CHAPTER 5

LEAD

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I. Introduction

Lead mainly exists as Pb (II) carbonate, sulfide or oxide in the earth's crust and has an average concentration of \( \approx 13 \mu g \, g^{-1} \) and in uncontaminated soils it is \( \approx 10 \mu g \, g^{-1} \) (Craig, 1986). Uncontaminated open ocean and fresh surface waters may contain 0.1 \( \mu g \, l^{-1} \) and 0.5 \( \mu g \, l^{-1} \) respectively. But rivers flowing adjacent industrialized centres may contain levels up to \( \approx 100 \mu g \, l^{-1} \). Considerable atmospheric addition of Pb has also been reported from various parts of the world (Alloway, 1990). The high enrichment of Pb may be a direct contribution from vehicle exhausts. Lead, one of the most abundant toxic pollutants in the environment, becomes a real concern as a contaminant because of its constant and continuous release into the air, water and soil in appreciable amounts (Branica, 1980). Lead toxicity appears to cause brain damage, mental deficiency and serious behavioural problems generally known as "Plumbism". Another consequence of lead poisoning is the kidney trouble known as "nephritis". Several studies have demonstrated a strong positive correlation between blood lead levels and drinking water concentrations (Sherlock et al., 1982; Pocock et al., 1983). In appreciation of the public health risk, the USA, Canada and the European community have restricted the total Pb concentration in tap water to be 50 \( \mu g \, l^{-1} \) (de Mora et al., 1987). So far there is no evidence that Pb plays any essential role in metabolism.
The widespread and general use of lead is due to its high ductility and low corrosiveness. Ever since the introduction of tetra alkyl lead (TAL) as an antiknock additive in fuels used in the internal combustion engines, Pb contamination has become a major problem in the environment. The TAL species are sparingly soluble in water and saturation solubilities in freshwater are probably about 15 mg Pb l\(^{-1}\) for tetra methyl lead (TML) and 0.1 mg Pb l\(^{-1}\) for tetra ethyl lead (TEL) (Grove, 1980). A major pathway of lead is the organo metallic form whereas many other metals are released in the inorganic form (eg. Zn, Cd, etc.). Lead also shows great affinity to particulate phase retention (Windom et al., 1988; Paulson et al., 1989). It has been proved that Pb is unique among trace metals in the marine environment, because of its short residence time in the water column (Klomp, 1990). This feature makes the distribution of Pb respond quickly to input changes and the profile being perturbed because industrial lead inputs to the marine lead cycle have increased considerably beyond natural inputs (Schule and Patterson, 1981). It appears that most of the fluvial lead is removed over the continental shelves near the coasts by rapidly settling particles which sequester metals like Pb (Turekian, 1977). Wilhelmy and Flegal (1991) observed a separation of Pb from the cluster of nutrients and other trace metals, indicating that the source and transport processes affecting the distribution of Pb are considerably different from those for other metals. They also suggested that Pb distributions are most likely to be dominated by atmospheric inputs.

Available data on lead in estuarine waters are limited and include those of Danielsson et al., (1983); Elbaz-Poulichet et al., (1984 & 1991); Windom et al., (1985 & 1988); George (1989), Paulson et al., (1989); Forstner et al., (1990) and Harper (1991). All of them have reported considerable particulate association for Pb. So far, the only data available for the Cochin estuary are those of Ouseph (1987); Nair et al., (1990) and Nair et al., (1991) on the sediment associated lead. In the Cochin estuary, the major source of Pb contamination has been identified as being the industrial and
sewage effluents, shipping lines and atmospheric fall-out.

II. Results

In the Cochin estuary, the dissolved form of lead accounts for about 75% of the total metal. The other forms studied, principally total particulate Pb, though less in magnitude, exhibited significant features. Equally important was the exchangeable particulate form observed in this estuary which varied both seasonally as well as spatially. The results have been used to compare the abundance of the metal fractions on a percentage basis during the three seasons. The monthly distribution of the different Pb fractions is presented Station-wise in Fig. 5.1, averaged seasonally in Fig. 5.2a and as percentage abundance in Fig. 5.2b.

Chelex-100 Labile Metal (CLM).

The Chelex-100 eluted AAS read dissolved lead exhibited low content in fresh water and higher amounts towards the seaward side. The CLM values ranged from near detection limits at Station 3 in July 1989 to 9.64 μg l⁻¹ at the same Station in December 1988. Intermediate Stations lying in the estuarine zone were composite in nature but evidently pointed to an increase of this fraction progressively from the freshwater zone. During the entire survey consistently ranged but varying values were observed for this fraction but for the three lone values observed at Stations 1, 3 & 6 in December 1988 and September 1989. The amount of Pb-CLM fraction as pointed out earlier was generally low at Station 5 & 6 except during the postmonsoon months at Station 5 (Fig. 5.2a). Elevated levels were noticed at Stations 3 & 4 during two seasons, the premonsoon and the postmonsoon. During the months from June to September, the above Stations (Stations 3 & 4) were characterized by low to very low amounts of dissolved CLM-lead. The values at Station 2 indicated some amount of scatter during the early part of the survey. The location at the barmouth (Station 1) showed considerable abundance even during the intervening period of the monsoon while during other periods of
Fig. 5.1 Monthly distribution of lead fractions at Stations 1 to 6
(D-December 1988 to N-November 1989)
Fig. 5.2 Seasonal variation of lead fractions
   a) absolute values  b) percentages
the year the values were still higher. Thus the general
distribution trends pointed out to an increase of this metal
fraction longitudinally from upper estuarine reaches to the
lower estuary.

The seasonally segregated feature (Fig. 5.2a) exhibited a
steady increase of this metal fraction both during premonsoon
and postmonsoon from Station 6 to Station 1 i.e. from upper
estuarine reaches to the lower estuarine reaches. The monsoon
season was characterised by a mid-estuarine minimum. The range
of values in monsoon was lower than the values during the other
two seasons. This figure also helps to point out the
occurrence of higher amounts of this fraction of the metal
during postmonsoon season except at Station 6 where the averaged
monsoonal value predominates.

Organically Bound Metal (OBM).

Results on the studies of the organically bound metal in
the lead fractionation scheme delineated two areas of the
estuary, one in which the content was considerably low
(freshwater to low saline - Stations 6, 5 & 4 ) and the other
with marginal to high values in the lower estuary (Stations 3,
2 and 1). The contribution of OBM - Pb by the river as
observed from the data at Station 6, varied from near detection
limits to $\approx 5 \mu g l^{-1}$. Exceptionally high value were recorded
in January and March 1989 at this Station. The adjacent
downstream Stations (Stations 5 & 4) too contained only low
amounts of the bound metal while the features drastically
changed at Station 3. The trend at Station 3 was a gradual
decrease from premonsoon period to monsoon months followed by a
recovery to the initial levels. At this Station too a single
peak was encountered in February 1989. The distribution
feature at Station 2 was no different from that of Station 3
except that during monsoon the level of metal was enhanced at
this Station compared to Station 3. A more equitable
distribution was observed at Station 1 during the initial four
months of the survey as well as towards the end of the survey.
Considerable variation was noticed in the metal levels between
April and October 1989. To generalise the OBM profile, Stations 1 to 6 may be segmented into the upper estuary (Stations 4 to 6) with comparatively low content and the lower estuary (Stations 1 to 3) with high OBM content. Fig 5.2a analyses both seasonal as well as the spatial abundances. The behaviour of Pb associated with organics hence have to be viewed more critically in their spatial variation than inter-seasonal. A marked seasonal increase was observed at Station 1 during postmonsoon and Stations 2 & 3 incorporated low monsoon values compared to the higher values in the preceding and succeeding seasons.

Particulate Exchangeable Metal (PEM)

The content of PEM varied between 2.55 μg g⁻¹ at Station 6 in September 1989 and 1425 μg g⁻¹ at Station 5 in April 89. It has not been possible to derive any major feature in the distribution of PEM from Station 1 to 6. However it may be generally stated that the freshwater Station (Station 6) contained intermediate values which increased sharply at Station 5 and then gradually decreased towards the lower reaches of the estuary. It was also noted that the content of PEM fraction was generally high during postmonsoon with still higher values in premonsoon followed by a fall during monsoon season. This fact was quite evident in the three uppermost Stations (Stations 4, 5 & 6) than at Stations 1, 2 & 3 in the lower estuary. There was always a likelihood that this fraction of Pb was found in abundance at any Station irrespective of the month / season. The pattern of variability indicated that:

a) the monsoonal values were very low at all Stations to produce any appreciable trend in the distribution

b) in the freshwater region the premonsoon and the postmonsoon value were higher than during the monsoon and the difference was still further enhanced at Stations 4 & 5. However at Stations 1 & 2 no seasonal differences were noted when the abundance of PEM was at the minimum. The large peaks at Stations 4 & 5 indicative of premonsoonal enrichment mainly referred to the high single value observation made in the month of April.

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T9 §a1 Particulate setal (PTM)

The trends and abundance of Pb - PTM were more or less the same as that of Pb - PEM. The PTM values ranged between 34.24 µg g⁻¹ at Station 4 in September 89 and 6194 µg g⁻¹ at Station 5 in May 89. Once again during April 89 Station 5 exhibited anomalously high value. The range of PTM values was more susceptible to changes during premonsoon and postmonsoon whereas no such variations could be observed during monsoon. PTM and PEM distribution profiles closely resembled each other except that the observed values were scaled an order higher.

Percentage Abundance of Different Fractions

The results of this analysis serve to bring out the relative proportions of seasonal abundance in percentages among the four fractions in which the PEM has already been included in the PTM fraction. Fig.5.2 b indicates sharp variations in the seasonal abundance of the three fractions at Station 6. The content of OBM far exceeded that of CLM and PTM during premonsoon but occurred as the least during monsoon when either of the other species (PTM & CLM) were equitably distributed. It was the PTM and OBM fractions which dominated in content during postmonsoon season. However these inter-seasonal variability gradually minimised to a well graded and near uniformly patterned difference as the analysis was extended to Stations nearer the seaward side. e.g. at Station 3 exhibited an OBM content of ~ 60% during all seasons whereas 20 to 30% of CLM was followed by 10 to 15% of the PTM lead in two seasons namely premonsoon and postmonsoon. In the case of changes observed during monsoon CLM and to some extent the PTM also showed consistent fall from Station 6 to Station 3 compensated by the enhancement in the OBM fraction. Noteworthy were the changes of trends in the case of CLM and PTM at Stations 1, 2 & 3 during monsoon when the former tended to increase towards the lower estuary and the content of PTM decreased. At the same instance the proportion of OBM fraction in monsoon remained a constant. As recorded in Fig.5.2a, the pattern of changes in PEM, a true replica of variations of Pb - PTM, the seasonal
abundance on a percentage basis also followed similar and identical changes. On the whole, comparing percentages of all the four fractions, Pb-associated with organic matter was found to play an important role followed by PTM in deciding the relative proportions of Pb abundance within the Cochin estuary.

Regression Analyses

The results of the regression analyses showed significant positive correlations between CLM and OBM ($r = 0.40$, $P < 0.001$). With different environmental parameters CLM and OBM showed significant positive correlations with salinity ($r = 0.51$ and $r = 0.60$); pH ($r = 0.3$ and $r = 0.32$) and only OBM showed a positive correlation with DOC ($r = 0.39$, $P < 0.001$). The particulate fractions PEM and PTM showed significant negative correlations with salinity ($r = -0.30$ and $r = -0.35$); pH ($r = -0.35$ and $r = -0.37$); SS ($r = -0.54$ and $r = -0.46$) and with POC only the PEM showed significant positive correlation ($r = 0.41$). (For all the above cases $P < 0.001$ and $n = 72$

III. Discussion

i. Spatial and Seasonal Variation

The behaviour of Pb fractions in Cochin estuary highlights distinct features with regard to each of the estimated species. Between species themselves and between Stations too, variations though existent, were found to be within a rather uniform range of values. To start with, Pb in the freshwater zone (Station 6) contains low amounts of all the four fractions during all the seasons when compared to low saline Stations. The values at this location may be taken to represent aquatic environments which are relatively unpolluted and clean. The fractions of Pb surveyed at Station 5, which is downstream of the cleaner location, gave rise to enhanced amounts of particulate Pb attributable to the anthropogenic inputs at this region. This observation is no exception as elevated levels of many other metal fractions are being distinctly noted at this site. Since the initial months of the study (January to May), both the
particulate fractions showed enhanced values at Stations 4, 5 & 6. The elevated levels occur during the period of low river discharge when effects of industrial effluents, if any, will be noticeable and the possibility of high to very high values cannot be ruled out.

The Stations 3 & 4 in the intermediate salinities and Stations 1 & 2 in the lower estuary exhibit two different trends: one of increasing amounts in the dissolved fractions and the other of decreasing contents in the particulate fractions. The decrease of the particulate fractions may be either due to the dilution of the metal-rich limnic particles with metal depleted oceanic particles or to the desorption of Pb from the particulate phase in the presence of water with higher ionic strength. The non-conservative behaviour of PEM and PTM discussed later negates the possibility of particle dilution. On the contrary the dissolved fractions were observed to increase towards the saline region. Analogous to this increase, the labile Pb has been reported to magnify quantitatively towards the seaward side in the Gironde estuary (Elbaz-Poulachet et al., 1984). This feature may be attributed to factors like desorption from the particulate phase, remobilization from sediments, eolian inputs as industrial Pb, shipping activities and dredging operations. It is certain that all or some of these factors will be operative in the Cochin estuary too. Surveys performed in the Brazos river estuary is a pioneer of lead cycling between dissolved and particulates (Keeney - Kennicutt and Presley, 1986). It has been observed as well as experimentally proven in the laboratory that increase in the dissolved phase, has been accounted more by the remobilization from the sedimentary phase, than the dissolution of the metal from the particulate phase. This gives rise to the situation of low riverine values and high estuarine values which has been true in the Cochin estuary too. Another causitive factor for the high dissolved Pb in the estuarine Stations is the dredging activities in the harbour area. Amongst many heavy metals Pb in its labile form has been shown to be released into the water column during dredging operations (De Groot et al., 1976; Luther et al., 1986). Within the
dissolved fractions the relative enhancement occurs to the OBM fraction of Pb in the lower estuary. The occurrence of this feature is more associated to extensive motorised watercraft plying in this region giving rise to introduction of TAL compounds.

On focussing attention on the seasonal behaviour of Pb fractions, the CLM fraction which indicated a mid estuarine minimum during monsoon specified a condition of higher riverine inputs associated with higher river discharge but on mixing with seawater in the estuarine region nearer to the seaward side, rapid desorption from other phases do occur to cause the increase in CLM lead. The lower values occur in a region where particulate precipitation is maximum (low salinity region) bringing down the concentration of CLM—Pb. The seasonal variations (Fig. 5.2 a.) also indicate a progressive increase of the OBM fraction in each of the seasons, in the down estuary. Relatively the enhancement occurs mostly during postmonsoon followed by monsoon and the least in premonsoon for which the causitive factors have already been discussed. The trends with regard to two other fractions within the particulate is surmised, for premonsoon as due to low river discharges (alternatively this affects the dilution of effluents discharged) coupled with settling of coarser particles (containing depleted amounts of metals) leaving the finer texture in suspension. The differential settling of particles have accounted for the higher values of particulate metals in the studies conducted in the Rhine estuary (Duinker, 1983).

ii. Estuarine Metal Reactivity

In the Cochin estuary, the CLM fraction was found to increase towards the estuarine region (Stations 6 to 1). This may be attributed, among various factors, to the salinity induced desorption from particulates and sediments. The salinity—CLM plots for premonsoon and postmonsoon are given in Figs. 5.3 a & b. No presentable features are available for dissolved fractions (CLM and OBM) versus salinity in monsoon.
Fig. 5.3 Salinity - CLM plots
a) premonsoon b) postmonsoon
In both premonsoon and postmonsoon the CLM increases sharply up to salinity 5%. and then maintains a steady state with increasing salinities. The distribution of CLM as well as OBM with respect to salinity changes in the Cochin estuary is significantly different from those reported elsewhere (Duinker, 1983 in the Rhine estuary and Windom et al., 1988 in the Bang Pakong estuary). The enrichment of dissolved Pb in the low salinity region is a major finding in the estuarine behaviour of element lead in Cochin estuary.

The major source of organic lead in the aquatic environment has been identified as the atmospheric fallout (Windom et al., 1985). They also postulated that the fluvial contribution to the total lead concentrations are insignificant compared to atmospheric inputs. In Cochin estuary too, atmospheric fallout may be in reasonable amounts due to the proximity of metropolis of Cochin and the extensive water traffic in the adjoining backwaters. This additional source may be a reason for a negative mass balance of Pb in this estuary. The attempt to understand the behaviour of Pb-OBM with respect to salinity changes (Figs. 5.4 a & b) seasonally reveals two distinct behavioural patterns. In the first case, during premonsoon the organic lead is enriched in the low salinity (5%) region followed by its depletion up to salinity 12%. In salinities > 12%, a well marked increase was observed in the distribution of OBM. In the second case during postmonsoon, initially the Pb-OBM fraction gets enriched up to salinity 6% and thereafter gradually levels off to a constant value in higher salinities. The characteristics emerging from these two figures are concomitant with those of the Pb-CLM fraction except for the decrease of OBM in the low / intermediate salinities of the Cochin estuary during premonsoon. With available data on the organically bound Pb at the above specified salinities, it has not been possible to categorise the perturbations quoted above. Similar analysis on the behaviour of organically bound metals with respect to salinity changes in the Cochin estuary does not however give rise to a similar situation. A closer inspection may reveal sharp discontinuities in the association of Pb with organic matter or a major influencing factor on organo-lead
Fig. 5.4 Salinity - OBM plots
a) premonsoon b) postmonsoon
compound by the ionic behaviour of seawater. On an average, 51% of the total Pb (CLM + OBM + PTM in μg l⁻¹) is in the organic form (OBM). Higher quantities of non-labile Pb have been reported from elsewhere, 12 to 58% (Luther et al., 1986); 16 to 45% (Nilsen and Lund, 1982) and 45 to 70% (Batley and Florence, 1976 a & b.)

As reported by Chau and Wong (1980), methylation mechanisms can play an important role in the transport of Pb from sediment to the aqueous layer. This fraction of Pb shows another significant positive correlation with DOC (r = 0.39 p < 0.001). The co-variance of organic lead with DOC (Figs. 5.5 a, b & c for premonsoon, monsoon and postmonsoon) suggests a natural relationship between the two and indicates that Pb is transported primarily in chemical association (complexed or adsorbed) with dissolved organic substances or as Pb concentrates in highly weathered organic rich drainage basins. A peculiarity of organic Pb in the environment compared to other metals is that Pb is predominantly added in the organic form, while other metals are usually added in the labile form and later get organically associated in the environment. It is also reported that "organic-rich" rivers contain the highest Pb concentrations (Windom et al., 1985).

From Figs. 5.1 and 5.2a it was noted that both the particulate fractions decreased towards the saline region. The non-conservative behaviour of PEM and PTM for premonsoon and postmonsoon is shown in Figs. 5.6 a & b and 5.7 a & b. In monsoon no such trend could be observed. During premonsoon and postmonsoon these fractions undergo a sharp removal in the very low salinity region (salinity < 5%). This is due to the turbulence aided coagulation processes followed by desorption caused by seawater with high ionic strength. The process of coagulation has been shown to occur at salinities even as low as 0.3% in the Delaware Bay (Gibbs et al., 1983) and the Gironde estuary (Gibbs et al., 1985). Duinker (1983) also has suggested that in most of the estuaries, the fine grained river-borne material would be flocculated in the early stages of mixing. In the Elbe estuary also the Pb content of
Fig. 5.5 DOC - OBM trend plots
a) premonsoon b) monsoon c) postmonsoon
Fig. 5.6 Salinity - PEM plots
a) premonsoon b) postmonsoon
Fig. 5.7 Salinity - PTM plots
a) premonsoon  b) postmonsoon
suspended particulate matter decreased considerably in the saline region during periods of low river discharge (Vollmer et al., 1990) and the feature was attributed to the high sedimentation rate of SPM combined with dilution by material transported upstream. The PEM fraction shows a significant positive correlation with POC (r = 0.41, P < 0.01). Hence it may be inferred that a part of the decrease of PEM can be the result of a decrease in POC content. The PEM and PTM are also found vary inversely with suspended solids (Figs. 5.8 a & b and 5.9 a & b). The regression analysis shows r = -0.54 & r = -0.46 for PEM and PTM versus suspended solid load respectively.

IV. Transport and Species Transformations

The available reports on the transport of Pb shows that it is mainly associated with the particulate phases, ~ 45% in the fresh water region & ~ 69% in the estuarine region of the Yarra river system, (Hart and Davies, 1981); ~ 47% in the Susquehanna river, (Mc Duffie et al., 1976); ~ 72% in the Rhine estuary, (de Groot et al., 1976) and ~ 50% in the Mandovi and Zuari estuaries, (George, 1989). Contradictory to the above observations, in the Cochin estuary, Pb is found to be transported mainly in the dissolved form (~ 75%), whereas the particulate-phase transport is only ~ 25% of which 8% is in the exchangeable form (Table 5.1). During premonsoon and postmonsoon ~ 23% is transported in the particulate phase and ~ 77% in the dissolved phase. The monsoonal transport is characterised by a slightly increased particulate association (~ 28%). The organic phase transport varied between ~ 48% during postmonsoon and ~ 55% during premonsoon. The transport in the labile form varied between ~ 20% in monsoon and ~ 29% during postmonsoon.
Fig. 5.8 Suspended solids - PEM plots
(a) premonsoon  b) postmonsoon
Fig. 5.9 Suspended solids - PTM plots
a) premonsoon b) postmonsoon
Table 5.1

<table>
<thead>
<tr>
<th>Season</th>
<th>CLM %</th>
<th>OBM %</th>
<th>PEM %</th>
<th>PTM %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Premonsoon</td>
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<td>54.73</td>
<td>07.66</td>
<td>22.54</td>
</tr>
<tr>
<td>Monsoon</td>
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<td>52.41</td>
<td>10.02</td>
<td>28.00</td>
</tr>
<tr>
<td>Postmonsoon</td>
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<td>48.39</td>
<td>05.85</td>
<td>22.96</td>
</tr>
<tr>
<td>Annual Average</td>
<td>23.66</td>
<td>51.84</td>
<td>07.84</td>
<td>24.50</td>
</tr>
</tbody>
</table>

The species transformations taking place during estuarine transport are shown in Fig. 5.10. During premonsoon the PEM decreases from 11.81% in the upper estuary (UE) to 2.45% in the lower estuary (LE). In monsoon it decreases from 16.04% to 1.85% and in postmonsoon from 9.42% to 1.39%. During premonsoon PTM showed a sharp decrease from 31.82% in the UE to 18.57% in the middle estuary (ME) and then gradually decreases to 15.88% in the LE. In monsoon the decrease of PTM is considerable from 40.61% in the UE to 6.16% in the LE. In postmonsoon the decrease is from 39.2% in the UE to 4.7% in the LE.

The CLM fraction marginally increases during premonsoon from 21.62% in the UE to 23.01% in the LE. In monsoon a sharp decrease was observed from 23.58% in the UE to 12.71% in the ME and then it increased to 21.35% in the LE. The postmonsoon showed a marginal decrease from 27.84% in the UE to 25.31% in the LE with a maximum in the ME (30.31%). During premonsoon the OBM fraction showed a sharp increase from 46.5% in the UE to 58.04% in the ME and then gradually increased to 61.11% in the LE. The monsoonal variation showed a sharp increase from 35.81% in the UE to 67.28% in the ME and then gradually increased to 72.49% in the LE. In postmonsoon the increase was steady from 32.96% in the UE to 70% in the LE.

The net result of species transformations of lead during estuarine mixing is given below:

The net result is a gain in the OBM content during all the seasons and a marginal gain for CLM during premonsoon. All the
Fig. 5.10 Seasonal Species transformations during estuarine transport
LE-lower estuary ME-middle estuary UE-upper estuary
other fractions experienced a net loss. In monsoon the mid­
estuarine minimum associated with CLM fraction is
proportionally reflected in the enhanced OBM levels.

V. Mass Balance

Given,

\[
\begin{align*}
C_R &= 6.92 \, \mu g \, l^{-1} \\
C_B &= 18.78 \, \mu g \, l^{-1} \\
C_E &= 13.59 \, \mu g \, l^{-1} \\
Q_R &= 5.192 \times 10^{12} \, l \, \text{Yr}^{-1} \\
Q_B &= 1.780 \times 10^{12} \, l \, \text{Yr}^{-1} \\
Q_E &= 6.970 \times 10^{12} \, l \, \text{Yr}^{-1}
\end{align*}
\]

Flux in from the river

\[
= Q_R \times C_R \\
= 35.93 \times 10^{3} \, Kg \, \text{Yr}^{-1}
\]

Flux in from the barmouth

\[
= Q_B \times C_B \\
= 33.43 \times 10^{3} \, Kg \, \text{Yr}^{-1}
\]

Total Pb flux into the estuary

\[
= (35.93 + 33.43) \times 10^{3} \, Kg \, \text{Yr}^{-1} \\
= 69.36 \times 10^{3} \, Kg \, \text{Yr}^{-1}
\]

Flux out from the estuary

\[
= Q_E \times C_E \\
= 94.72 \times 10^{3} \, Kg \, \text{Yr}^{-1}
\]

Mass balance of lead:

\[
\text{flux in - flux out} = (69.36 - 94.72) \times 10^{3} \, Kg \, \text{Yr}^{-1} \\
= -25.36 \times 10^{3} \, Kg \, \text{Yr}^{-1}
\]

The mass balance of lead in this estuary shows an excess of
25.36 \times 10^{3} \, Kg \, \text{Yr}^{-1}. It has been reported that fluvial
contributions to the total lead are insignificant compared to
atmospheric fallout in the estuaries of southern United States
(Windom et al., 1985). In the Cochin estuary the fluvial
contribution of Periyar river is 35.93 \times 10^{3} \, Kg \, \text{Yr}^{-1} and the
excess lead is 25.35 \times 10^{3} \, Kg \, \text{Yr}^{-1}. This shows that an amount
equal to about 70% of the fluvial lead is added from some other
sources. A significant increase in the total lead
concentrations was reported in the Yarra river system when
river water enters estuarine water (Hart and Davies, 1981). Evans and Cutshall (1973) attributed this sort of increase to a possible leaching from the sediments that occur at higher salinities. The mass balance calculations of Klinkhammer and Bender (1981) for the Hudson river estuary and that by Fanger et al., (1990) for the Hamburg harbour area however showed a higher input flux of lead than the output flux. The remobilization from the sediments along with atmospheric fallout, sewage effluent, shipping and dredging activities may be some of the reasons for the observed excess lead output from this estuary.