Chapter 7

SPECIATION - A CRITICAL APPRAISAL

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I. Overview

A critical evaluation of the metal speciation in the Cochin estuary is provided in this chapter. This part of the work which serves as the summary is presented under different sub-headings.

I.i. Inter-metallic comparison

This chapter deals with the comparative behaviour of the four metals during estuarine transport. Several attempts have been hitherto made (Kuwabara et al., 1988; Windom et al., 1988) to categorize the metals according to their behaviour in the estuarine environment. The complexity and diversity of different estuaries along with differences in the chemistry of these metals make the proposition beyond contemplation. The studies, when enlarged to accommodate speciation aspect too, become all the more complicated. However, very useful and directional results could be achieved by closely following the processes as revealed from the behaviour of each of the metals investigated in this study. Of the four metals studied, the
dissolved labile fractions (CLM) of cadmium and zinc were found to decrease towards the saline region (Figs. 4.2a and 6.2a) whereas those of copper and lead showed an appreciable increase in the same direction. Notedly the CLM fraction of all the four metals showed enhancement at Station 5 compared to values at Station 6.

The organically bound fractions of copper, cadmium and lead were found to increase towards the lower reaches of the estuary, but the same fraction of zinc was found to decrease in the same direction. The OBM fraction of cadmium and zinc only showed considerable increase at Station 5 compared to Station 6.

With regard to the particulate exchangeable and total metal fractions (PEM and PTM) - all the four metals followed similar distribution patterns; elevated levels at Station 5 compared to Station 6 and thereafter a decrease towards the lower reaches of the estuary. It may be concluded at this point that the anthropogenic inputs at Station 5 (see Fig. 7.2) was mainly in the CLM and particulate fractions (PEM and PTM) for copper; all fractions in the case of Cd and Zn and only as the particulate fraction (PEM and PTM) for lead.

The results of the intermetallic correlation studies (r values) for each fractions of the four metals are given in Table 7.1. The CLM fraction of cadmium showed an excellent positive correlation (r = 0.87) with Zn and to a lesser extent with Cu (r = 0.35). This fraction of Cu vs Pb also showed significant positive correlation (r = 0.44).

In the OBM fraction lead showed significant positive correlations with Cd (r = 0.50) and Cu (r = 0.42). Cd also showed moderate positive correlation with Cu and Zn (r = 0.33 each). The exchangeable particulate fraction of Zn showed excellent positive correlations with Cu (r = 0.79) and Cd (r = 0.66).
<table>
<thead>
<tr>
<th>Fraction</th>
<th>Metal</th>
<th>Cu</th>
<th>Cd</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>CLM</td>
<td>Cd</td>
<td>0.35</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pb</td>
<td>0.44</td>
<td>0.22</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Zn</td>
<td>0.10</td>
<td>0.87</td>
<td></td>
</tr>
<tr>
<td>OBM</td>
<td>Cd</td>
<td>0.33</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pb</td>
<td>0.42</td>
<td>0.50</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Zn</td>
<td>0.17</td>
<td>0.33</td>
<td>-0.1</td>
</tr>
<tr>
<td>PEM</td>
<td>Cd</td>
<td>0.49</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pb</td>
<td>0.26</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Zn</td>
<td>0.79</td>
<td>0.66</td>
<td>0.26</td>
</tr>
<tr>
<td>PTM</td>
<td>Cd</td>
<td>0.36</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pb</td>
<td>0.32</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Zn</td>
<td>0.75</td>
<td>0.55</td>
<td>0.45</td>
</tr>
</tbody>
</table>

Cadmium also showed a significant positive correlation with copper Cu \( (r = 0.49) \). The total particulate fraction of Zn showed excellent positive correlations with Cu \( (r = 0.75) \), Cd \( (r = 0.55) \) and Pb \( (r = 0.45) \). Also there existed significant positive correlation between Cu and Cd \( (r = 0.36) \). It may be surmised that Cd and Zn are closely similar in its behaviour in the different phases in this estuary. Alloway (1990) also reported that Cd was closely associated with Zn in its geochemistry. The behaviour of Cu and Pb in the dissolved phase was well correlated but the 'exchangeable' fractions did not co-vary.

To generalize, Cd and Pb in this estuary show significant relationship in their organic association where as copper,
cadmium and zinc are related in their particulate association.

To sum up, the order of intermetallic CLM relation would be expressed as: Cd & Zn > Cu & Pb > Cu & Cd > Cd & Pb > Cu & Zn > Pb & Zn. In the OBM fraction, the sequence would be Cd & Pb > Cu & Pb > Cd & Zn = Cu & Cd > Cu & Zn > Pb & Zn. The order for both the particulate fractions (PEM & PTM) would be as follows Cu & Zn > Cd & Zn > Cu & Cd > Pb & Zn = Cu & Pb > Cd & Pb.

I. ii. Metal Reactivity in the Estuary

Both the particulate fractions of all the metals studied in this estuary showed a sharp decrease in their content in the salinity range 0 - 5%. Among the dissolved fractions, Cu-CLM did not exhibit any noticeable trend with salinity. The OBM fraction of cadmium showed a broad maximum in the 20 - 25% salinity range whereas the CLM fraction of the same metal did not show any such trend. The CLM and OBM fractions of lead showed an initial increase upto salinity ~ 5%, and thereafter, the CLM remained at a steady level. But the OBM fraction decreased within the salinity range 5 - 12%, and then increased sharply with increase of salinity. In the case of zinc both CLM and OBM fractions showed a sharp removal in the low salinity region (< 5%). The particulate fractions (PEM & PTM) of copper was found to decrease with increasing amounts of suspended solids during both premonsoon and monsoon seasons. However it increased sharply in the initial stages (of low suspended solids) and fell back to a steady state during postmonsoon as turbidity increased. Lead showed a decrease with increase of suspended load only during premonsoon and postmonsoon. In the case of cadmium and zinc the decreasing trend was consistent during all the three seasons.

In the analysis of results of metal vs organic carbon, both the PEM and PTM of copper showed excellent positive correlations with POC ($r = 0.55$ and $r = 0.64$); other metals did not show any significant correlation. The feature of decrease of particulate copper towards the lower reaches of the estuary was commented upon earlier as being due to the decrease of POC.
contents. The metal species discussed in relation to DOC indicates that the OBM fractions of copper, cadmium and lead showed significant positive correlations while zinc did not exhibit any such relation. Additionally the organophillic nature of the four metals studied in this estuary follows the order Cu > Pb > Cd > Zn.

I. iii. Metal Transport

The Cochin estuary, a typically tropical one, portrays interesting features on metal transport and associated phenomenon. On an annual average basis all the four metals studied (two phases - dissolved and particulate) are transported mainly in the dissolved form. This phase (CLM + OBM) accounts for Cu - 59.76%, Cd - 81.04%, Pb - 75.50% and Zn - 64.91%. Within this dissolved phase (CLM + OBM) the maximum organic association (OBM) was for Cu (72.59%) followed by Pb (68.67%), Cd (64.45%) and the minimum was for Zn (52.00%). Corresponding CLM fraction values are indicated in Table 7.2. The particulate associated transport in this estuary followed the order Cu (40.24%) > Zn (35.09%) > Pb (24.50%) > Cd (18.96%). The particulate phase accounted for the total particulate metal (PTM) of which the PEM fraction i.e., the exchangeable form was in the following order: Zn (56.73%) > Cd (54.48%) > Cu (34.00%) > Pb (32.00%). The table also provides the T - E percentage values which is the difference between the two particulate metal fractions.

Apart from calculating the annual average basis, the metal transportation was checked during the monsoon season when the amount of suspended solids in the river runoff peaks to a maximum. In this context the monsoonal transport was characterised by an increased particulate association in the order Cu (57.40%) > Zn (45.04%) > Pb (28.00%) > Cd (22.14%). This seasonal rating indicates the higher particulate associated copper (compared to dissolved) as well as other metals (compared to annual averages) to be on the greater side, which is an important feature.
The budget calculations for this estuary (condensed from previous chapters) show that annually $1.77 \times 10^3$ kg of copper, $2.27 \times 10^3$ kg of cadmium and $25.36 \times 10^3$ kg of lead are removed in excess of inputs from this estuary. It implies that this part of the Cochin estuary acts as a source for the above mentioned metals. On the other hand, the mass balance of zinc showed $79.57 \times 10^3$ kg yr$^{-1}$ to be deposited in the estuary. This estuary, hence acts as a sink for the metal zinc.

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### II. Anthropogenic Inputs

This investigation has proved beyond doubt the existence of anthropogenic inputs between Stations 5 and 6. Hence it became imperative to calculate the time average annual value for the extent of such inputs within the river reach. The 3D overlap figure (Fig.7.1) for the four metals (CLM + OBM + PTM) at
Fig. 7.1 Annual mean concentration (CLM + OBM + PTM) of metals Cu, Cd, Pb & Zn at Stations 1 to 6
Stations 1 to 6 is also presented as pie diagrams indicating the annual mean concentrations in the same figure. The calculations are presented on the basis that the mean concentration at Station 6 is used to calculate the fluvial contribution and the difference of the same from the calculations made at Station 5 will indicate the amount of anthropogenic input. The input values are calculated for each metals as below:

**Discharge of Periyar river**  
= 5.192 x 10^{12} \text{ l yr}^{-1}

**Copper:**

Fluvial input at Station 6  
= 1.92 \mu g l^{-1} \times 5.192 \times 10^{12}
= 9.969 \times 10^3 \text{ kg yr}^{-1}

Amount at Station 5  
= 3.08 \mu g l^{-1} \times 5.192 \times 10^{12}
= 15.992 \times 10^3 \text{ kg yr}^{-1}

Anthropogenic input  
= 6.023 \times 10^3 \text{ kg yr}^{-1}

**Cadmium:**

Fluvial input at Station 6  
= 0.63 \mu g l^{-1} \times 5.192 \times 10^{12}
= 3.271 \times 10^3 \text{ kg yr}^{-1}

Amount at Station 5  
= 1.50 \mu g l^{-1} \times 5.192 \times 10^{12}
= 0.203 \times 10^3 \text{ kg yr}^{-1}

Anthropogenic input  
= 4.932 \times 10^3 \text{ kg yr}^{-1}

**Lead:**

Fluvial input at Station 6  
= 6.81 \mu g l^{-1} \times 5.192 \times 10^{12}
= 35.358 \times 10^3 \text{ kg yr}^{-1}

Amount at Station 5  
= 9.16 \mu g l^{-1} \times 5.192 \times 10^{12}
= 47.559 \times 10^3 \text{ kg yr}^{-1}

Anthropogenic input  
= 12.201 \times 10^3 \text{ kg yr}^{-1}

**Zinc:**

Fluvial input at Station 6  
= 17.96 \mu g l^{-1} \times 5.192 \times 10^{12}
= 93.248 \times 10^3 \text{ kg yr}^{-1}

Amount at Station 5  
= 86.50 \mu g l^{-1} \times 5.192 \times 10^{12}
III. Enrichment Factors

The enrichment factors at Stations 1 to 6 were worked out on the basis of the background value at Station 6 (Table 7.3) and it is shown in Fig 7.3. This table shows that the factors of enrichment for copper and lead are comparatively higher in the estuarine Stations (Stations 1, 2 & 3) than at Stations 4 and 5. Zinc is considerably enriched at Stations 3, 4 & 5 and noticeably depleted at Station 1. On the other hand, cadmium is enriched to about 2.5 times throughout the estuary. Obviously, the anthropogenic inputs at the industrial site (upstream of Station 5) cause extensive enhancement in the content of zinc and cadmium.

Table 7.3

<table>
<thead>
<tr>
<th>Station</th>
<th>Cu</th>
<th>Cd</th>
<th>Pb</th>
<th>Zn</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>1.93</td>
<td>2.46</td>
<td>2.71</td>
<td>0.67</td>
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<td>2</td>
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<td>1.93</td>
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<td>1.13</td>
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<tr>
<td>5</td>
<td>1.60</td>
<td>2.51</td>
<td>1.35</td>
<td>4.82</td>
</tr>
</tbody>
</table>

IV. Selective Processes in Metal Cycling in the Environment

To explain the processes in simple terms the environment is subdivided as water media, sandwiched between atmosphere and sediment. The four metal species, CLM, OBM, PEM and PTM form the nuclei of processes in the aquatic environment. External sources such as industrial and sewage effluents are also incorporated. The regulating processes of metal cycling in the environment, pertaining to Cochin estuary are given in Fig. 7.3. The CLM fraction is found to be transformed to PEM and
Fig. 7.2 Enrichment factors at Stations 1 to 6
Fig. 7.3 Selective processes in metal cycling in the environment
vice-versa by processes as shown. In estuaries, modifications in the distributions of river-born components in dissolved and particulate phases may occur in response to sharp gradients of parameters like salinity, pH, concentrations of dissolved organic and suspended matter. Thus particles play an important role in the formation and distribution of metal species. The most important processes which control metal concentrations are the sorption processes which include:

i) non-specific adsorption of species on particle surface which is a physical process originating from electrostatic forces

ii) chemisorption of species, which takes place as hydrolytic adsorption or condensation reactions, including co-precipitations with Fe and Mn hydroxides and

iii) ion-exchange, also a chemical process.

The above processes are better understood in terms of competition for surface sites with protons and cations (Bourg, 1983). This concept leads to the determination of surface complex formation constants, corresponding to interface reactions such as:

\[
\text{SOH} + \text{M}^{z+} \rightleftharpoons \text{SOM}^{(z-1)+} + \text{H}^+
\]

(where SOH: surface and M: metal). In solution chemistry, activity coefficients do affect the value of the surface constant. The adsorption of Cu is not affected by a greater number of Na⁺ or NO₃⁻ ions; Cd, however, is not as competitive with Na⁺ with respect to adsorption. The Ca²⁺ and Mg²⁺ ions present in solution are capable of replacing the metal ions thus leading to desorption. For the sorption of trace metals in aquatic systems, the more important sites generally are comprised of thermodynamically metastable phases, which exhibit extensive isomorphous substitution. This is mainly true for Fe and Mn oxyhydrates.

The CLM fraction also would be transformed to OBM either by organic complexation or biological uptake. The major processes by which the sediment associated metal is converted to the CLM form include tidal resuspension followed by desorption, diagenetic processes and microbial activity. The major process in the reverse direction is the scavenging by Fe and
Mn oxyhydrates and subsequent settling.

The variations in OBM content are well reflected in sediment metal levels. This may be explained as the relationship between the amount of primary productivity in the overlying waters and the extent to which the organically associated metal would be preserved in the bottom sediments; the greater the magnitude of primary productivity the greater the extent of preservation of the metal in the sediment media as also reported earlier (Chester et al., 1988). The other possible mechanism by which the OBM gets transferred to sediments is the flocculation process and the opposite is mainly by microbial degradation and diagenetic remobilization.

The processes by which the exchangeable particulate metal is converted to strongly bound form are lattice incorporation and chelation. The major processes by which the particulate metals and sediment metals equilibrated are thought to be purely physical (settling and resuspension).