A study on seasonal accumulation of metals in Tirumalairajan river estuary and adjacent coastal track, Tamil Nadu, east coast of India

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Seasonal accumulation of metal concentrations (Fe, Mn, Zn, Pb, Cu, Cr, Co and Ni) in surface sediments from the Tirumalairajan estuary and its adjacent coastal track of east coast of India were studied. Fe, Mn, Cr, Co and Ni are relatively high enrichment factor in both estuary and beach environments. Calculated enrichment factor (EF) with respect to the upper continental crust values show that the analyzed sediments are depleted in Fe, Mn, Co, Cr, Ni and enriched in Zn, Pb, Cu. Moreover, metal concentrations have positive correlations with to the particle size and organic matter content of the sediments, which strongly suggests that the influence of irrigation and industrial wastewaters discharged from the neighboring irrigation land and industries. Factor analysis clearly reveals that fine particles and organic matter control the distribution of metals in the sediments.

[Keywords: Heavy metals, Enrichment Factor, Sediments, Irrigations and Industrial Wastewater East Coast of India.

Introduction

Due to the rapid industrialization and economic development along the estuarine region heavy metals are continuing to be introduced to estuarine and coastal environments around the world¹²³. Various studies have demonstrated sediments from coastal areas, which are greatly contaminated by heavy metals; therefore, the evaluation of metal distribution in surface sediments is necessary to assess pollution monitoring in the marine environment⁴⁵⁶⁷. Heavy metals are natural constituents and some of them are even essential for many living organisms but become toxic at higher concentrations⁸⁹¹⁰¹¹. Most of the studies deal with the contamination of sediments by heavy metals using only the total metal content as a criterion to assess its potential effect as contaminant. Hence, the sediments are widely used as indicators of environmental contamination by heavy metals in estuarine and coastal environment¹²¹³. Further, it has been proved in many studies that the contamination due to heavy metals leads to severe health problems¹⁴¹⁵¹⁶¹⁷.

Materials and Methods

Tirumalairajan river is a tributary of major river Cauvery in the central part of Tamil Nadu. Tirumalairajan Estuary and its adjacent coastal track are noted for its geographic location within the central part of Nagapattinam district, east coast of India and extensive irrigational activity, urbanization and light to medium industrialization along its shores. The influence of tide was noticed upto 8-10 km in the upstream direction¹⁸. The geology of the catchment area comprises of various rock types such as granite, charnockite and gneisses. Tirumalairajan river flows through recent alluvium deposits which are composed of clays and silts before it enters into the sea. Estuary also receives discharges from a number of irrigation channels. The average annual rainfall in summer...
season is 43.12 mm and 451.48 mm in monsoon. The main purpose of the present study is to identify the concentration pattern of metals in the estuary and adjacent beach sediments in Nagapattinam City in east coast of India.

Surface sediment samples were collected during the monsoon (December 2009) and summer (June 2010) seasons. Sample collection preceded initially in the mouth, estuary and freshwater zone, along the Tirumalairajan estuary, and adjacent to the beach of Karaikal (Fig.1). Five sampling locations were distributed along the Tirumalairajan estuary and six sampling stations along the Karaikal beach. Beach sediments were collected from the top 5 cm along the beach, whereas the estuary sediments were collected by using Van Veen grab sampler. Pipette analysis was carried out to compute sand, silt and clay fractions. For the determination of organic matter is followed by loss on ignition. Metal concentration in sediment samples was determined by total metal extraction method proposed by Tessier et al., with hydrofluoric acid (HF) in combination with perchloric acid (HClO₃), and heated on a hot plate at 200°C for about 8 hours and evaporated to dryness. After cooling, the residue was dissolved with 0.5 mL HNO₃ and the solution was made up with Milli-Q water to a volume of 25 mL in a volumetric tube. Supernatant liquid was removed by pipette and stored for final quantification of the trace metals using ICP-OES (Inductively Coupled Plasma Optical Emission Spectrometry, Perkin Elmer Optima 5300 DV). Accuracy of the analytical method was analyzed by the standard reference material MAG-1 (marine mud from the United States Geological Survey). Below detection limits for metal analysis were Fe-0.004 µg/g, Mn-0.001 µg/g, Zn-0.005 µg/g, Pb-0.042 µg/g, Cu-0.009 µg/g, Cr-0.007 µg/g, Co-0.007 and Ni-0.015 µg/g. Percent recoveries of metals were Fe-82.3, Mn-74.6, Zn-83.5, Pb-77.6, Cu-78.3, Cr-71.4, Co-68.3 and Ni-68.6. Factor analyses between metals, sand, silt, clay and organic matter in surface sediments of two different seasons were performed. It was attempted to understand source and association by using the software STATISTICA (Ver.8). EF is calculated according to the following equation:

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EF = \frac{M_x \times Feb}{M_b \times Fex}
\]

where Mx and Fex are the sediment sample concentrations of the heavy metal and Fe (or other normalizing element), while Mb and Feb are their concentrations in a suitable background or baseline reference material.

Results and Discussion

Chemical data set (Table 1) of the present study are presented as bivariate plots (Fig. 2 a and b). Sand content for the studied samples varied from 68.85–96.55% whereas silt, clay and organic matter content varied from 2.43–23.09%, 1.02–8.06% and 2.05–3.44% respectively in monsoon. During summer, the sand, silt, clay and organic matter contents varied from 64.2–96.65%, 2.07–25.76%, 1.28–10.04% and 2.57–5.03% respectively. It indicates the sediments are relatively coarse-grained and represent bed load derived from the Cauvery river basin. Due to selective deposition, the silt and clay particles are transported into the mouth bar area and outer estuary, while the sand particles far away to the mouth bar. In this study, the higher percentage of organic matter was observed at stations 2 (4.35%), 3 (5.03%) and 4 (4.22%). It indicates that estuary is possibly accomplished by the high productivity of the region besides death and burial of huge population of biota increase the concentration of organic matter. The rate of deposition of the organic matter and inorganic constituents are more in this environment, which results in the retarded decomposition of organic matter and its better
have passed to the open ocean and later dispersed by littoral current. The littoral current pattern also substantiates the possibility of sand accumulation by the above-mentioned mechanism. In summer season, most of the sediment samples fall in sand category. This is may be due to the limited inputs and weak wave energy condition. So, the beach sediments contain a very large amount of sand and meager amount of silt and clay. The beach sediments show comparatively low amount of organic matter than the estuarine environments. Even though, the beach environment is having more productivity with high rate of deposition of organic and inorganic constituents owing to the coarse-grained nature of sands, the organic matter is unable to concentrate in the sediments.

In the Tirumalairajan river estuary, during monsoon, the bulk metal concentrations of Fe, Mn, Zn, Pb, Cu, Cr, Co and Ni in the sediments vary from 1804.23-2721.5 μg/g, 8.34-15.4 μg/g, 23.4-39.7 μg/g, 1.73-5.87 μg/g, 13.65-28.17 μg/g, 0.96-1.28 μg/g, 0.20-0.33 μg/g and 0.52-1.04 μg/g respectively. In summer season, the metal concentrations of Fe, Mn, Zn, Pb, Cu, Cr, Co and Ni in the sediments vary from 1736.7-3144 μg/g, 30.24-42.45 μg/g, 38-56.3 μg/g, 2.83-6.74 μg/g, 21.7-28 μg/g, 2.79-4.01 μg/g, 0.24-0.5 μg/g and 1.66-2.01 μg/g respectively. The concentration of Fe and Mn within the estuarine sediments can be related to various natural processes and also these metals were derived from the Karaikal harbor. Relatively higher concentration of Zn, Pb, Cu, Co, Cr and Ni found in the estuary sediments (station 2, 3 and 4) are due to the irrigation runoff and anthropogenic activities.

In the beach sediments, the concentration of bulk metals (Fe, Mn, Zn, Pb, Cu, Cr, Co and Ni) ranged from 1267.3-2287.5 μg/g, 10.4-20.4 μg/g, 4.03-8.46 μg/g, 0.29-1.33 μg/g, 0.54-1.56 μg/g, 2.04-3.56 μg/g, 0.56-0.79 μg/g and 0.35-0.88 μg/g respectively during the monsoon season. During summer season, sand, silt, clay and organic matter varied from 96.71-98.21%, 1.20-2.55%, 0.21-0.88% and 0.38-0.56% respectively. During the study period, the Tirumalairajan River retains most of the coarse sediments and some may retainment. The fine texture of the sediments reported in this environment also favor for the accumulation of organic matter in this region. Along the coastal track, the percentage of sand, silt, clay and organic matter varied from 96.34-97.43%, 2.03-3.27%, 0.32-0.96% and 0.38-0.53% respectively during the monsoon season. During summer season, sand, silt, clay and organic matter varied from 96.71-98.21%, 1.20-2.55%, 0.21-0.88% and 0.38-0.56% respectively. During the study period, the Tirumalairajan River retains most of the coarse sediments and some may
respectively. It is mainly due to the natural occurrence of these metals in sediments and rocks in the catchment area and drainage region and they being the input of metals to Tirumalairajan rivers and its tributaries.  

The studied heavy metals can be ranked according to mobility in the following descending order: Fe > Mn > Zn > Cu > Pb > Cr > Co > Ni in estuarine and Fe > Mn > Zn > Cu > Cr > Pb > Co > Ni in beach environment. The characteristics of estuarine sediments show silty sand nature. Fe is enriched, while other elements are depleted during monsoon and vice-versa in summer season. Whereas the beach sediments show sandy in nature and all the metals are depleted in monsoon and enriched in summer season. Variation in the metal concentrations is due to the continual resuspension of bottom sediments occurring in the Tirumalairajan estuary and the part of the Karaikal coast may serve to scavenge and concentrate metals that are naturally present in water column as well as those introduced by irrigation runoff and industrial discharge. The distribution pattern resembles the anthropogenic contribution of metals and the role of sediment type, organic matter become major factors affecting the distribution of metals in this region.

Factor analysis

In order to establish the natural and geochemical processes responsible for enrichment of heavy metal with respect to textural parameters, organic matter content of the sediments, the R-mode varimax factor analysis was applied. Factor analysis of the present data set further sorted by the contribution of less significant variables (<0.5 factor score). Factor analysis extracted two common factors viz. Factor 1 (F1), Factor 2 (F2) with significant loadings within each factor for all the two seasons, which are

| Table 1—Concentration of heavy metals in the study area (minimum and maximum) |
|-----------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Metals (µg/g)                     | Estuary Monsoon | Estuary Summer  | Coastal track Monsoon | Coastal track Summer |
| Fe       | 1804.2   | 2721.5   | 1736.3   | 3144     | 1267.3   | 2287.5   | 1503.7   | 2389.3   |
| Mn       | 8.34     | 15.4     | 30.3     | 42.45    | 10.41    | 20.40    | 25.91    | 54.82    |
| Zn       | 23.4     | 39.73    | 38.04    | 56.32    | 4.03     | 8.46     | 4.41     | 11.09    |
| Pb       | 1.73     | 5.87     | 2.83     | 6.74     | 0.29     | 1.33     | 0.97     | 1.53     |
| Cu       | 13.65    | 28.17    | 21.73    | 28.06    | 0.54     | 1.56     | 1.41     | 5.65     |
| Cr       | 0.96     | 1.28     | 2.79     | 4.01     | 2.04     | 3.56     | 4.15     | 5.67     |
| Co       | 0.20     | 0.33     | 0.24     | 0.50     | 0.56     | 0.79     | 2.12     | 3.00     |
| Ni       | 0.52     | 1.04     | 1.66     | 2.01     | 0.35     | 0.88     | 0.54     | 1.50     |
| Sand %   | 68.85    | 96.55    | 64.20    | 96.65    | 96.34    | 97.43    | 96.71    | 98.21    |
| Silt %   | 2.43     | 23.09    | 2.07     | 25.76    | 2.03     | 3.27     | 1.20     | 2.55     |
| Clay %   | 1.02     | 8.06     | 1.28     | 10.04    | 0.32     | 0.96     | 0.21     | 0.88     |
| Organic matter % | 2.05 | 3.44 | 2.57 | 5.03 | 0.38 | 0.53 | 0.38 | 0.56 |
presented in the Figure. 3a and b. Association of metals in the estuary and beach sediments is very well supported by the high absorption and scavenging capacity of Fe–Mn and other metals like Co, Cu, Pb, Zn in factor 1 and Ni in both factors. In addition, the results also suggest that the metals are mostly related to the sand or mud fraction rather than organic matter, indicating that they are all recently deposited due to the external input. The concentration pattern and association of metals clearly infers that the manifold irrigation activities contribute a huge amount to the enrichment of metals like Zn, Cu and Pb in the estuary and beach sediments of the city in both seasons.

Enrichment pattern

A common approach for estimating the anthropogenic impact on sediments is to calculate a normalized enrichment factor (EF) for bulk metal concentrations above uncontaminated background levels29,30. Enrichment method normalizes the measured heavy metals content with respect to sample reference metal such as Fe or Al. In this approach the Fe or Al is considered to act as a ‘proxy’ for the clay content31. A similar approach and used Mn for enrichment calculations in a study of marine sediments near Christchurch32. Fe is an acceptable normalization element to be used in the enrichment factor33. Since, Fe is relatively high in natural concentration and is therefore nor expected to be substantially enriched from anthropogenic source in estuarine sediments33. The enrichment factor of metals can be distinguished, whether it is from natural or anthropogenic origin. Metals having EF values <1 reveal a natural origin, whereas >1 indicate enrichment due to anthropogenic inputs34, based on suitable background reference material21. In this study, the enrichment factor for metals Cu, Zn and Pb are >1 in estuarine sediments indicating the influence of anthropogenic source and possibly it may be attributed the agricultural runoff and industrial waste in both seasons (Fig. 4a). Similarly, the EF value of >1 obtained for the metals Cu, Zn, Pb, Cr, and Co in beach sediments reveals that they were derived from the adjacent irrigation field and also through river inputs (Fig. 4b).

Conclusions

Slightly higher concentration of metals (Fe, Mn, Zn, Pb, Cu, Cr, Co and Ni) was observed in the summer season when compared to the monsoon season. The calculated sequence of metals based on the average of estuary and beach environment presents the following sequence: Fe > Mn > Zn > Cu > Pb > Cr > Co > Ni (estuary) and Fe > Mn > Zn > Cu > Cr > Co > Pb > Ni (beach). Factor analysis has helped in identifying associations of different metals in sand and mud fraction and organic matter. Difference between the estuary and beach sediments indicates that Zn, Cu, Pb are slightly above the background levels in the estuarine. Moreover, the estuarine sediments indicate two to three fold increase in its geochemical composition than the adjacent coastal sediments due to irrigation and industrial activities. It is proposed that continuous monitoring and further studies in the area should be carried out in the near future to ascertain long-term effects of anthropogenic impact and to assess the effectiveness of minimizing the human activity to upgrade the marine environment in the Tirumalairajan estuary on the east coast of India.

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