

Dispersion and Accumulation Trend of Heavy Metals in Coastal and Estuarine Sediments and its Textural Characteristics, a Case Study in India

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ABSTRACT This study evaluated the persistence of heavy metals, cadmium (Cd), lead (Pb) and mercury (Hg) in surficial marine sediments and their relationship with textural characteristics. Furthermore, heavy metal distribution was studied against organic carbon concentration within the sediments. Our results suggest that Cochin estuary is highly polluted in the case of all heavy metals (Pb of $29.48 \pm 4.37 \mu\text{g/g}$, Cd of $0.21 \pm 0.17 \mu\text{g/g}$ and Hg of $0.17 \pm 0.15 \mu\text{g/g}$). All the studied trace elements showed negative correlation with sand particles. However, significant positive correlations were observed between lead and mercury with silt and organic carbon ($P < 0.01$), presumably metal accumulation increases with decrease in sediment grain size. The concentrations of the trace elements reported in this work are useful as reliable baselines and can be used for comparison in future studies.

INTRODUCTION

Trace metals have shown to be significantly hazardous pollutants in aquatic environments, even at very low concentrations (Nriagu and Pacyna 1988; Salomons and Stigliani 1995) and accumulate in sediments through complex physical and chemical adsorption mechanisms, depending on the nature of the sediment matrix. Bryan and Langston (1992) reported that sediments may carry heavy metals up to five orders of magnitude above the overlying water.

Under changing environmental conditions, these sediment bound heavy metals may be remobilized and enter the water or food chain. Especially heavy metals like Cd, Hg, Pb, may exhibit extreme toxicity even at low levels under certain conditions, thus necessitating regular monitoring of sensitive aquatic environments (Peerzada et al. 1990). So it is vital to understand the prevailing scenario of the ecosystem for the environmental health regards. In the present study an attempt is made to quantify the natural and anthropogenic contaminants of toxic heavy metals in sediment at selected areas (Veli, Kochi and Mangalore) along the south-west coast of India and to ascertain if there is any correlation between the metal levels and grain size of the samples taken. Additionally, the element concentrations reported here can be used to de-

velop a regional database against which future sediment analyses could be compared. Measurements of some major elements were also used to normalize and used to examine the trace elements behavior.

MATERIALS AND METHODS

The present study has been taken as a part of the project entitled Coastal Ocean Monitoring and Prediction System (COMAPS) under the Ministry of Earth Sciences (MoES)-Government of India. The study area comprises three industrially important coastal regions (Veli, Kochi and Mangalore lying between latitude $8^{\circ} 29' 39'' - 12^{\circ} 50' 26''\text{N}$ and longitude $76^{\circ} 53' 48'' - 74^{\circ} 44' 02''\text{E}$), each with four sampling sites in addition to the estuary and are located 1, 3, 5 and 10 km respectively from the shore region, towards the offshore (Fig. 1). Studies were limited to premonsoon season of 2006 only. Sediments were collected using Van Veen grab during the cruises of CRV Sagar Purvi (Coastal research vessel, MoES), collected carefully by avoiding contamination and kept frozen till analysis. Textural characteristics (sand, silt and clay) were determined following pipette analysis (Krumbein and Pettijohn 1938) and organic carbon of the composite samples using chromic acid digestion followed by back titration with ferrous ammonium sulphate (El Wakeel and Riley 1957). For cadmium (Cd) and lead (Pb) sediments were finely powdered, dried (at 70°C) and digested

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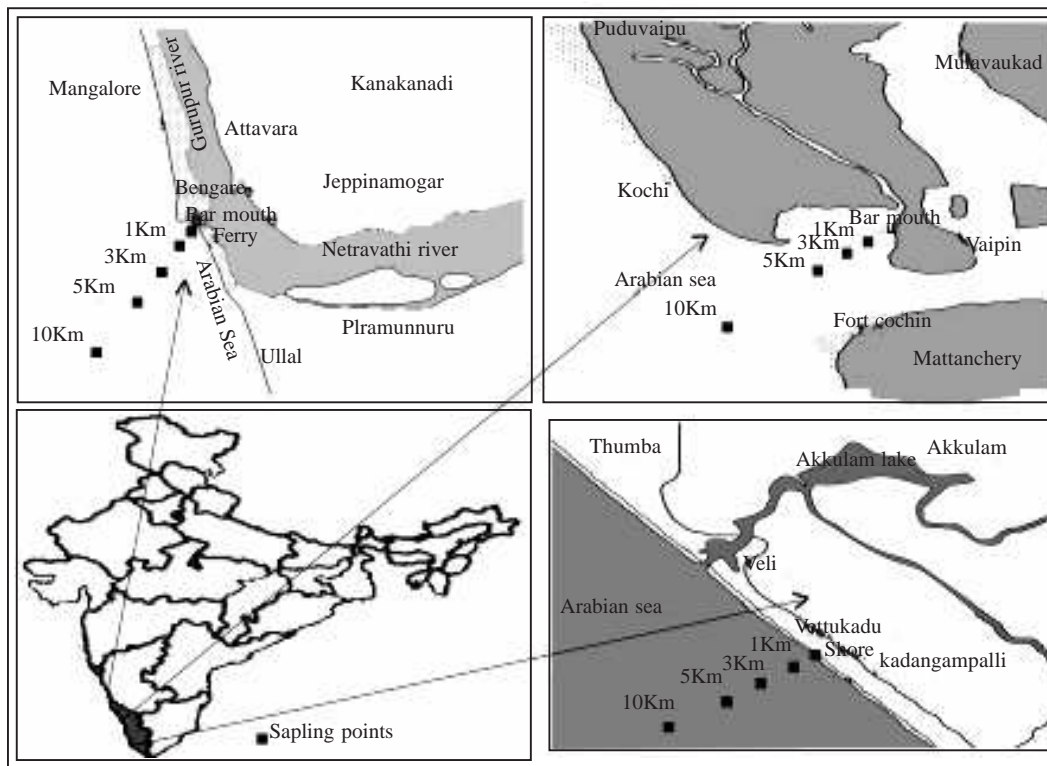


Fig. 1. Map showing the study area

in a mixture of HF-HClO₄-HNO₃ using the Microwave digester until a clear solution was obtained and made up to 25 ml using Milli Q water. Samples were analyzed on a flame AAS (AAAnalyst 100 Perkin Elmer) after calibration with suitable E Merck elemental standards. Cold vapour technique was adopted for mercury (Hg) analysis.

All determinants were performed in duplicate for single samples and the results for each sampling sites were expressed as their mean. Correlation was achieved by the Pearson correlation, performed with SPSS software. Correlation level less than 0.05 and 0.01 were considered significant

RESULTS AND DISCUSSION

1. Sediment Characterization

The particle size distribution and organic carbon of the study area are given in Figures 2 and 3. The percentage of clay, silt and sand in the overall study area were within the range of

4.1-20.19 % for clay, 2.21-26.22 % for silt and 55.12-92.46 % for sand. The concentrations of organic carbon (OC) were from of 0.65 to 3.16 mg/g. The maximum sand concentration and minimum silt, clay and organic carbon were obtained from Veli nearshore region. However, the minimum sand concentration was reported from the Kochi estuary and subsequently the maximum silt, clay and organic carbon were also reported from the same station at different sites, respectively of 10km, 3km and estuary itself. Generally the distributional status of total organic carbon closely followed the distribution of sediment type, that is, sediment low in clay content was low in organic carbon and as the clay content increased, the total organic carbon content also increased which was reported by Reddy et al. (1986). Sand, silt, clay and organic carbon reported the mean concentration respectively of 78.12± 15.56 %, 11.38± 8.98 %, 9.44± 6.81 % and 1.53± 0.78 mg/g in Veli, 60.39± 3.25 %, 20.63± 4.06 %, 17.23± 3.61 % and 2.70± 0.42 mg/g in Kochi and 69.21± 6.69%, 17.01± 5.60%, 12.63± 2.02 % and 1.58± 0.31 mg/g in

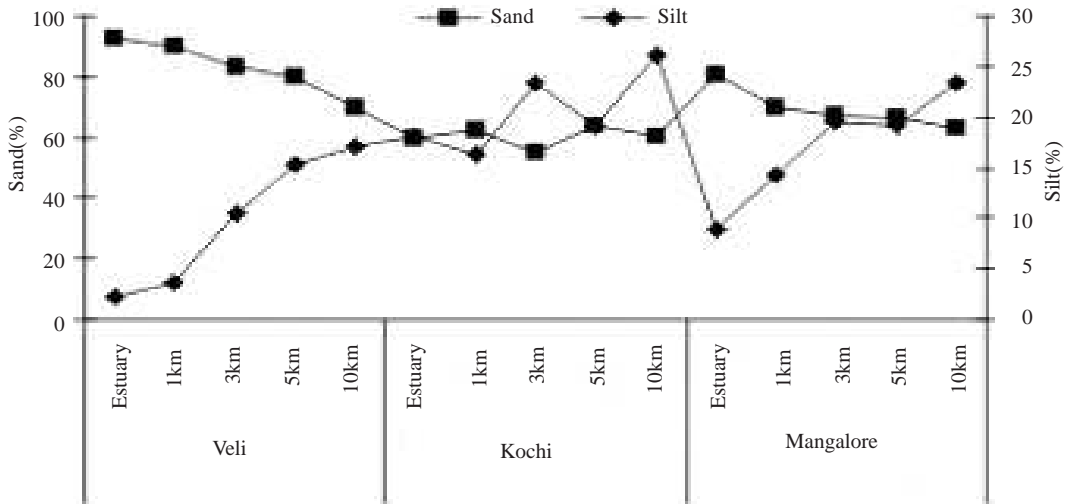


Fig. 2. Distributional status of sand and silt (%)

Mangalore. Spatial distribution (Table 1) of silt, clay and organic carbon were highly varied from the distribution of sand in which the former were more prominent towards the offshore region and the latter towards the shore region. In the overall study, Veli station (Table 2) reported with the maximum sand concentration (37.61%) and Kochi with the maximum silt (42.08 %), clay (43.85 %) and organic carbon (46.45%).

2. Heavy Metal Distribution

The regional variations of total concentration of heavy metals (Pb, Cd and Hg) were illustrated in the Figures 4 and 5 and they were within the range (13.18 - 33.81µg/g) for Pb, (0.1-0.19µg/g) for Cd and (0.01-0.20µg/g) for Hg. The higher values of, Pb, Cd and Hg were reported the Kochi estuary. Pb, Cd and Hg reported their

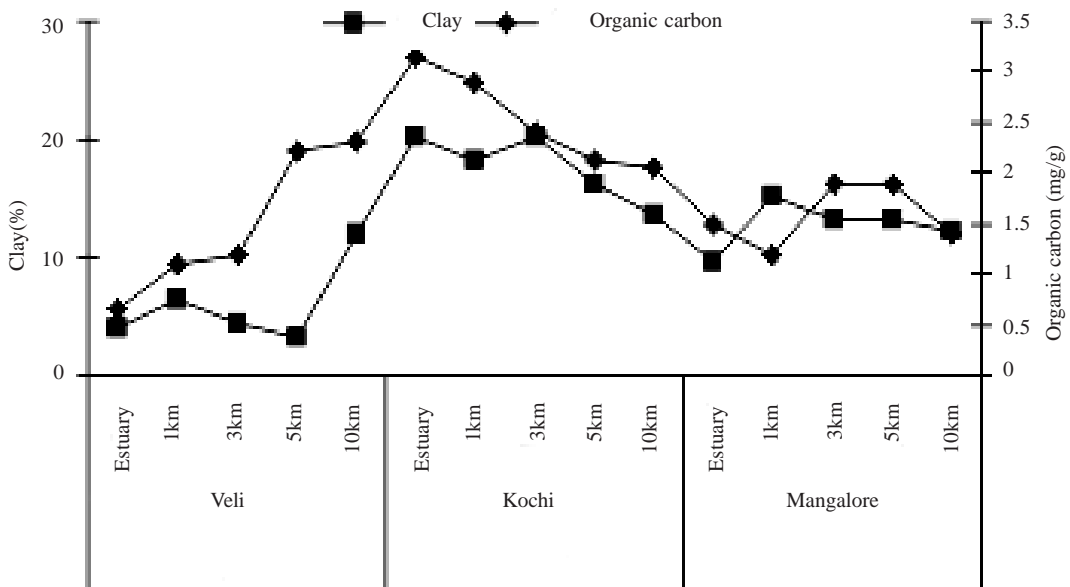


Fig. 3. Distributional status of clay (%) and organic carbon (mg/g)

Table 1: Percentage distance wise distributional status of textural characteristics and chemical parameters at all stations

Parameters	Estuary	1km	3km	5km	10km
Sand	22.4	21.15	19.77	17.82	18.86
Silt	11.92	13.93	21.78	25.13	27.24
Clay	17.22	20.23	19.19	25.18	18.18
Organic carbon	18.28	17.91	18.94	22.14	22.73
Lead	13.88	18.85	20.3	23.79	23.18
Cadmium	18.64	14.55	16.36	16.36	34.09
Mercury	18.11	14.18	14.96	13.38	39.37

Table 2: Percentage station wise distributional status of textural characteristics and chemical parameters in all transects

Parameters	Veli nearshore	Kochi estuary	Mangalore estuary
sand	37.61	29.07	33.32
Silt	23.21	42.08	34.71
Clay	24.02	43.85	32.13
Organic carbon	26.34	46.45	27.21
Lead	24.27	38.32	37.41
Cadmium	24.55	48.18	27.27
Mercury	17.32	66.93	15.75

mean concentration respectively of $18.68 \pm 6.32 \mu\text{g/g}$, $0.11 \pm 0.01 \mu\text{g/g}$ and $0.04 \pm 0.03 \mu\text{g/g}$ in Veli, $29.48 \pm 4.37 \mu\text{g/g}$, $0.21 \pm 0.17 \mu\text{g/g}$ and $0.17 \pm 0.15 \mu\text{g/g}$ in Kochi and $28.78 \pm 6.96 \mu\text{g/g}$, $0.12 \pm 0.01 \mu\text{g/g}$ and $0.04 \pm 0.01 \mu\text{g/g}$ in Mangalore respectively. Spatial distribution (Table 1) of Pb, Cd and Hg showed a similar pattern distribution in which they were more dominant towards the offshore region, especially at 10km from shore (23.18% lead, 34.09% cadmium and 39.37% mercury). Fostner and Wittman (1983) showed that the distribution of heavy metals in marine deposits was influenced by sediment texture, clay content and organic carbon. As relatively finer sediments were comparatively high towards the offshore region, the sediment bound metals were also high. In the overall study (Table 2), Kochi reported with the maximum percentage accumulation of heavy metals, Pb, Cd and Hg in the ratio of (38.32%), (48.18%) and (66.93%) respectively. The higher total metal concentration in Kochi estuary than the observed values show that there is an increased anthropogenic input of these metals into the region. Joseph et al. (2008) pointed out that the industrial discharge at the riverine end, domestic sewage discharge and movement of ships, barges, fishing and passenger boat with in the estuary may be responsible for this increase.

3. Correlation Analysis

Correlation matrix (Table 3) revealed the existence of a strong correlation between heavy metal concentration and sediment characteristics. Lead showed a positive correlation with silt at 0.01 level ($p < 0.01$), with clay at 0.05 level ($p < 0.05$), and also with organic carbon at 0.05 level ($p < 0.05$). Mercury also showed strong positive correlation with silt and also with organic carbon. Libes (1992) reported that finer sediments have a larger surface area, which allows heavy metals and other contaminants to be adsorbed easily. Positive correlations found between organic carbon and studied metals have indicated high affinity among them (Langston 1982; Coquery and Welbourn 1995). In contrast, Cd has presented no significant relationships with organic carbon, presumably the fact that Cd does not tend to form stable organic complexes (Campbell et al. 1988). However, all the studied heavy metals showed negative correlation with sand particles which presumably may have low surface area.

Table 3: Correlation matrix showing the interrelationship of heavy metals and sediment characteristics

Parameters	S. No.	1	2	3	4	6
Sand	1	1.000				
Silt	2	-0.938**	1.000			
Clay	3	-0.901**	0.700**	1.000		
Organic carbon	4	-0.793**	0.699**	0.758**	1.000	
Lead	5	-0.824**	0.875**	0.611*	0.525*	
Cadmium	6	-0.294	0.456	0.041	0.493	1.000
Mercury	7	-0.428	0.527*	.240	0.655**	0.954**

CONCLUSION

Of all the stations studied, coastal sediments of Kochi reported to have the high heavy metal accumulation and seemed to be under stress. Pearson correlation in the estuary indicated a definite association of heavy metals with fine particles (silt-clay) and organic carbon content. Based on these results, we suggest that the variation of grain-size distribution is one of the most important factors influencing the spatial variations of trace element concentrations on the area under study. The present study reflects the impact of anthropogenic input as a source for heavy

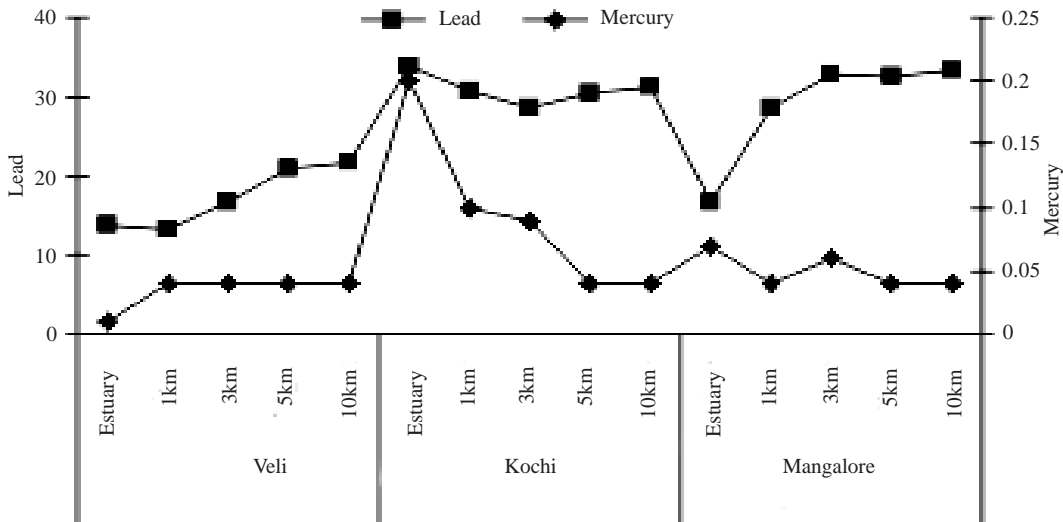


Fig. 4. Distributional status of lead and mercury ($\mu\text{g/g}$)

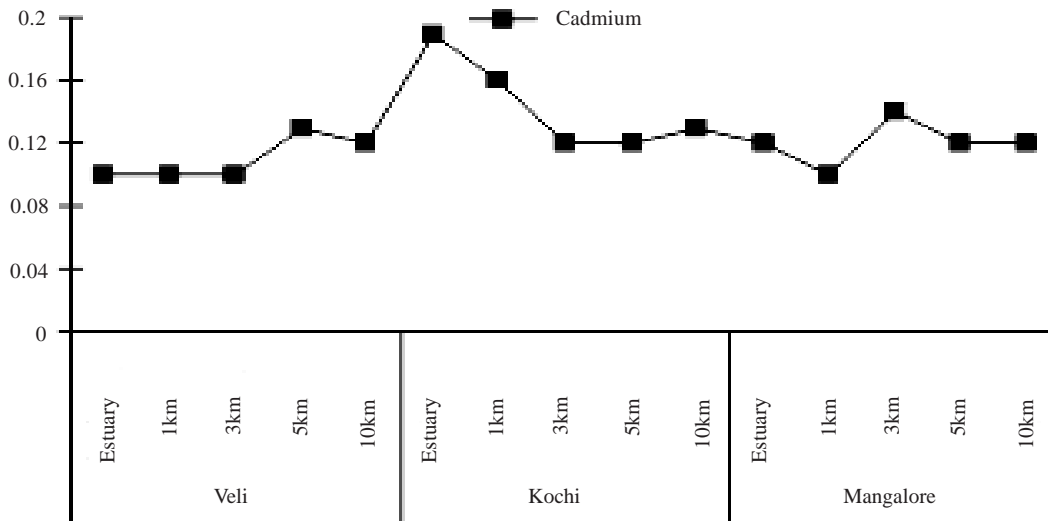


Fig. 5. Distributional status of cadmium ($\mu\text{g/g}$)

metals in this region, and it is recommended that a permanent monitoring programme be established to assess confined pollution problems

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REFERENCES

- Bryan GW, Langston RJ 1992. Bioavailability, accumulation and effects of heavy metals in sediments, with special reference to United Kingdom estuaries: A review. *Environ Poll*, 76: 89-131.
- Campbell P, Lewis A, Chapman P, Crowder A, Fletcher W, Imber B, Luoma S, Stokes P, Winrey M 1988. Biologically available metals in sediments. *National Research Council Canada Publication No. NRCC No 27694*, Ottawa, Canada.
- Coquery M, Welbourn P 1995. The relationship between metal concentration and organic matter in sediments and metal concentration in the aquatic macrophyte *Eriocaulon septangulare*. *Wat Res*, 29(9): 2094-2102.

- El Wakeel, Riley JP 1957. The determination of organic carbon in marine muds. *Journal of Du Conseil International Exploration*, 22: 180.
- Fostner U, Wittman GTW 1983. *Metal Pollution in the Aquatic Environment*. Berlin: Springer-Verlag.
- Krumbein WC, Pettijohn FJ 1938. *Manual of Sedimentary Petrography*. New York: Appleton Century Crofts Inc.
- Langston WJ 1982. The distribution of mercury in British estuarine sediments and availability to deposit-feeding bivalves. *Journal of the Marine Biological Association of the UK*, 62: 667-684.
- Libes SM 1992. *An Introduction to Marine Biogeochemistry*. Singapore: John Wiley and Sons. Inc.
- Nriaju JO, Pacyna JM 1988. Quantitative assessment of worldwide of air, water and soil by trace metals. *Nature*, 333: 134-139.
- Peerzada N, Mc Morrow L, Skiliros S, Guinea M, Ryan P 1990. Distribution of heavy metals in rove harbors. *Sci of Tota Environ*, 92: 1 - 12.
- Reddy, Venkadaswamy HR, Hariharan V 1986. Distribution of nutrients in the sediments of the Netravathi-Gurupur estuary. *Mangalore Ind J Fish*, 33: 123-125.
- Salomons W, Stigliani WM 1995. *Biogeochemistry of Pollutants in Soils and Sediments. Risk Assessment of Delayed and Non-linear Responses*. Heidelberg, Germany: Springer-Verlag.
- Joseph SM, Haseeb, Abhilash PP, Ouseph PP 2008. Water and sediment quality assessment of Cochin estuary, south -west coast of India. *Ind J Environ Sci*, 12(1): 77-81.