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Distribution and Accumulation of Metals in the Surface Sediments of Coleroon River Estuary, East Coast of India

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Abstract This study deals with the geochemical nature of distribution of metals (iron, manganese, lead and zinc) in bulk sediments and its association with sand, silt, clay and organic carbon. Ten numbers of surface sediment samples were collected during summer season of 2009 from Coleroon estuary. The sediments are mostly sandy silt in nature. The organic carbon distribution indicates that they are brought in the surroundings of coastal areas. Correlation analysis clearly indicates that fine particles and organic carbon control the distribution of metals. The most evident the significant correlations where zinc vs manganese (r = 0.641), manganese versus iron (r = 0.618), lead versus manganese (r = 0.574). The correlation between organic carbon versus manganese (r = 0.768), organic carbon versus sand (r = 0.872), organic carbon versus silt (r = 0.902), organic carbon versus clay (r = 0.793). The degree of correlation between metals and other major constituents is often used to indicate the origin of the metals. Strong positive correlation coefficient of all the above said metals and organic carbon are mainly associated with the fine grained sediments.

Keywords Coleroon estuary · Metals · Correlation matrix · East coast of India

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Metal pollution is one of the world-wide environmental problems. It is believed that organisms in different tropic levels are suffering from metal toxicities. Major indicators of pollution in aquatic environments are contaminated sediments that can be defined as soils, sand, organic matter, or minerals accumulated at the bottom of a water body. Under certain conditions, contaminants contained in sediments can be released to overlying waters and sediments can be important sources of contaminants in waters (Gao et al. 2010; Sundaray et al. 2011). Sediments of rivers, lakes and estuaries in a large number of locations have been contaminated by inorganic and organic materials. Among the inorganic materials, metals are frequent and important contaminants in aquatic sediments. They become a number of reactions in the system including sorption and precipitation, and they are greatly influenced by redox conditions in the sediments. Metals are transported as either dissolved species in water or an integral part of suspended solids. They may be volatilized to the atmosphere or stored in riverbed sediments. They can remain in solution or suspension and precipitate on the bottom or can be taken up by organisms. The metals content of sediments comes from natural sources (rock weathering, soil erosion, dissolution of water-soluble salts) as well as anthropogenic sources such as municipal wastewater-treatment plants, manufacturing industries, and agricultural activities, etc.

The Coleroon River is an ephemeral and carries floods during monsoon. They generally flow from west towards east and the pattern is mainly sub parallel. The eastern coastal part near Pazhayar is characterized by back water. Coleroon River, a major waterway of the Trichy and Thanjavur district, is formed by the bifurcation of the Cauvery flows at Trichy and finally joins the Bengal Pazhayar. Since the districts are underlined by sedimentary formation, the major land forms that occur are natural levees and near Maliaduthurai coastal plain covering almost the entire district with beaches beach ridges, mudflats swamps, and backwater along the coastal stretch. The deltaic plains are found near the confluence of River Coleroon with sea in the east and also in the south. Flood plain deposits are observed along the river course (Fig. 1).

The objectives of the present study were (1) to estimate the total concentration of metals (iron, manganese, lead and zinc) in surface sediment of Coleroon estuary and, (2) to evaluate the grain size effect on metal levels in the sediments.

Materials and Methods

The sediment samples collected in Coleroon estuary during summer season in 2009. Totally ten samples were collected in mouth, estuarine, and freshwater region. The sediment samples were collected by using a Van Veen grab sampler on board hired fishing trawler. Sub-sampling of the sediments was done by taking from the upper portion 5 cm of the sample from the grab with the help of plastic spatula. Sediment samples were then frozen to 4°C prior to analysis. Sampling locations were obtained by the global positioning system (GPS). Sediment samples were then kept in an oven and dried at 60°C for further analysis. Pipette analysis was carried out to compute sand, silt and clay fractions (Folk 1974). For the determination of organic matter, 20 g of air-dried sample was taken in silica crucible, which can withstand at higher temperature and heated up to 550°C for 6 h. After 6 h heating the sample was reweighed. The difference in weight was the total organic matter present in the sediments. The determination organic matter followed method loss on ignition by Fishmen and Friedman (1985). The organic carbon determined organic matter divided by 1.742. The results were expressed in percentage. The metal concentration in sediment samples was determined by total metal extraction method proposed by Tessier et al. (1979), with hydrofluoric acid (HF) in combination with perchloric acid ($HClO_3$), and heated on a hot plate at 200°C for about 8 h and evaporated to dryness. After cooling, the residue was dissolved with 0.5 mL HNO_3 and the solution was made up with Milli-Q water to a volume of 25 mL in a volumetric tube. The final acidic solution was transferred into a 50 mL centrifuge tube and was centrifuged at a speed of 10000 rpm for 10 min. The clear supernatant was stored in acid-cleaned polypropylene tubes and was analyzed for metals (iron, manganese, lead and zinc) and analysis with an ICP-OES (Perkin Elmer Optima 5300 DV). Below detection limits for metal analysis were iron—0.004 µg/g, manganese—0.001 µg/g, lead—0.042 µg/g and zinc—0.005 µg/g. The accuracy of the analytical method was analyzed by the standard reference material MAG-1 (Marine mud from the United Geological Survey). Percent recoveries of metals were iron—82.3, manganese—74.6, lead—83.5 and zinc—87.6. Pearson correlation analyses between metals, sand, silt, clay and organic carbon in surface sediments were performed (STATISTICA VER.5).

Results and Discussion

The estuarine and coastal environment is influenced continental and marine factors. In general, is a combination of mineral, metals and organic detritus, the characteristic of which vary according to the depth and distance from the mouth of the river or the entrance of the sea. Variation in

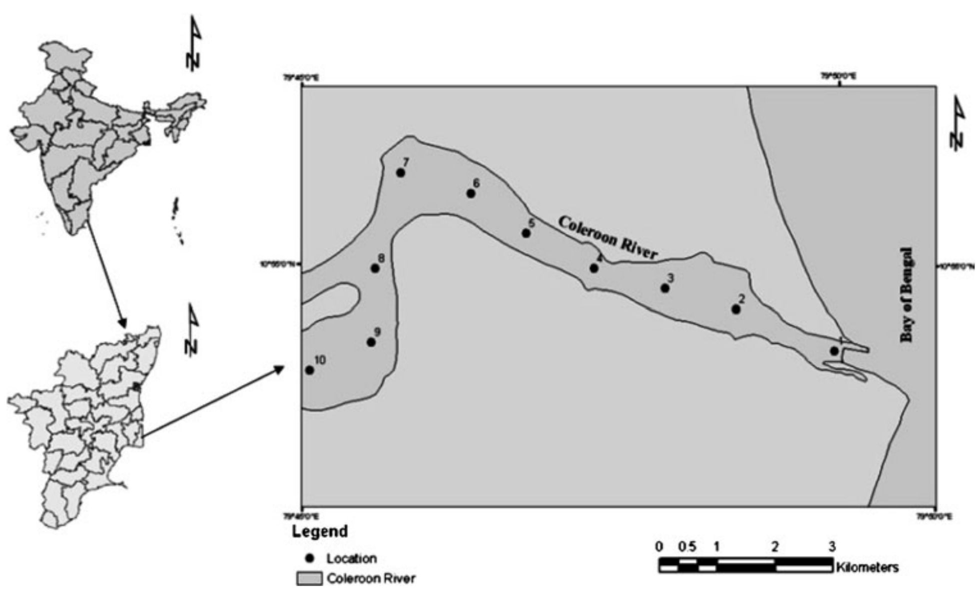

Fig. 1 Location map of the study area

size characteristics of the different sediment types are directly related to water movement patterns (tidal and wave energy regimes). During the study period, sand content for the studied samples varies from 43.87% to 96.89% where as silt and clay content varies from 3.01% to 37.98% and 0.04% to 4.57% respectively. It indicates the sediments are relatively coarse and represent bed load derived from the Cauvery river basin. Due to selective deposition, the fine particle sediments are transported into the mouth bar area and the outer estuary, while the coarse sediments are deposited in the upper reaches of the estuary. The organic carbon concentration in the same study period varies from 0.57% to 4.57% which follows the similar trend as that of silt and clay (Table 1). The sediment sample is classified as sandy silt in middle estuarine region and mostly sand type was observed in mouth and upper estuarine region. It is due to intense hydrodynamic action from waves and tidal currents (Baptista Neto et al. 2006; Venkatramanan et al. 2011; Anithamary et al. 2011). It has been reported that the distribution of grain size and organic carbon content were two critical factor influencing the metal distribution in sediments. Condensed humic substances form coatings and complexes with particles in smaller fractions, while organic material in the larger fractions comprises floes of algae and small pieces of degraded plant material. Sorption behavior is known to differ according to the origin and composition of the organic material. The low content of Organic carbon was observed in mouth and upper estuary, may be due to the combined result of limited fine grained sediment deposition and rapid organic carbon oxidation in sediments through sulphate reduction (Lin et al. 2000). Metals are more adsorbed by the smaller particles, especially clay, than by the coarser fractions. The organic content of the samples plays a minor role in metal adsorption. In contrast to the organic content, the metal content decreases continuously from the clay to the coarse silt fraction. This aggregated fine inorganic material is responsible for the increase in metal content associated with the fine silt and clay fraction. Comparison of metal compositions in Coleroon River estuary sediments with results shown in Table 2.

The correlation co-efficient for the metals are shown in Table 2. Most of the metals show good correlations. The most noticeable significant correlations were zinc versus manganese ($r = 0.641$), manganese versus iron ($r = 0.618$), lead versus manganese ($r = 0.574$). The correlation between organic carbon versus manganese ($r = 0.768$), organic carbon versus sand ($r = 0.872$), organic carbon versus silt ($r = 0.902$), organic carbon versus clay ($r = 0.793$). The degree of correlation between metals and other major constituents is often used to indicate the origin of the metals. Previous studies have demonstrated that grain size is a major factor in controlling sedimentary metal concentration (Lin et al. 2000; Baptista Neto et al. 2006). Strong positive

Table 1 Comparison of metal compositions in Coleroon River estuary sediments with results from other studies

S.No	Location	Fe	Mn	Pb	Zn	References
1	Belgian coast and Scheldt estuary	19	0.06	2.1	1.2	Fatima et al. (1988)
2	Cauvery estuary, East coast of India	5,780	264	12	14	Ramanathan et al. (1993)
3	Yangtze River, intertidal zone China	33,394	766	27.3	94.3	Weiguo Zhang et al. (2009)
4	Zuari estuary, central west coast of India	8,361	2,936.72	–	90.18	Dessai and Nayak (2009)
5	Mahanadi basin, India	88.93	59.36	66.54	56.21	Sundaray et al. (2011)
6	Coleroon estuary East coast of India	2,744	32.1	7.02	51.4	Present study

Metal concentrations are μg/g

Table 2 Correlation between metals, sand, silt, clay and OC in different fractions of the surface sediments for summer season

	Fe	Mn	Zn	Pb	Sand	Silt	Clay	Organic carbon
Fe	1.00							
Mn	0.62	1.00						
Zn	0.28	**0.64**	1.00					
Pb	0.63	0.57	0.30	1.00				
Sand	−0.17	−0.42	−0.47	0.21	1.00			
Silt	0.25	0.50	0.50	−0.16	**−0.99**	1.00		
Clay	0.05	0.29	0.40	−0.29	**−0.98**	**0.93**	1.00	
OC	0.41	**0.77**	0.58	0.19	**−0.87**	**0.90**	**0.79**	1.00

Bold figures are statistically significant at $p < 0.05$

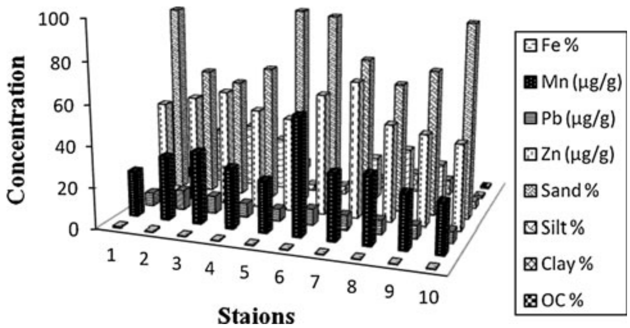

Fig. 2 Distribution of heavy metal and distribution of sand silt clay in study area

correlation coefficient of all the metals and the organic carbon with the silt and clay content of the sediments were found, indicates higher metals and organic carbon concentration are associated with the fine-grained sediments, as these components are more readily adsorbed on clay minerals. Significant and positive correlation coefficients were also observed between organic carbon versus metals revels their common accumulation into the fine grained fraction of sediments. However silt, clay and organic carbon contents in the surface sediments are themselves correlated, as organic components adhere to clay mineral as well. The combined importance as a geochemical substrate for metals concentration is significant for these sediments. Correlation analysis also reveals close relationship between individual metals, which indicates the similar processes governed by the behavior of all metals. The significant and good correlation in iron and manganese metals are found co-precipitate with or adsorbed in sediments. These characters are due to their large surface area, extensive cation exchange capacity and widespread availability. This strong degree of association between the main metals (iron, manganese, lead and zinc) was also reported in the literature for different urbanized and polluted areas (Ayyamperumal et al. 2006; Accornero et al. 2008). However, when the correlation data are compared with metal distribution it is possible to observe that metal concentration are much more influenced by the source areas than the organic matter or particle size. The bar diagram clearly indicate the variation in sand, silt, clay and organic carbon and metals more observation present in various location of the estuary (Fig. 2).

This present study has allowed us to determine the bulk metals levels in surface sediments of Coleroon estuary. The distribution of metals may be linked to lithogenic sources and current patterns in adjacent coastal area. Metals associated with silt and clay particles tended to be deposited at the interface between the freshwater and marine water zones due to the processes of adsorption and coagulation. The correlation coefficient for relationships between the metals shows a strong degree of association between the fine fractions. When the comparing level of metals in the studied area to other areas, the levels of metals content are lower than in other areas. This also justifies the need to a have regular monitoring and other stringent measures to control the level of metals before any major catastrophic event affects this area.

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