noticed after the tsunami in almost in all the samples. The high Cu concentration may be due to anthropogenic wastes (Vernet 1993) from near by soils brought back by tsunami waves. Fungicides and algaecides used in fish farming are other sources of pollutants, mainly consisting of copper compounds (Spencer and Green 1981). During the past decades there has been a rapid increase in the number of aquaculture ponds as well as the cultivation pattern that has changed drastically (Ranjan et al. 2007). During 1970s, there were no aquaculture ponds in the area, whereas in 1984 it increased to 3.99 sq Km and in 1996 to 6.99 km^2 (Hong Yeon et al. 2004; Kathiresan 2004, 2005). As results the waste are being transferred to the estuarine complexes through Vellar Estuary, Uppnar Estuary and Khan Sahib Canal. This may have lead to the accumulation of Cu in the sediments of Pichavaram mangrove ecosystem.

After the tsunami, significant variations in the Nickel concentration are observed. Effluent discharge from nearby chemical industries could be a potential source for Ni in mangrove sediments (Khan et al. 2004) (Fig. 5). The mean concentration of Ni in present study is 252.1 μg/g. The minimum and maximum concentration observed was 132 and 567 μg/g respectively, whereas pre-tsunami average Ni concentrations in this area were 62 μg/g (Ramanathan et al. 1999).

High concentrations of Lead were also reported in all samples, with a mean of the mean concentration of which was 143.8 μg/g. The minimum and maximum concentrations were 119.3 and 173.2 μg/g respectively. The highest concentrations were found higher in the Vellar estuary area, MGR Tittu area, and Chinnavaikal area than the central forest area (near Uppnar river area) and the Coleroon river area (Fig. 6). Szczucinski et al. (2005) suggested two possible explanations of high Pb concentrations in the tsunamigenic sediments. One of the possibilities was that the seawater translated on land with the tsunami wave had distinctly different Pb concentrations than the average seawater. The second possibility may be that high amounts of lithogenic or anthropogenic Pb was released during the event which was associated mainly with salt compounds (Szczucinski et al. 2005). In Pichavaram, increases in Pb concentrations may be due to the direct input of nitrate compounds from external sources, mainly from the aquaculture effluents, agricultural runoff and domestic sewage (Purvaja and Ramesh 2000; Subramanian 2004). Furthermore, the negative correlation of Pb (Table 2)

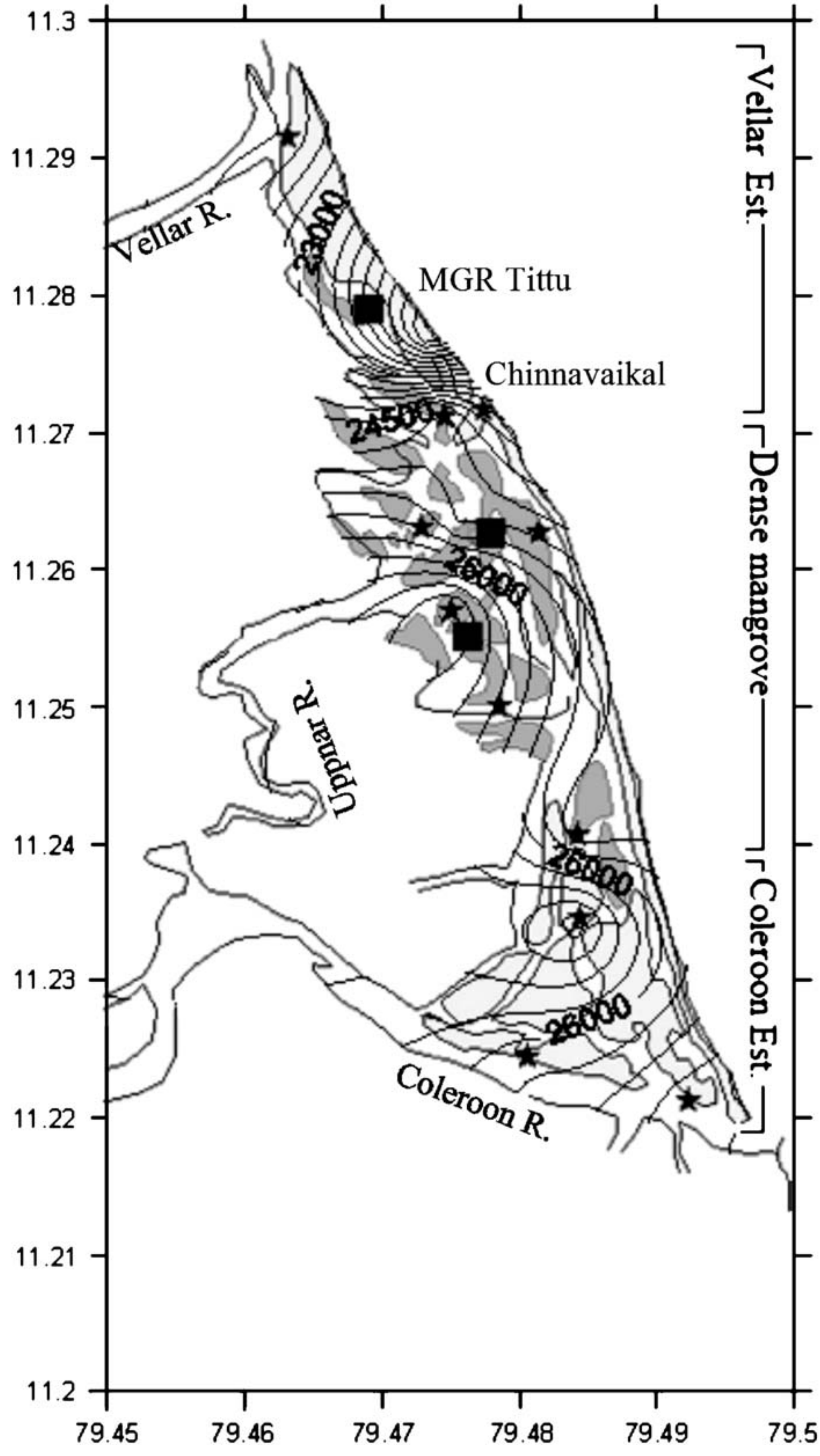


Fig. 7 Spatial distribution of Iron (in μg/g) in post-tsunami sediments of Pichavaram

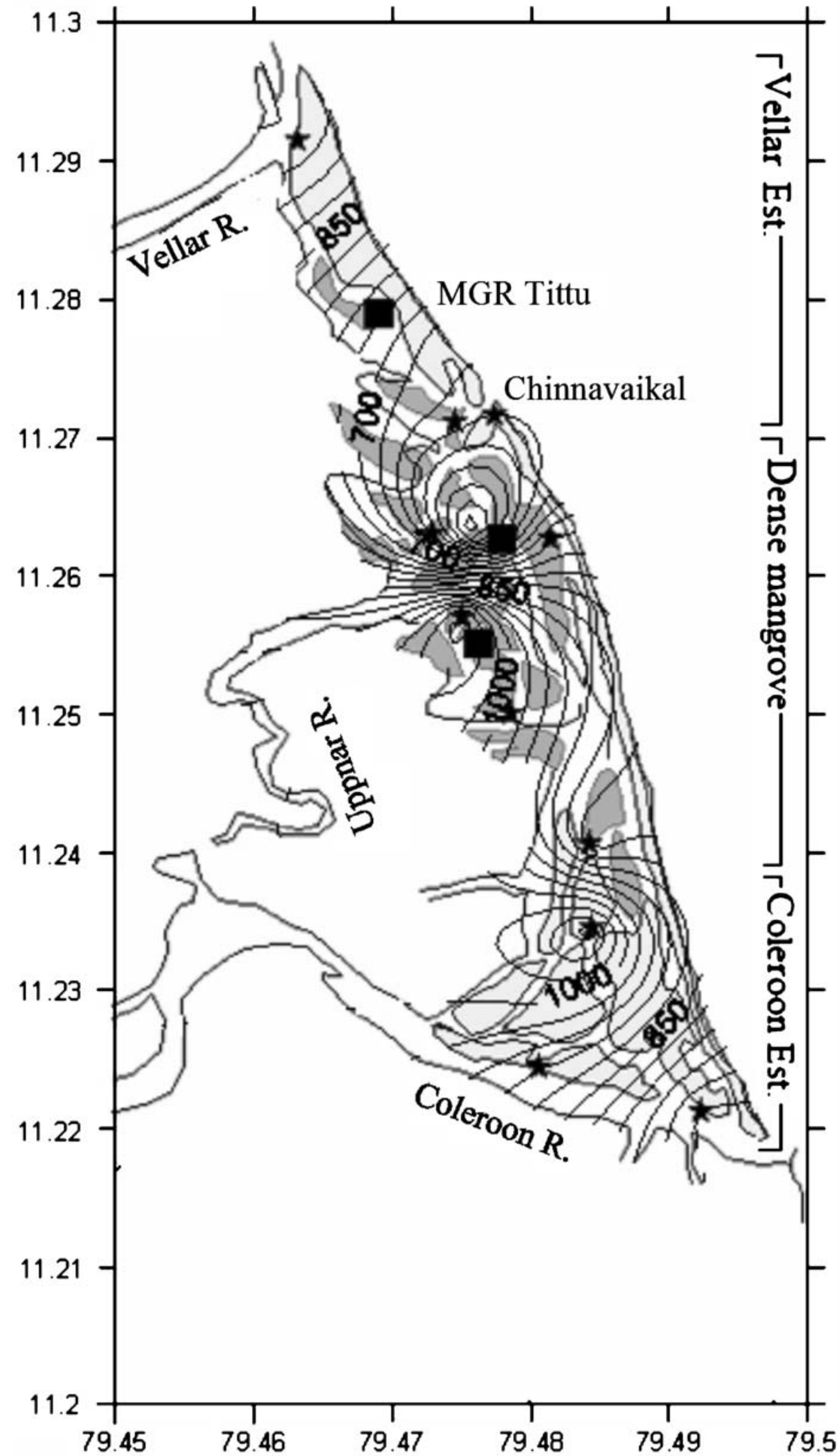
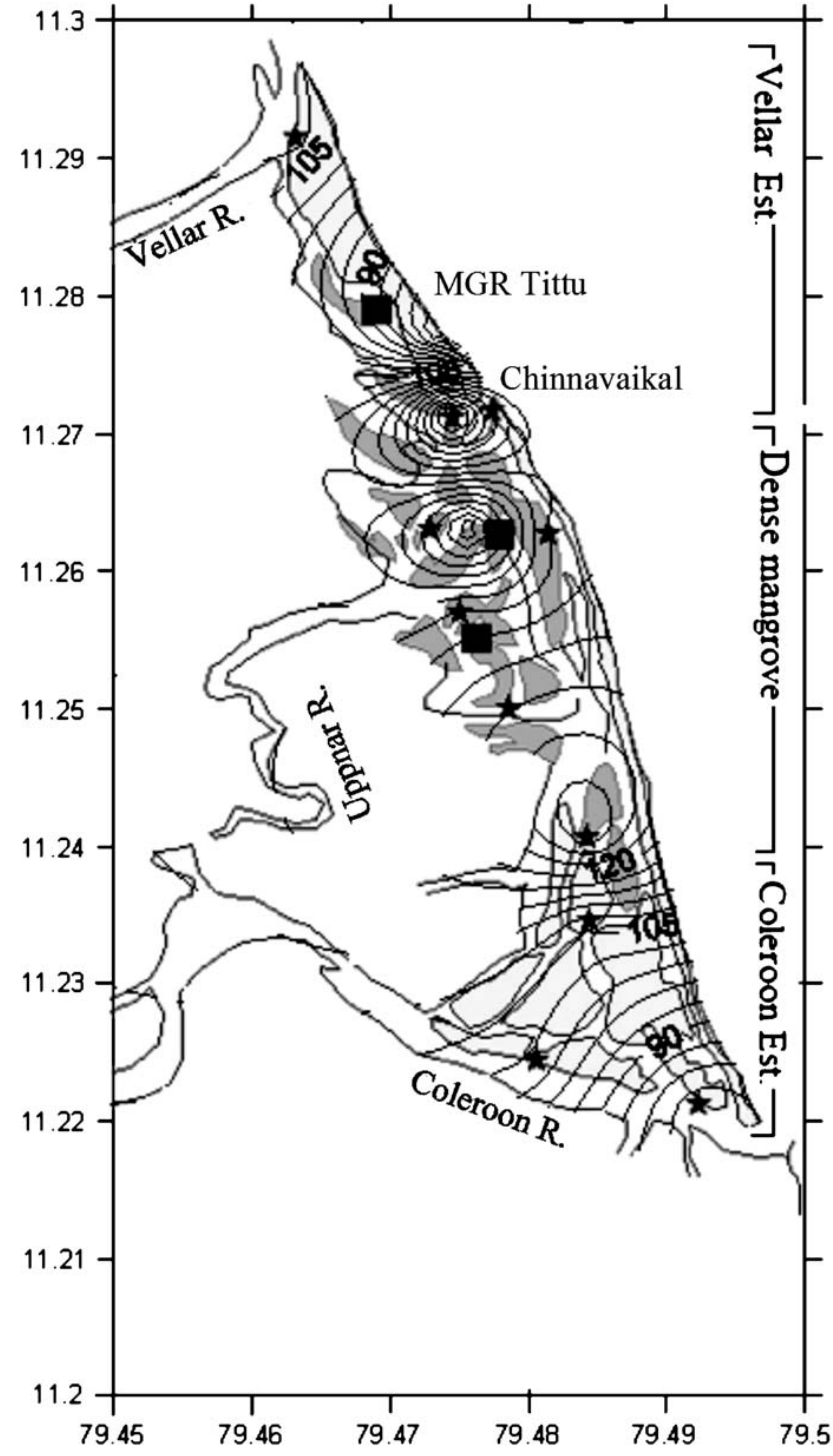


Fig. 8 Spatial distribution of Manganese (in μg/g) in post-tsunami sediments of Pichavaram

Fig. 9 Spatial distribution of Zinc (in μg/g) in post-tsunami sediments of Pichavaram



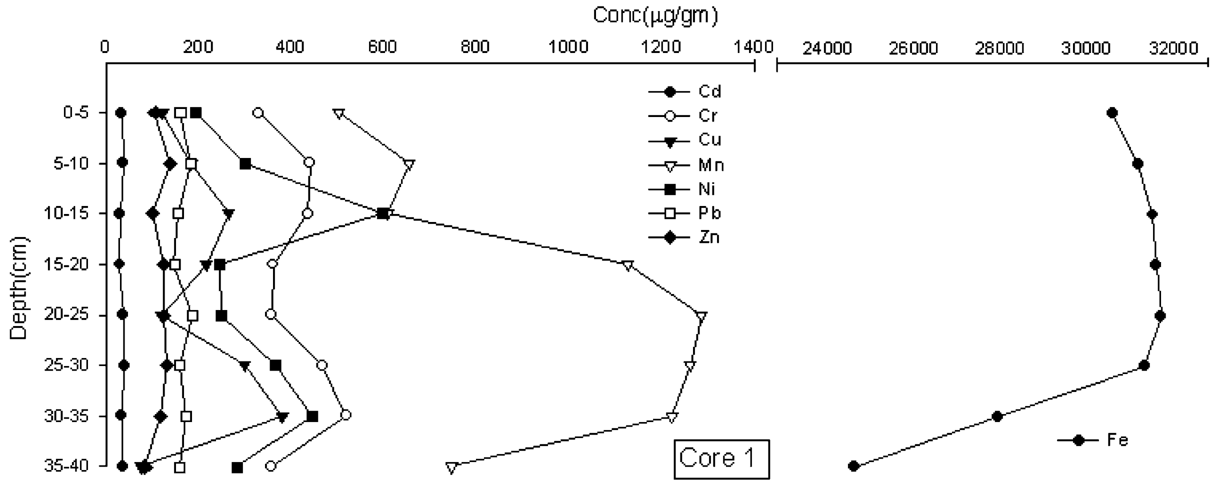


Fig. 10 Depth profile of heavy metals in the sediments of Pichavaram (Post Tsunami)—Core 1

with all the elements and organic matter suggested that the source of this Pb might be from the inundated tsunamigenic sediments which were returned after being impacted by agricultural and aquaculture derived Pb. However in present study the exact source of lead could not be delineated.

The mean concentration of Iron In the surface sediments was highest (24,998 μg/g, Table 1) as compared to other heavy metals. Before the tsunami, the mean concentration of Fe was 32,482 μg/g (Ramanathan et al. 1999). The prime source of iron is weathering and construction of dam over Coleroon river has checked the fresh water inflow into the mangrove estuarine complexes (Prasad 2005), resulting in the decrease of iron concentration in the sediments (Fig. 7). Manganese concentration in the present study varied from 425 to 1,111.19 μg/g, with a mean concentration of 801.38 μg/g. Before tsunami, its mean concentration was 701 μg/g (Fig. 8).

The minimum Zinc concentration after the tsunami was observed as 74 μg/gm with maximum concentration up to 140.5 μg/gm and mean concentration of 106 μg/gm (Fig. 9; Table 1). Before tsunami, the Zn concentration was reported as 89 μg/gm (Ramanathan et al. 1999) that is no significant change in Zinc concentration was observed after the tsunami.

Vertical distribution of variation of heavy metals in Pichavaram

In core 1, Cr concentration was observed least where as it was highest in core 3 and it showed decreasing

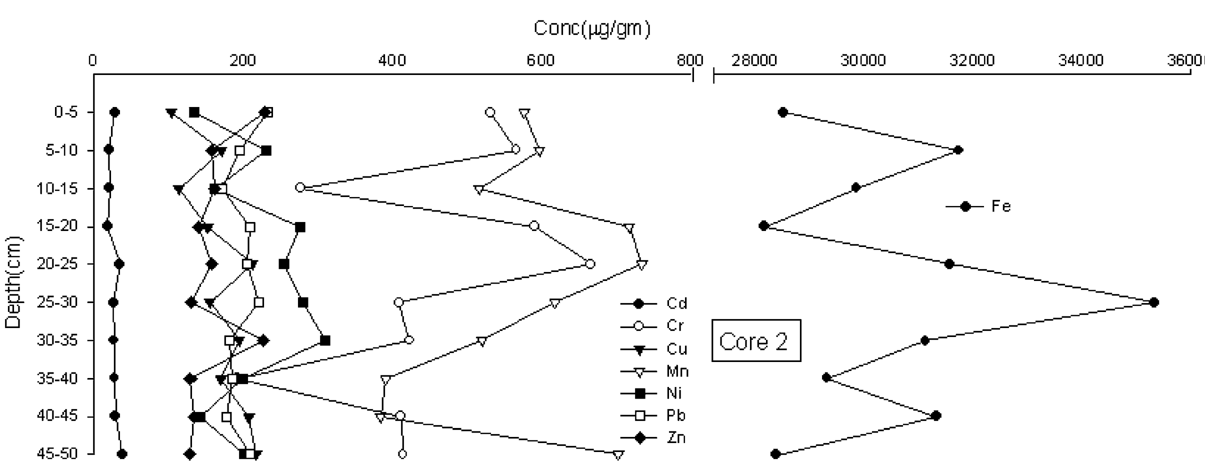


Fig. 11 Depth profile of heavy metals in the sediments of Pichavaram (Post Tsunami)—core 2

pattern. In all cores, Cr and Cu concentration decreased with the depth. In the core1 and core 2, the Ni concentration decreased with depth. However, in core 3, the Ni concentration increased up to 20 cm depth, after that it followed a decreasing pattern (Figs. 10, 11 and 12). Fe was the dominant heavy metal in the core sediment of the Pichavaram. Fe concentration was found minimum at the top and increased with depth up to 30 cm and then decreased in bottom (Figs. 10, 11 and 12). However, core 2 and 3 showed irregular trend in Fe distribution which may be due to the complex post-digenetic process including tsunami turbulence processes occurring in mangrove sediment. In core 1, the Mn concentration increased from the top (501 μg/g) to the depth of 20–25 cm (1,284 μg/g) and then decreased (Figs. 10, 11 and 12). In the core 2 and 3, it showed similar behavior. Pb showed a decreasing pattern with depth in all core sediments suggesting the excess anthropogenic loading occurring in the recent past. The concentration of Zn was higher in central region than the other regions. In all the cores, distribution of Zn was almost constant from top to bottom (Figs. 10, 11 and 12). Overall, the impact of Tsunami on the top and middle layer showed post depositional change and bioturbation adding heavy metal to biota and deeper layer. The inconsistency in the heavy metals trend may be due tsunamigenic turbulence which might have stirred the top layers temporarily.

Grain size control on the heavy metal concentration

The variation of the heavy metal concentration with grain size is shown in Table 3 and Fig. 10. The grain size analyses showed that Cd concentration was highest in <125–63> micrometer size, whereas samples from Vellar Estuary (Table 3; Fig. 13) show that maximum concentration was present in <63–10> μm size particles. In samples from Coleroon Estuary, (Table 3; Fig. 13) the maximum concentration was found in >125 and <10 μm size. The finer grain size fraction is rich in clay and organic matter, thus enhancing the Cd concentration. Cu concentration was more dominated in >125 μm in the Vellar area, whereas in Coleroon and Pichavaram zones its concentration was dominated in <10 μm grain size. In case of Fe, maximum concentration was present in > 125 μm in samples 7, and 10, whereas in case of sample no. 1 6, 8, and 9 the maximum concentration was present in 125–63 μm size particle respectively. After the tsunami, the silt fraction contained more iron due to dominance of heavy minerals. Maximum concentration of Mn was present in <10 μm in samples 6, 9 and 10 whereas in sample 7 and 8 maximum concentration was present in >125 μm size particles. Particle size analysis showed that maximum concentration of Ni was present in >125 μm in most of the samples. Pb was predominant in > 10 μm size particles. Grain size analysis showed that maximum concentration of Zn was present in >250 μm in samples 6, and 7, whereas in sample 1, 8, 9 and 10 maximum concentration was present in <10 μm size particles.

In general, concentrations of heavy metals tend to increase as the size fractions get finer. However for certain metals (Cu, Ni and Pb), the coarser particles show similar or even higher heavy metal concentrations than finer ones (Fig. 13). The higher residence time and/or presence of coarser particles from agriculture and industrial wastes are possibly responsible for higher metal content in the coarser size fractions (Singh et al. 1999).

Discussion

Spatial variation of metals

From the Figs. 2, 3, 4, 5, 6, 7, 8 and 9, it is clear that tsunami sediments were contaminated by heavy metals. The source of these heavy metals can be attributed to adjacent terrestrial factors as well as to the rivers supplying higher load of effluents to Pichavaram mangroves. These sediments are contaminated by both natural (tsunami) and anthropogenic activities like agriculture, aquaculture and land use patterns.

When the pre-tsunami and post-tsunami concentrations of Cd and Cr at different locations were compared, it was observed that concentration in estuarine complex has increased drastically with areas dominated by mangrove vegetation. This indicates that mangrove sediments act as a trap for these heavy metals (Lacerda 1998). Mn, Cu, Ni and Pb show similar behavior as that of Cd and Cr. However in the case of Pb, the contour map (Fig. 8) shows high concentration patches near Vellar estuary indicating that it may have come from the local deposition of Pb caused by the burning of diesel fuel. Excess heavy

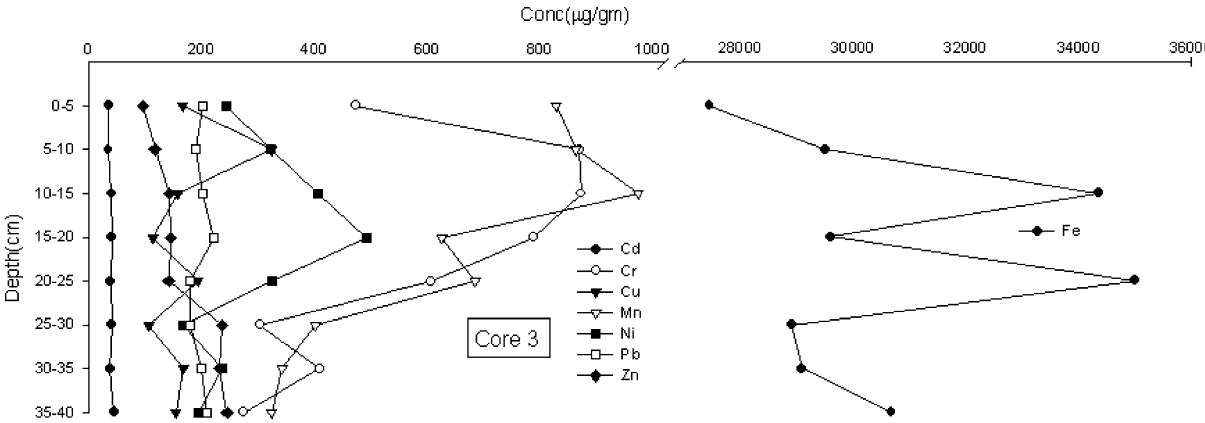


Fig. 12 Depth profile of heavy metals in the sediments of Pichavaram (Post Tsunami)—Core 3

Table 3 Variation of heavy metals (in µg/g) with grain size (µm) in tsunamigenic sediments of Pichavaram

Metal concentration in µg/g									
Size in µm	Sample no	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
<10	S1	21	574	206	29,780	640	194	181	146
	S2	19	564	217	26,714	672	210	193	162
	S5	24	234	74	31,390	1,538	183	181	169
	S6	35	189	1,127	29,760	676	183	219	145
	S7	26	189	1,053	30,880	1,963	340	155	153
	S8	11	738	171	30,140	1,138	244	194	179
	S9	39	250	118	31,920	998	206	245	173
	Mean	25	391	424	30,083	1,089	223	195	161
<63–10>	S1	18	240	48	27,790	992	206	116	89
	S2	16	243	41	27,519	872	261	142	93
	S5	44	160	65	28,320	1,071	382	207	142
	S6	43	167	70	25,810	634	107	181	109
	S7	34	167	136	28,480	970	229	103	142
	S8	16	157	57	29,600	892	118	90	139
	S9	20	285	79	25,720	772	198	191	126
	Mean	27	203	71	27,606	886	214	147	120
<125–63>	S1	42	695	125	30,990	3,893	531	142	84
	S2	38	693	118	31,567	4,251	501	152	79
	S5	13	321	22	25,850	892	164	116	100
	S6	14	247	148	28,710	752	145	168	136
	S7	59	247	92	29,310	777	217	232	104
	S8	28	183	67	26,150	1,023	108	181	109
	S9	19	186	43	24,020	802	179	181	85
	Mean	30	367	88	28,085	1,770	264	167	100
>125	S1	38	759	1,352	28,340	3,521	2,270	124	61
	S2	27	706	1,287	27,654	3,412	2,412	143	58
	S5	12	366	136	19,680	559	191	207	170
	S6	18	286	1,200	30,750	863	2,230	172	152
	S7	24	286	180	27,513	2,131	4,508	142	138
	S8	31	186	96	29,750	1,093	2,830	159	89
	S9	23	196	257	34,810	905	1,173	194	92
	Mean	25	398	644	28,357	1,783	2,231	163	109

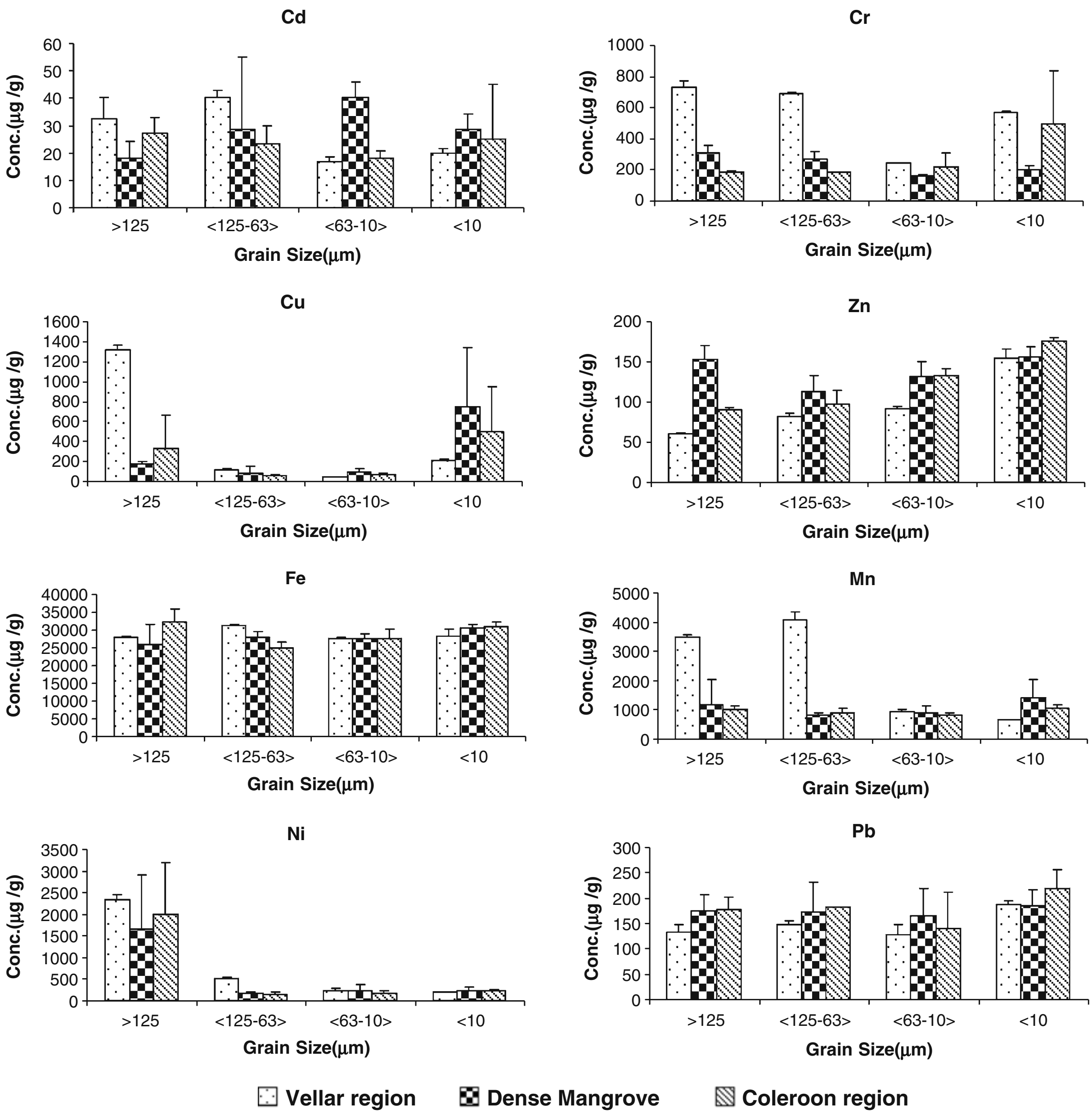


Fig. 13 Grain size control on heavy metals' distribution in tsunamigenic sediments of Pichavaram

vehicular traffic in the populated stretch of this river/estuary as well as due mechanized boats for fishing may have lead to the emission of Pb and its deposition at local scale. As mentioned earlier, the exact source of Pb contamination the sediments of Pichavaram could not be delineate. There is little variation in the case of Zn and Fe, which reveals absence of any anthropogenic source, indicating the conservative nature of these metals.

Correlation between various heavy metals

A statistical analysis of the spatial distribution of heavy metals revealed that the high degree of correlation and significant relation among the metals (Table 2). This indicates the identical behaviour of metals during transport in the mangrove environment. Significant inter-elemental correlations (i.e. Fe–Mn, Fe–Cu, Fe–Cr, Fe–Zn, Cr–Cu, Cr–Ni, Cr–Mn, Cu–

Table 4 Index of geoaccumulation in tsunamigenic Pichavaram sediment

Index of geoaccumulation												
Description of sediment quality	I_{geo}	I_{geo} Class	Polluters									
			S1	S2	S3	S4	S5	S6	S7	S8	S9	S10
Extremely contaminated	>5	6	Cd	Cd	Cd	Cd	Cd	Cd	Cd	Cd	Cd	Cd
Strongly to extremely strongly contaminated	4–5	5	–	–	–	–	–	–	–	–	–	–
Strongly contaminated	3–4	4	–	–	–	–	–	–	–	–	–	–
Moderately to strongly contaminated	2–3	3	Cr, Pb	Pb	Cr, Pb	Cr, Pb	Pb	Cr, Ni, Pb	Cr, Ni, Pb	Cr, Pb	Pb	Cr, Pb
Moderately contaminated	1–2	2		Cr		Cu, Ni, Pb	Cr, Ni	Cu	Cu	Cu	Cr	
Uncontaminated to moderately contaminated	0–1	1	Cu, Ni	Cu, Ni	Cu, Ni		Cu			Ni	Cu Ni	Cu, Ni
Uncontaminated	<0	0	Fe, Mn, Zn	Fe, Mn, Zn	Fe, Mn, Zn	Fe, Mn, Zn	Fe, Mn, Zn	Fe, Mn, Zn	Fe, Mn, Zn	Fe, Mn, Zn	Fe, Mn, Zn	Fe, Mn, Zn

Ni) and inverse correlations (i.e. Cd–Cr, Cd–Pb, Fe–Pb, and Mn–Pb) were observed in the mangrove sediments. In the present study, the poor association of Mn with other metals (Ni, Zn, and Cu) suggests that Mn-oxide may be only a minor host phase for these elements in the mangrove environment.

Fe showed a good correlation with Mn, Ni and Organic matter, where as Fe is negatively correlated with Pb. In the mangrove zone, significant concentration with organic carbon have been observed implying that oxic to sub-oxic and then to anoxic vertical gradients might be present in the mangrove sedimentary environment. Organic matter has direct control over the redox potential of the sediments, thereby controlling the concentration of Fe and Mn in the intertidal sediments. Due to changes in redox potential, desorption of metals (Fe and Mn) from the crystalline sedimentary matrix to the water occurs (Marchand et al. 2006). Fe–Mn complexes seem to have a strong bearing on the dispersal patterns of other metals in this aquatic sedimentary environment mainly due to their geochemical affinity (Forstner and Wittman 1983).

Significant correlations of organic carbon with most of the metals (except Ni and Cd) indicates that the sediment organic matter is acting as metal carrier and plays an important role in their distribution pattern (Samuel and Phillips 1988). Individual correlations reveal that Cr and Cu have significant correlations with Fe, while, Cr has significant correlation with Mn indicating the probable adsorption of these metals on to the oxides-hydroxides of Fe and Mn. Non-significant correlations of Cd, Ni, Zn and Pb with most of the metals may be possibly due to the different processes like biological effects and external inputs operating in the mangrove and adjacent estuarine sediments. Ni and Cd having significant correlations with Cr reveal that these metals are carried by industrial waste discharges into the nearby environment. There is not much change observed in metal concentration in the surface sediments after Tsunami except for Cr, Cd, Cu, Ni, Pb, Zn indicating the enrichment of the heavy metals by the heavy minerals brought by tsunami water from the shelf region and from the adjoining agriculture and aquaculture.

Geoaccumulation index

I_{geo} was calculated and was applied for the Pichavaram mangrove sediments shown in Table 4. Elevated I_{geo}

values identified for the concentration of Fe, Mn and Zn concentrations observed in present study were quite similar in accordance with the pre-tsunami concentration reported in sediments of various Indian mangrove forests (Badarudeen et al. 1996, Ramanathan et al. 1999 and Ray et al. 2006).

Increase of heavy metals in the mangrove sediment may be attributed to the abundance of fine particle with greater surface area (Forstner and Wittman 1983; Salmons and Forstner 1984) and precipitation of metals as hydroxide coating (mainly Fe and Mn) over finely dispersed particles (De Groot and Allersma 1975). Factors like enhanced organic matter content, flocculation due to varying salinity regimes (Sholkovitz 1976) and transportation of deep shore sediments to the coastal zone (Rubio et al. 2000; Seralathan et al. 2006 and Ramesh et al. 2006) also contribute significantly towards the enrichment of heavy metals in sediments.

The I_{geo} values for tsunamigenic sediments indicate that the sediments are extremely contaminated with Cd (Tables 1 and 4). The heavy metals like Pb and Cr are moderately to strongly contaminated nature. Pichavaram Estuarine sediment was moderately contaminated with Cu and Ni. As tsunami waves leave behind a clearly identifiable sediment deposit (Dawson and Shi 2000; Scheffers and Kelletat 2003) if buried and preserved then in due course of time a geologic record of that tsunami will be created. However, the interpretation of their origin requires study of many diagnostic sediment properties—for example: grain-size fining trends, character of lower and upper contacts, presence of intraclasts, marine diatoms, foraminifera and other microfossils, etc. (Goff et al. 2001). Sediment chemical composition was also used as a proxy helping identification of paleotsunami sediments. The residence time of post-tsunami seawaters in the sediments and resulting amount of bounded contaminants may be partly related to grain-size distribution (Szczucinski et al. 2005). The exception is Pb, which in seawater belongs to the least common heavy metals, (Bruland 1983) but here in the sediments, the Pb concentration were highest (Tables 1 and 4). This would which indicate anthropogenic sources. Aquatic sediments are the primary sinks for lead in the environment (Craig and Wood 1980). Lead values in bay, estuarine and other coastal sediments (marsh environments) have been much altered by man's activities (Martin and Meybeck 1979; Dekov et al. 1997). Enrichment of Pb, Cd, Co, and Ni in the Pichavaram sediments (Tables 1 and 4) suggests the effect of discharge of industrial and agricultural wastes through the Vellar, Uppanar, and Coleroon Rivers and Khan Saheb canal. The concentration of trace metals in the present study area is relatively high when compared to the reported pre-tsunami values (Ramanathan et al. 1999) of heavy metals concentrations in the sediments of this area. This difference may be due to the difference in the magnitude of input for each metal in the sediment (Ghrefat and Yusuf 2006). High concentrations of these trace metals in mangrove sediments indicates that the mangrove systems are physical traps for fine material, and their transported load of metals constitutes a chemical trap for precipitation of metals from solution (Harbison 1986).

Conclusion

The present study suggests that tsunamigenic sediments are rich in heavy minerals, thus resulting in increases in concentrations of heavy metals such as cadmium, chromium, nickel and lead in the Pichavaram mangrove forest of India. The calculation of the geoaccumulation index for the tsunamigenic sediments represents the heavy metal enrichment. Some heavy metals such as iron, zinc and manganese show little or no variation after the tsunami. Thus it can be concluded that after tsunami, there is a significant alteration in the sediment composition and characterization with respect to heavy metal concentration. I_{geo} calculations suggested that the sediment has behaved as a sink for the heavy metals Cd, Pb and Ni. As a result of changes in geochemistry these metals may be released to the ecosystem and create a threat for its sustainability. More extensive and long-term studies involving the various component of the ecosystem are needed.

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