INTRODUCTION

Trace metals in aqueous environment may occur in various chemical forms like dissolved, particulate, sediment and interstitial water. The suspended matter can act as a scavenger for heavy metals in water (De Groot et al., 1976). A large part of heavy metals present in the aqueous environment is associated with suspended particles. When the flow velocity slackens, the coarser grained particles and aggregates will settle. This sedimentation takes place especially in estuaries and harbours. This will lead to the accumulation of trace metals in sediments. A large part of the anthropogenic discharge of trace metals into the environment becomes part of the suspended matter and gets deposited in river sediments. Therefore, sediment reflects the extent of the pollution in the given area. Anthropogenic inputs of some heavy metals, however, exceed those of natural inputs due to weathering (De Groot, et al., 1976). Estuarine sediments act as a sink for metals regardless of whether the metal rich waste is discharged into the river as solids or solutions (Elderfield and Hepworth, 1975). The estuarine environment is the last area for the removal of trace metals before their passage from the terrestrial to the marine environment. The role of rivers in transporting material from the continents to ocean is paramount, being 10 times that of glaciers and 100 times that of winds (Goldberg, 1976).

MATERIALS AND METHODS

The Zuari river originates from the Dighi ghat of the Karnataka part of the Sahyadri Hills after flowing through a stretch of 67 kms joins the Arabian Sea near the Mormugao-Donapaula point. Its width at the mouth of the estuary is 5.5 km while, in the upstream, it narrows to less than 0.5 km. Similar to the Mandovi it is fed by monsoon precipitation and also receives the discharge from a catchment area of 550 km². Its basin constitutes about 27 % of the total land area of Goa. It carries drainage from 309 km² of the forest land. There are a total of 127 industries in its basin which discharge about 4.4 x 10⁶ m³ of effluents per year into the river and its tributaries. There are 10 large mines in its basin which generate 1000-4000 tonnes of rejects per day per mine, of which a good portion can be expected to reach the river. (NIO, 1979).

The station locations in the study area are given in Fig. 1. The area of investigation covers the Zuari river in Goa (west coast of India). It comprises

ABSTRACT

The bottom sediment samples were collected from the ten sampling stations located along the Zuari river of Goa, west coast of India. The sediment samples were analyzed for some trace metals content viz. Zinc, Iron, Manganese, Cadmium, Cobalt, Copper and Chromium. The collection of the sediment samples were carried out during three seasons viz. Pre-monsoon (February-May), Monsoon (June-September), Post-monsoon (October-January). In general, concentrations of the trace metals in the sediments broadly registered highest values during monsoon season except for cadmium and iron, which showed slightly higher concentrations during the Post-monsoon season. Relatively higher concentration of iron during the Post-monsoon and monsoon compared to Pre-monsoon can be attributed to mining and shipping activities along with increased river runoff.

KEY WORDS

Biodegradation
Tannery effluent
Pseudomonas putida

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of ten sampling stations. The stations were named (from mouth to head) ZE1, ZE2, ZE3, ZE4, ZE5, ZE6, ZE7, ZE8, ZE9 and ZE10 (extra stations, ZE4a, ZE6a, ZE9a, ZE9b). These stations cover the entire course of the river i.e. from the head to the mouth region. Sediment samples for the study were collected in three seasons viz. Pre-monsoon (May), Monsoon (July) and Post-monsoon (November). Bottom sediment samples were collected from different stations using a hand operated Van Veen Grab sampler. The analysis of trace metals from the sediments were done according to total decomposition method of Loring and Rantala (1992). In this method hydrofluoric acid (HF) and aquarea are used to release the total metal content from marine sediments into solutions in a sealed teflon bomb.

RESULTS AND DISCUSSION

The trace metal concentrations of the sediment samples from the estuarine regions of Zuari river in the different seasons are furnished in the Table 1.

Zinc

The concentration of zinc (µg g⁻¹) in sediments varied from 63.33 to 114.33 during pre-monsoon, from 52.67 to 126.0 during monsoon and from 23.67 to 165.33 during post-monsoon. The range and average values of zinc in sediments in the present study (Table 2) is slightly lower when compared with those reported earlier from Godavari estuary (Srinivas, 1998), Vamsadhara estuary (Devavarma

Table 1: Data on seasonal variation of trace metal in sediments of the Zuari river of Goa, West coast of India

<table>
<thead>
<tr>
<th>Station</th>
<th>Zn (µg g⁻¹)</th>
<th>Fe (µg g⁻¹)</th>
<th>Cr (µg g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZE1</td>
<td>84.00</td>
<td>7.38</td>
<td>0.274</td>
</tr>
<tr>
<td>ZE2</td>
<td>114.33</td>
<td>3.50</td>
<td>0.200</td>
</tr>
<tr>
<td>ZE3</td>
<td>63.33</td>
<td>2.65</td>
<td>0.199</td>
</tr>
<tr>
<td>ZE4</td>
<td>86.67</td>
<td>2.25</td>
<td>0.130</td>
</tr>
<tr>
<td>ZE5</td>
<td>114.33</td>
<td>3.50</td>
<td>0.200</td>
</tr>
<tr>
<td>ZE6</td>
<td>63.33</td>
<td>2.65</td>
<td>0.199</td>
</tr>
<tr>
<td>ZE7</td>
<td>86.67</td>
<td>2.25</td>
<td>0.130</td>
</tr>
<tr>
<td>ZE8</td>
<td>114.33</td>
<td>3.50</td>
<td>0.200</td>
</tr>
<tr>
<td>ZE9</td>
<td>63.33</td>
<td>2.65</td>
<td>0.199</td>
</tr>
<tr>
<td>ZE10</td>
<td>AVG 87.30</td>
<td>4.27</td>
<td>0.210</td>
</tr>
</tbody>
</table>

Figure 1: Map showing study area in the Zuari River of Goa, West Coast of India
Seasonal variation of zinc registered highest concentrations during the monsoon followed by pre-monsoon and post-monsoon seasons (Fig. 2a). High concentrations of zinc during monsoon are due to the effect of increased inputs of land derived metals due to runoffs. A large part of the anthropogenic discharge of heavy metals into the environment becomes part of the suspended matter in rivers. This suspended matter can act as scavenger for heavy metal in water (Burton and Liss, 1976). Similar observations were made by Srinivas (1998) in Godavari estuarine sediments and Pondicherry harbour by Senthilnathan and Balasubramanian (1999).

Iron

Concentration of iron (%) in different seasons varied from 2.25 to 6.5 during pre-monsoon, from 4.016 to 12.078 during monsoon and from 2.23 to 16.77 during post-monsoon. The range and average values of iron in the present study (Table 2) is slightly higher when compared with those reported earlier from Mandovi estuary (Bukhari, 1994), Godavari estuary (Srinivas, 1998), Vamsadhara estuary (Devavarma et al., 1993 and 1991), Krishna estuary (Krishna Rao and Swamy, 1991), Vellar estuary (Mohan, 1995), World river average (Martin and Maybeck, 1979), Surficial Rocks (Martin and Maybeck, 1979) and Tapti (Subramanian, 1985). Seasonal variation of iron in sediments registered higher values during post-monsoon and monsoon seasons followed by pre-monsoon (Fig 2b). Concentration of metals in sediments depends on several factors such as local conditions, particle size and organic matter content (Aston and Chester, 1976). Fine grained sediments (clays, clayey silts) are characterized by higher metal concentration in sediment (Deva Varma et al, 1993). Relatively high concentration during post-monsoon can be attributed to high organic matter content in sediments. Whereas, higher concentrations during monsoon may be due to the higher inputs from land runoff and influx of metal rich fresh water. The increased particulate matter along with suspended sediment load brought in by the river would also be a possible reason for the abnormally high values during monsoon (Senthilnathan and Balasubramanian, 1994).
Table 2: Comparison of range and average concentrations of trace metals in sediments of Mandovi and Zuari rivers of Goa with other regions

<table>
<thead>
<tr>
<th>Location</th>
<th>Zn (mg kg⁻¹)</th>
<th>Fe (%)</th>
<th>Mn (%)</th>
<th>Cd</th>
<th>Co</th>
<th>Cu (mg kg⁻¹)</th>
<th>Cr (mg kg⁻¹)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mandovi estuary</td>
<td>25.0-149.67</td>
<td>2.03-12.8</td>
<td>0.062-6.079</td>
<td>ND-4.3</td>
<td>3.33-32.0</td>
<td>3.67-80.67</td>
<td>68.0-403</td>
<td>Present study</td>
</tr>
<tr>
<td>Zuari estuary</td>
<td>23.67-165.33</td>
<td>2.23-16.7</td>
<td>0.04-0.62</td>
<td>Nd-4.6</td>
<td>12.0-36.33</td>
<td>7.0-74.0</td>
<td>60.33-388.0</td>
<td>Present study</td>
</tr>
<tr>
<td>Mandovi estuary</td>
<td>21.0-83.5</td>
<td>2.2-49.7</td>
<td>0.01-1.18</td>
<td>-</td>
<td>2.5-45.3</td>
<td>12.9-77.5</td>
<td>-</td>
<td>Alagarsamy, 1988</td>
</tr>
<tr>
<td>Mandovi estuary</td>
<td>38.0-102</td>
<td>3.15-11.05</td>
<td>0.085-1.01</td>
<td>-</td>
<td>15.35</td>
<td>31-88</td>
<td>224-580</td>
<td>Bukhari, 1994</td>
</tr>
<tr>
<td>Godavari estuary</td>
<td>66.0-323.0</td>
<td>2.67-8.03</td>
<td>0.04-0.17</td>
<td>-</td>
<td>22.0-89.0</td>
<td>61.0-157.0</td>
<td>88.0-243.0</td>
<td>Srinivas, 1998</td>
</tr>
<tr>
<td>Vamsadhara estuary</td>
<td>50.0-250.0</td>
<td>3.20-7.10</td>
<td>0.04-0.09</td>
<td>-</td>
<td>20.0-45.0</td>
<td>25.0-55.0</td>
<td>8.0-128.0</td>
<td>Devavarma et al., 1993-1991</td>
</tr>
<tr>
<td>Krishna estuary</td>
<td>97</td>
<td>6.6</td>
<td>0.2</td>
<td>-</td>
<td>32.0</td>
<td>37.0</td>
<td>106.0</td>
<td>1991 and 1993</td>
</tr>
<tr>
<td>Vellar estuary</td>
<td>196</td>
<td>3.93</td>
<td>0.4854</td>
<td>7</td>
<td>48</td>
<td>45</td>
<td>222</td>
<td>Mohan, 1995</td>
</tr>
<tr>
<td>Tuticorin coast</td>
<td>0.224-0.432</td>
<td>0.029-0.125</td>
<td>(0.316)</td>
<td>(0.078)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Ganesan and Kannan, 1995</td>
</tr>
<tr>
<td>Narmada 50</td>
<td>3.14</td>
<td>0.0514</td>
<td>-</td>
<td>36</td>
<td>46</td>
<td>55</td>
<td>Subramanian et al., 1985</td>
<td></td>
</tr>
<tr>
<td>Tapti 118</td>
<td>10.9</td>
<td>0.13</td>
<td>-</td>
<td>64</td>
<td>126</td>
<td>108</td>
<td>Subramanian et al., 1985</td>
<td></td>
</tr>
<tr>
<td>Indian 16</td>
<td>2.9</td>
<td>0.06</td>
<td>-</td>
<td>31</td>
<td>28</td>
<td>87</td>
<td>Subramanian et al., 1985</td>
<td></td>
</tr>
<tr>
<td>Average</td>
<td>350</td>
<td>4.8</td>
<td>0.105</td>
<td>-</td>
<td>20</td>
<td>100</td>
<td>100</td>
<td>Martin and Maybeck, 1979</td>
</tr>
<tr>
<td>Average</td>
<td>129</td>
<td>3.59</td>
<td>0.07</td>
<td>-</td>
<td>13</td>
<td>32</td>
<td>97</td>
<td>Martin and Maybeck, 1979</td>
</tr>
<tr>
<td>Average</td>
<td>129</td>
<td>3.59</td>
<td>0.07</td>
<td>-</td>
<td>13</td>
<td>32</td>
<td>97</td>
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</tr>
<tr>
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<td>0.07</td>
<td>-</td>
<td>13</td>
<td>32</td>
<td>97</td>
<td>Martin and Maybeck, 1979</td>
</tr>
</tbody>
</table>

N. D = Non-detectable; All values in parentheses are average values. All values in µg g⁻¹ except Fe and Mn.

Ganesan and Kannan (1995) had reported high content of iron during monsoon and post-monsoon in Tuticorin coast, which is attributed to increasing land runoffs. Srinivas (1998) while studying Godavari estuarine sediments observed higher concentrations during monsoon seasons.

**Manganese**

Concentration of manganese (%) in sediments varied from 0.139 to 0.413 during pre-monsoon, from 0.159 to 0.62 during monsoon and from 0.047 to 0.62 during post-monsoon. In general, the ranges and averages of manganese concentrations in the present study (Table 2) broadly agree with those reported from Mandovi estuary (Bukhari, 1994 and Alagarsamy, 1988). But, it revealed slightly higher concentrations when compared with those reported earlier from Godavari estuary (Srinivas, 1998), Vamsadhara estuary (Devavarma et al., 1993 and 1991), Krishna estuary (Krishna Rao and Swamy, 1991), Cauvery estuary (Ramanathan et al., 1988), Tuticorin coast (Ganesan and Kannan, 1995), Narmada (Subramanian et al., 1985), Narmada (Subramanian et al., 1985) World river average (Martin and Maybeck, 1979), Surficial Rocks (Martin and Maybeck, 1979) and Tapti (Subramanian, 1985). However, slightly lower values were observed when compared with that reported earlier from Vellar estuary (Mohan, 1995).

Seasonal variation of manganese in sediments showed highest concentration during post-monsoon and monsoon periods compared to pre-monsoon (Fig 2c). Higher concentration during post-monsoon season can be

![Figure 2c: Seasonal variation of Manganese in sediment of Zuari River of Goa, West coast of India](image-url)
attributed to high organic matter content during post-monsoon season. Srinivas (1998) reported high concentration of manganese in sediment during monsoon and post-monsoon in Godavari estuary. Similarly high concentration of manganese was reported during monsoon and post-monsoon season from Tuticorin coast (Ganesan and Kannan, 1995).

**Cadmium**
Concentration of cadmium (µg g⁻¹) in different seasons in sediments varied from ND (Non Detectable) to 2.16 during pre-monsoon, from ND to 4.6 during monsoon and from 0.33 to 3.3 during post-monsoon. The range and average values obtained in the study is slightly lower when compared with that reported earlier from Vellar estuary (Mohan, 1995).

![Variation of Cd at different seasons](image1)

**Figure 2c: Seasonal variation of Cadmium in sediment of Zuari River of Goa, West coast of India**

Seasonal variation of cadmium is found to be highest during post-monsoon period followed by monsoon and pre-monsoon (Fig 2d). Higher values during post-monsoon could be due to higher organic matter content in both the estuaries. This is also supported by significant positive correlation exhibited between cadmium and organic carbon during post-monsoon season in the Mandovi estuary (Singh, 2000). Senthilnathan and Balasubramanian (1999) while studying heavy metal distribution in Pondicherry harbour reported higher concentration of cadmium in sediments during monsoon and lower in summer. This was attributed to land runoff and influx of metal rich water.

**Cobalt**
Concentration of cobalt (µg g⁻¹) varied from 12.33 to 22.33 during pre-monsoon, from 12.0 to 35.67 during monsoon and from 11.0 to 36.33 during post-monsoon. The ranges and averages values of cobalt in sediments in the present study (Table 2) is slightly lower when compared with those reported earlier from Godavari estuary (Srinivas, 1998), Vamsadhara estuary (Devavarma et al., 1993 and 1991), Krishna estuary (Krishna Rao and Swamy, 1991), Cauvery estuary (Ramanathan et al., 1988), Vellar estuary (Mohan, 1995), Narmada (Subramanian et al., 1985), Tapti (Subramanian, 1985) and Indian river average (Subramanian et al., 1985). However, the ranges and average values of cobalt observed in the present broadly agree with those reported earlier from Mandovi estuary (Bukhari, 1994 and Alagarsamy, 1988), World river average (Martin and Maybeck, 1979), Surficial Rocks (Martin and Maybeck, 1979).

Seasonal variation of cobalt is found highest during monsoon period followed by post-monsoon and pre-monsoon (Fig 2e). The higher concentration of cobalt during monsoon period may be attributed to the land runoff and influx of metal rich fresh water. Similarly highest concentration of cobalt during monsoon season has been reported from Godavari estuary (Srinivas, 1998).

**Copper**
Concentration of copper (µg g⁻¹) varied from 30.67 to 43.33 during pre-monsoon, from 18.0 to 74.0 during monsoon and from 7.0 to 70.0 during post-monsoon. The ranges and averages values of copper obtained in the present study broadly agree with those reported earlier from Mandovi estuary (Bukhari, 1994 and Alagarsamy, 1988), Vamsadhara estuary (Devavarma et al., 1993 and 1991), Cauvery estuary (Ramanathan et al., 1988), Vellar estuary (Mohan, 1995), Indian river average (Subramanian et al.,
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Figure 2c: Seasonal variation of Copper in sediment of Zuari River of Goa, West coast of India

1985), Surficial Rocks (Martin and Maybeck, 1979). However, they are found to be lower when compared with those of Godavari estuary (Srinivas, 1998), Krishna estuary (Krishna Rao and Swamy, 1991) and World river average (Martin and Maybeck, 1979).

Seasonal variation of copper showed maximum values during monsoon followed by pre-monsoon and post-monsoon seasons (Fig 2f). This slight increase in the concentrations of copper in the sediments during the monsoon period may be due to downstream transport along with the monsoonal discharge. Settling of trace metals at the area of confluence between river and seawater could lead to such effects. Senthilnathan and Balasubramanian (1999) also reported higher concentration of copper in sediments from Pondicherry harbour during monsoon and lower in summer. This was attributed to land runoff and influx of metal rich water. Similarly, higher concentrations of copper in sediments were reported from Godavari estuary during monsoon season (Srinivas, 1998).

Chromium

The concentrations of chromium (µg g⁻¹) in different seasons varied from 93.33 to 175.33 during pre-monsoon, from 107.67 to 653.0 during monsoon and from 39.33 to 388.0 during post-monsoon. The ranges and averages values of chromium in the present study (Table 2) are slightly higher when compared with those reported earlier from Godavari estuary (Srinivas, 1998), Varsadhara estuary (Devavarma et al., 1993 and 1991), Krishna estuary (Krishna Rao and Swamy, 1991), Cauvery estuary (Ramanathan et al., 1988), Vellar estuary (Mohan, 1995), Narmada (Subramanian et al., 1985), Tapti (Subramanian, 1985), Indian river average (Subramanian et al., 1985), World river average (Martin and Maybeck, 1979) and Surficial Rocks (Martin and Maybeck, 1979). But, the range is found to be in broad agreement when compared with the earlier values reported from Mandovi estuary (Bukhari, 1994).

Seasonal variation in the concentrations of chromium registered highest values during the monsoon period followed by those in pre-monsoon and post-monsoon (Fig 2g). High concentrations observed during monsoon can be attributed to the land runoff and influx of metal rich fresh water. The increased particulate matter along with suspended sediment load brought in by the river would also be a possible reason for the abnormally higher values during monsoon (Senthilnathan and Balasubramanian, 1997). Similarly, Srinivas (1998) reported higher concentrations of chromium in sediments from Godavari estuary during monsoon season.

CONCLUSION

The range and average values obtained from the estuarine region of Zuari river for the trace metals in sediments are in broad agreement with those in other Indian estuarine and coastal sediments. In general, seasonal variation of all metals except for iron and cadmium showed higher...
concentrations during monsoon followed by those in pre-
monsoon and post-monsoon. High concentrations of 
metals during monsoon can be attributed to the large land 
runoff, the suspended matter from the catchment areas 
along with the runoffs from mining areas. The increased 
particulate along with suspended sediment load brought 
in by river would be the possible reason for the abnormally 
higher values during monsoon. Relatively higher 
concentration of iron during post-monsoon and monsoon 
compared to premonsoon can be attributed to the increased 
river runoff and the associated high organic carbon content 
along with above factors.

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