Textural and heavy metal distribution in sediments of Mahanadi estuary, East coast of India

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Surface sediment samples from the Mahanadi estuarine region were collected during May, 2008 to April, 2010 in three different seasons (pre-monsoon, post-monsoon and summer) annually. Present study focuses on the levels of Pb, Cd, Hg, texture pattern and organic carbon in order to assess the extent of environmental pollution. Concentration data were processed using correlation analysis. Contamination of sediments was assessed on the basis of contamination factor (CF), geo-accumulation index ($I_{geo}$) and pollution load index (PLI). Average concentration of Pb, Cd and Hg were 23.88±8.88 µg/g, 1.45±0.14 µg/g, 0.107±0.070 µg/g in 2008-09 and 23.89±7.27 µg/g, 0.65±0.50 µg/g, 0.102±0.058 µg/g in 2009-10 respectively. Texture pattern found to be sand dominated averaging over 96.00% in both the years followed by silt and clay fraction. Results of Pearson correlation matrix showed a positive correlation of grain size and organic carbon with concentration of Cd and Pb suggesting the influence of fine fraction in their incorporation into the sediments. Results of geo-accumulation index indicated that the sediments were uncontaminated with Hg, uncontaminated to moderately contaminated with Pb and moderately contaminated with Cd in the estuarine region.

[Keywords: Mahanadi estuary, Heavy metal, Geo accumulation index, Contamination factor, Correlation matrix]

Introduction

Mahanadi river system is the third largest in the peninsula of India and the largest river in Odisha state. The basin extends over an area of approximately 141,600 km$^2$, with a total length of 851 km and peak discharge of 44,740 m$^3$ s$^{-1}$ water$^1$. Major industrial establishment such as Mahanadi coal field Ltd., Jagatpur industrial estate, PPL, IFFCO, etc. discharge their effluent into this water body. Fishing harbor activities, municipal sewage and materials handling in Paradip Port further pollute the estuarine water as well as sediment. Present study is to evaluate the heavy metal pollution, particularly Pb, Cd and Hg, in the estuarine sediment of Mahanadi because of the fact that this estuary is under great environmental pressure due to the enormous discharge of the industrial and domestic sewage into it. Attempts have been taken to evaluate the heavy metal distribution, texture pattern and organic carbon trend, the sources of heavy metals and interrelationship between these sediment qualities by using statistical analysis.

Materials and Methods

Surficial sediments from the river mouth as a station (Lat $20^\circ 17' 37''$ N Long $86^\circ 42' 25''$ E) marked in Fig. 1 were sampled in June (pre-monsoon), October (post-monsoon) and April (summer) months between 2008-2010 annually using a Van Veen grab. Samples were then transferred to pre cleaned polythene bag and brought to the laboratory. Some part of the sediment samples were oven dried at 60°C to constant weight. Sand, silt and clay fractions in sediments were analyzed by weight sieving and pipette method$^{2}$. The oven dried sample was powdered with grinder (Tetsch, model RM100). Then required amount of ground sample was taken for organic carbon (OC) estimation following Walkley and Black method$^{3}$. For the estimation of lead and cadmium the powdered sediment samples was brought into solution by digesting with concentrated HF, HClO$_4$ and HNO$_3$ and the residue remaining after evaporation of acid was dissolved in dilute HCl$^4$. For mercury analysis sediment was digested in aquarea for 10 minutes at 60°C followed by oxidation with KMnO$_4$. The concentration of total mercury was measured by cold vapour atomic absorption spectroscopy (CVAAS) following standard procedure$^5$ on Atomic Absorpton spectrophotometer (Shimadzu model AA6300). All acids and chemicals used during the analysis were of special grade with low mercury content (E. Merck.
Germany). Analytical results of grain size distribution, organic carbon and heavy metals (Pb, Cd and Hg) are given in Table 1.

Geoaccumulation index (Igeo)

The index of geo-accumulation (Igeo) was computed using the equation:

$$I_{geo} = \log_2 \left( \frac{C_n}{1.5 \times B_n} \right)$$

Where \( C_n \) is the measured concentration of the element in the politic sediment fraction and \( B_n \) is the geochemical background value (average shale) in the earth’s crust. The constant 1.5 allow for natural fluctuations in the content of a given substance in the environment and very small anthropogenic influences. Six classes of the geo accumulation index have been distinguished as given below.

<table>
<thead>
<tr>
<th>Igeo value</th>
<th>Class</th>
<th>Quality of sediment</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;0</td>
<td>0</td>
<td>Unpolluted</td>
</tr>
<tr>
<td>0–1</td>
<td>1</td>
<td>From unpolluted to moderately polluted</td>
</tr>
<tr>
<td>1–2</td>
<td>2</td>
<td>Moderately polluted</td>
</tr>
<tr>
<td>2–3</td>
<td>3</td>
<td>From moderately polluted to strongly polluted</td>
</tr>
<tr>
<td>3–4</td>
<td>4</td>
<td>Strongly polluted</td>
</tr>
<tr>
<td>4–5</td>
<td>5</td>
<td>From strongly to extremely polluted</td>
</tr>
<tr>
<td>&gt;5</td>
<td>6</td>
<td>Extremely polluted</td>
</tr>
</tbody>
</table>

Contamination Factor

The level of contamination, expressed by the contamination factor (CF)

$$CF = \frac{\text{metal content in the sediment}}{\text{metal content in natural reference sediment}}$$

The contamination factor was classified into four groups, which are shown below.

1 ≤ CF  Low contamination factor
1 ≤ CF<3 Moderate contamination factor
3 ≤ CF<6 Considerable contamination factor
6 ≥ CF Very high contamination factor

Pollution load Index

Pollution load index was calculated using the formula

$$PLI = \left( \prod_{j=1}^{n} CF_j \right)^{1/n}$$

where \( CF_j \) = contamination factor of metal ‘j’ with respect to world rock average, \( n \) =number of metal, which indicates the Pollution status of a site or region considering all metal concentrations PLI >1 is polluted.

Results and Discussion

The analytical results of all the parameters studied viz. grain size distribution, organic carbon and heavy metals (Pb, Cd and Hg) are given in Table 1.

Table 1—Analytical Results of surficial sediments of Mahanadi estuary. [sand, silt and clay are in %, OC in mg/g, Cd, Pb and Hg are in µg/g]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>2009—2010 Min-Max</th>
<th>Mean ±SD</th>
<th>2008—2009 Min-Max</th>
<th>Mean ±SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sand</td>
<td>94.16 - 98.91</td>
<td>97.62 ± 1.85</td>
<td>94.81 - 99.48</td>
<td>96.93 ± 1.92</td>
</tr>
<tr>
<td>Silt</td>
<td>0.38 - 4.96</td>
<td>1.74 ± 1.77</td>
<td>0.10 - 4.18</td>
<td>2.18 ± 1.67</td>
</tr>
<tr>
<td>Clay</td>
<td>0.44 - 0.90</td>
<td>0.64 ± 0.22</td>
<td>0.42 - 1.17</td>
<td>0.89 ± 0.32</td>
</tr>
<tr>
<td>OC</td>
<td>0.70 - 5.43</td>
<td>2.48 ± 2.11</td>
<td>1.05 - 6.97</td>
<td>3.70 ± 2.47</td>
</tr>
<tr>
<td>Cd</td>
<td>0.01 - 1.12</td>
<td>0.65 ± 0.50</td>
<td>1.25 - 1.56</td>
<td>1.45 ± 0.14</td>
</tr>
<tr>
<td>Pb</td>
<td>16.22 - 36.58</td>
<td>23.89 ± 7.27</td>
<td>17.30 - 36.90</td>
<td>23.88 ± 8.88</td>
</tr>
<tr>
<td>Hg</td>
<td>0.035 - 0.205</td>
<td>0.102 ± 0.058</td>
<td>0.048 - 0.189</td>
<td>0.107 ± 0.070</td>
</tr>
</tbody>
</table>
estuarine region is the fine material transfer from seaside during flood tide, bottom topography and shoreline configuration. Texture pattern found to be sand dominated in both the year in all seasons averaging over 96.00% (97.62% in 2009-10, 96.93% in 2008-09) followed by silt and clay fraction.

The organic matter content in estuarine sediments is controlled mostly by the rate of supply of terrestrial materials, rate of deposition of organic to inorganic constituents, primary productivity, composition and texture of sediments. Textural control over organic carbon is indicated by the positive correlation of organic carbon with silt and clay percentages (Table 2) in the sediments. It was experimentally proved that various clay minerals adsorbed substantial amount of organic matter formed by the decomposition of phytoplankton. Co-sedimentation of organic matter with fine particles due to similarity in settling velocity help for the sympathetic relationship of organic matter content with fine particles of sediments. Organic coating onto clay minerals may greatly affect size distribution and settling rates of inorganic sediments flocculation at the estuarine zone and contribute to the ubiquitous increase of organic matter in coastal marine sediments. Organic carbon (mg/g) during the study period ranged from 0.70 - 5.43, avg. 2.48 in 2009-10 and from 1.05 - 6.97, avg. 3.70 in 2008-09. Sediment samples of year 2008-09 recorded higher organic carbon content supported by greater clayey fraction as compared to 2009-10.

Heavy metal concentrations of the sediments are potentially good indicators of the state of an environment. Once heavy metals are discharged in estuarine and coastal waters, they rapidly become associated with particulates and are incorporated into bottom sediments. Accumulation of metals from the overlying water to the sediments is dependent on a number of external environmental factors such as pH, Eh, ionic strength, anthropogenic input, the type and concentration of organic and inorganic ligands and the available surface area for adsorption caused by variation in grain size distribution. Textural analysis and the heavy metal concentrations in the study area are presented in Table 1. The concentration of heavy metals (in µg/g) ranged between Pb: 17.30 - 36.90, Cd: 1.25 - 1.56, Hg: 0.048 - 0.189 with average values Pb: 23.88, Cd: 1.45, Hg: 0.107 in 2008-09 and Pb: 16.22 - 36.58, Cd: 0.01 - 1.12, Hg: 0.035 - 0.205 with average values for Pb: 23.89, Cd: 0.65, Hg: 0.102 (µg/g) in 2009-10. Average shale values (Pb: 20.00, Cd: 0.3, Hg: 0.4 µg/g) are commonly used as background values in sediment values. Hg and Pb values of the sediment samples were similar to those for average shale, which indicates that there are no major sources of pollution for these elements in the estuarine region. However for Cd, a comparison of metal concentration with average shale value reveals that the sediment samples were moderately polluted with Cd. This result is understandable if we bear in mind that this river is highly affected by the fertilizer based industrial effluents that has taken place in the river basin. Using the heavy metal concentration, Igeo (Fig. 2), CF and PLI (Table 2) were calculated. The obtained Igeo value revealed that Cd is moderately

![Fig. 2—Variation of Igeo value in estuary sediment.](image-url)

<table>
<thead>
<tr>
<th>Year</th>
<th>Min</th>
<th>Max</th>
<th>Avg</th>
<th>Cd CF</th>
<th>Pb CF</th>
<th>Hg CF</th>
<th>PLI</th>
</tr>
</thead>
<tbody>
<tr>
<td>2009-10</td>
<td>0.0</td>
<td>3.7</td>
<td>2.2</td>
<td>0.8</td>
<td>1.8</td>
<td>0.5</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>0.9</td>
<td>0.3</td>
<td>0.2</td>
<td>1.2</td>
<td>0.1</td>
<td>0.8</td>
</tr>
<tr>
<td>2008-09</td>
<td>5.2</td>
<td>5.2</td>
<td>4.8</td>
<td>1.8</td>
<td>1.2</td>
<td>0.5</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td>0.4</td>
<td>0.9</td>
<td>0.3</td>
<td>1.1</td>
<td>0.8</td>
<td>1.5</td>
<td>1.1</td>
</tr>
</tbody>
</table>
polluted in all seasons of the year 2008-09 and showed a positive signal in the year 2009-10. Lead is unpolluted to moderately polluted in pre-monsoon season of both the years and for Hg it is unpolluted in all the seasons of both the years. The CF value for Cd (Table 2) inferred that it comes under unpolluted to moderately polluted category in the estuarine region, much in agreement with the finding from Igeo value.

The data on heavy metal concentration, grain size fraction along with organic carbon in sediments of the study area was processed using SPSS 10.0 statistical software and are given in Table 3. Textural control over OC is indicated by the correlation of OC with sand, silt and clay percentage of the sediments. OC showed positive correlation with both silt (r=0.107) and clay (r=0.588) and an inverse relation with that of sand (r=0.188). These results showed that the OC concentration in the sediment increases as the particle size of the sediment decreases. Positive correlation of OC with clay and silt indicates its size dependant. Increase in OC with decreases in particle size is also attributed to the increase in surface area of fine particles. Among metals Cd and Pb showed positive correlation with silt and clay fraction of sediment suggesting fine sediments i.e. silt clay type sediments which are rich in organic content have higher cation exchange capacities and are able to trap metal rich sediment while sandy type sediments, organically poor sediments have little ability to retain metal ions. Results of statistical analysis revealed positive correlation between OC and Cd (r=0.118), OC and Pb (r=0.337) and negative relation with Hg (r=-0.100). Hg also showed negative correlation with silt (r=-0.155) and clay (r=-0.377). Such a negative relationship between Hg with OC and finer fraction of sediments could be due to the dominance of coarse sediment fraction in the estuary and absence of local polluting sources. The positive correlation between heavy metal concentrations suggested either a common source or a similar geochemical behavior origin.

### Conclusion

Various anthropogenic sources may be the main reasons contributing insignificant heavy metal to the estuary sediment. Relatively low level of sedimentary Pb and Cd indicates that the overall Pb and Cd contamination in the study area is not serious. There were no serious heavy metal contaminations in Mahanadi estuary. Present observation predicted the level of Pb, Cd and Hg pollution as unpolluted to moderately polluted, unpolluted and unpolluted to moderately polluted respectively throughout the year. In the absence of reliable information, further biomonitoring programme for heavy metals in the sediment and living resources from the Mahanadi estuary is highly essential to minimise ecological damage and cumulative impacts of these hazardous metals.

### Acknowledgement

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### References