Trace metal partitioning in a shallow estuary, Muthupet, India

Priya K L¹ and Haddout S²
¹ Assistant Professor, Department of Civil Engineering, TKM College of Engineering, Kollam, Kerala, India
² Department of Physics, Faculty of Science, Ibn Tofail University, B.P. 133 Kenitra, Morocco.

Email: klpriyaram@gmail.com; haddout.ens@gmail.com

Abstract. Dissolved trace metal concentrations of Fe, Cd, Cu and Zn were analysed in the Muthupet estuary, a well-mixed micro-tidal estuary in India during the post-monsoon and pre-monsoon in 2014. There was a significant variation in the salinity and suspended sediment concentration over the seasonal scale with peak salinity occurring at the downstream mouth during the post-monsoon and at intermediate locations during the pre-monsoon. Strong seasonal variations were observed in the concentration of trace metals. The concentration of Fe, Cd and Zn exceeded the USEPA standards, while that of Cu was within the permissible limits. Fe, Cu and Zn showed non-conservative behavior with peak concentrations at mid-estuarine reaches, irrespective of the location of salinity maxima, while the peak concentration of Cd occurred at high salinity reaches. The complexation of Cd as chlorocomplexes enhanced the mobilization of Cd, resulting in a peak value at high salinity reaches. The study indicated that the estuary is influenced by oceanic water and the anthropogenic input is secondary. Resuspension of bed sediments is identified as the major process controlling the trace metal concentration. Partition coefficient (Kd) of Fe, Cu and Zn was observed to be an increasing function of salinity, of which, the effect on Fe was much significant. The coagulation of suspended sediments at high salinity reaches enhanced the removal of Fe as Fe oxyhydroxides.

Keywords: Trace metals; partition coefficient; salinity; suspended sediment concentration; resuspension; Muthupet, India.

1. Introduction

Sediments are one of the ultimate sinks for the trace metals in a marine environment [1]. The trace metals may not be fixed permanently by the sediments, but may get released to the water column due to the dynamics of estuarine processes happening over a spatial and temporal scale [2]. In an aquatic environment, the transport of trace metals depends on the physio-chemical and biological processes [3]. The metals may exist in dissolved form or suspended form. The change of phase of the trace metal is affected by the physio-chemical characteristics of the estuary. A universal behaviour of trace metals cannot be arrived at because of the characteristic differences of estuaries [4, 5]. A common feature of many estuaries is the formation of turbidity maximum zone, where the concentration of suspended sediments is higher than the upstream and downstream locations [6, 7, 8]. There is a general consensus that the trace metal concentration is greatly affected by this turbidity zone, where the processes are...
different from the other parts of the estuary. The estuarine turbidity maximum (ETM) may have an effect on the flushing of the trace metals from the estuary. Even very small variations in the concentration of trace metals may affect the ecosystem, as they are toxic even at trace concentrations [9].

Earlier studies highlighted the role of pH, salinity, temperature, and composition of suspended sediments on the trace metal speciation [10]. The partitioning coefficient ($K_d$) is generally used to describe the partitioning of metals from adsorbed to dissolved phase and vice versa. It explains the equilibrium and reversibility of the solid-solution reaction. However, in many studies, $K_d$ is used descriptively without implicating to the state of the reactions [11, 10].

The studies on trace metal concentration of Indian estuaries are limited. Muthupet estuary, located in the south-east coast of India, is a part of the Point Calimere Ramsar site. The trace metal distributions of the estuary have been studied rarely [12, 13, 14, 15]. In the earlier studies, the trace metal concentrations of the bed sediments and the variation of trace metals with salinity and suspended sediment concentration (SSC) have been reported [15]. It was observed that Fe, Cd, Cu and Zn behaved non-conservatively within the estuary. The cause of this behavior is due to the variation in water chemistry over a temporal scale. This can be well explained by studying the partitioning of trace metals between solid and liquid phase. In the previous study, the total metal concentration in solid and liquid phase were considered, which do not give the exact picture of the partitioning of the metal between the two phases. Thus, in the present study, the behavior of metals in the dissolved form has been analysed and the influence of salinity and suspended sediment concentration (SSC) on the partitioning from solid phase to liquid phase has been investigated.

2. Materials and Methods

2.1 Study area
The Point Calimere is a wetland of international importance and is declared as a Ramsar site in August 2002. It is located in the delta of Cauvery river which has a drainage area of 87900 sqkm. The river discharges into the Bay of Bengal. Muthupet estuary forms one of the tributaries of Cauvery river and falls under Point Calimere Ramsar site. The estuary is bordered by mangrove forest, *Avicennia marina* being the dominant species. The estuary is shallow having an average depth of 1m. Fig. 1 shows the location of the study area.

The major tributaries of Cauvery that drains its water into the estuary are Korayar and Paminiyar rivers. Even though other minor tributaries join the estuary, the freshwater input from these is negligible. The freshwater flow into the estuary is seasonal with negligible discharge during the pre-monsoon season. Hence, there is a wide variation in the salinity values in the estuary. Salinity varies between 1 g/L and 40 g/L during a seasonal cycle. During the dry season, salinity value greater than that of sea has been observed in the estuary [16]. Formation of salt plug is a peculiar feature of this estuary. The salt plug controls the transport of salt within the estuary [17]. The bed of the estuary is predominantly clay at the downstream reaches, while silt is dominated at the upstream river side. The estuarine turbidity maximum zone has been identified in the estuary at approximately 5 km upstream of the mouth [16] and hindered settling was observed at this zone [18].
2.2 Sample collection and analysis
Samples were collected from seven sampling stations (Fig. 1) during the post-monsoon (10 January 2014) and the pre-monsoon (21 April 2014) at a depth of 0.3H (H being the water depth) above the bed of the estuary. The results of total metal concentration of the near surface samples during the post-monsoon and pre-monsoon in 2012 were already discussed [15]. The river flow at the time of sample collection was 60 m$^3$/s during the post-monsoon and there was no flow during the pre-monsoon. At each station, a depth sampler was used to collect the water samples from a depth of 0.3H above the bed of the estuary. Samples were collected in polyethylene bottles, which were pre-cleaned with deionized water. The bottles were closed and transferred to the laboratory and analysed within 24 hours. Salinity was determined in the field using a water quality analyser (Systronics Water Analyser 371, Ahmedabad) after calibrating the sensors using standard solutions. SSC was determined using gravimetric method wherein aliquots of 1000 mL water were filtered through 0.45 µm Millipore filter paper (Merck Specialities Pvt Ltd, Mumbai). In order to remove the salt content, the filters were washed using deionised water and then dried in an oven for 1.5 hours at 65$^\circ$C. The dried filters were

![Figure 1 Location map showing sampling stations](image-url)
kept in a desiccator for half an hour to bring them to room temperature and then weighed. The total concentration of trace metals were determined by atomic absorption spectroscopy. For this, the water samples were acidified using 1-2 mL L⁻¹ concentrated nitric acid and then filtered through 0.45 µm cellulose acetate filters which were cleaned with concentrated nitric acid and rinsed with deionised water. The filtered samples were anaysed for trace metals such as Fe, Cd, Cu and Zn using atomic absorption spectrometer (AAS) (240AA, Agilent Technologies, Bangalore). Initially, the AAS was calibrated by different concentrations of standard solutions of all metals. Three replicates of each sample were carried out for each metal. For the determination of dissolved trace metals, aliquots of 1000 mL samples were filtered through 0.45 µm cellulose acetate filters. The filters were cleaned using concentrated nitric acid and rinsed with deionised water prior to filtration. Further, the samples were acidified with concentrated nitric acid and were subjected to analysis using AAS. The concentration of trace metals in the adsorbed form was calculated from the difference of total concentration and dissolved concentration. The partition coefficient was then calculated as the ratio of adsorbed concentration to dissolved concentration.

3. Results and Discussion

3.1 Seasonal and longitudinal variations of salinity, SSC

Statistical summary of salinity and SSC are given in table 1. Salinity varied widely during the post-monsoon and the pre-monsoon with a peak concentration of 28.5 g/l during the post-monsoon and 32.2 g/l during the pre-monsoon. The salinity value was as high as 17.5 g/l at the river inlet during the pre-monsoon while it was 0.75 g/l during the post-monsoon. A seaward increase in salinity was noted during the post-monsoon while the peak salinity occurred at a distance of 5 km upstream of the mouth during the pre-monsoon (Fig. 2). The formation of a salinity maximum zone in the Muthupet estuary is well documented [16]. The low salinity zone (0 – 5 g/l of salinity) was absent during the pre-monsoon while it was clearly visible during the post-monsoon.

Suspended sediment concentration ranged between 0.04 and 0.63 g/l during the post-monsoon and between 0.05 and 0.78 g/l during the pre-monsoon. Peak SSC was observed at intermediate distances from the mouth of the estuary (Fig. 2). A zone of turbidity maxima occurs in the Muthupet estuary and is reported [16]. The SSC were marginally higher during the pre-monsoon compared to the post-monsoon.

Table 1 Summary of analysis of salinity, SSC and trace metals in the Muthupet estuary

|                  | Salinity (g/l) | SSC (g/l) | pH   | Fe (mg/l) | Cd (mg/l) | Cu (mg/l) | Zn (mg/l) | Zn/Cd |
|------------------|----------------|-----------|------|-----------|-----------|-----------|-----------|-------|
| **Post monsoon** |                |           |      |           |           |           |           |       |
| Min              | 0.75           | 0.039     | 7.39 | 0.16      | 0.002     | 0.015     | 0.3862    | 10    |
| Max              | 28.5           | 0.63      | 8.29 | 2.04      | 0.047     | 0.129     | 1.945     | 277   |
| Average          | 16.15          | 0.28      | 7.77 | 0.84      | 0.02      | 0.08      | 0.71      | 94    |
| STD Dev          | 9.24           | 0.21      | 0.37 | 0.70      | 0.02      | 0.04      | 0.55      | 104   |
| **Pre monsoon**  |                |           |      |           |           |           |           |       |
| Min              | 17.5           | 0.05      | 7.39 | 0.488     | 0.008     | 0.007     | 0.1183    | 1     |
| Max              | 32.2           | 0.78      | 8.42 | 1.492     | 0.136     | 0.015     | 0.407     | 21    |
| Average          | 27.57          | 0.37      | 7.90 | 1.05      | 0.08      | 0.01      | 0.20      | 6     |
| STD Dev          | 4.91           | 0.19      | 0.42 | 0.40      | 0.05      | 0.00      | 0.11      | 7     |
| USEPA stdb       |                |           |      |           |           |           |           |       |
|                  | 6.5-8.5        | 0.2       | 0.005| 1.0       | 5.0       |           |           |       |

b USEPA (2017)
3.2 Seasonal and longitudinal variations of dissolved trace metal concentration

Table 1 shows the statistical summary of dissolved trace metal concentration during the post-monsoon and the pre-monsoon. Seasonal variability of trace metals was significant during the study period (P≤0.05; table 2). The variations of trace metal concentration over a spatial scale during the post-monsoon and the pre-monsoon are presented in Fig. 3a - 3d. The concentration of Fe was high in all the samples with a peak concentration of 2.04 mg/l during the post-monsoon and 1.492 mg/l during the pre-monsoon. However, on an average, the concentration of Fe was higher during the pre-monsoon (1.05 mg/l) than that during the post-monsoon (0.84 mg/l). The maximum concentration of Fe exceeded the permissible limits as per USEPA standards. The concentration of Cd ranged between 0.002 and 0.047 mg/l during the post-monsoon and between 0.008 and 0.136 mg/l during the pre-monsoon (Table 1) and the seasonal variation was significant (P≤0.05; Table 2). Cd was higher than the permissible limits of USEPA standards. The concentration of Cd was observed to be higher near the mouth during the post-monsoon (Fig 3.). Nevertheless, a peak concentration of Cd at mid-estuary was observed during the pre-monsoon. Mid-estuary maximum of Cd has been reported elsewhere [19, 20, 10].

The concentration of Cu varied from 0.015 to 0.129 mg/l during the post-monsoon while the concentration was low during the pre-monsoon ranging between 0.007 and 0.015 mg/l. The post-monsoon concentration of Cu was higher than the pre-monsoon concentration. However, the values were within the permissible limits as per USEPA. Similar is the case of Zn with a higher post-monsoon concentration than the pre-monsoon concentration recording a peak concentration of 1.945 and 0.407 mg/l during the post-monsoon and the pre-monsoon respectively (Table 1). The seasonal variations of Cu (P≤0.005) and Zn (P≤0.05) were significant (Table 2). The location of peak concentration of Cu and Zn was at the mid-estuary and was similar to that of Fe and Cd (Fig. 3). Maximum concentration of Cu and Zn at the mid-estuary has been reported in other estuaries [21, 22, 10, 23]. The concentration of all the trace metals was lower near the mouth and head of the estuary.
Figure 3 Longitudinal variation of trace metals during the study period

3.3 Metal salinity plots
The general appearance of metal-salinity plots was similar for all the trace metals for the post-monsoon and the pre-monsoon. During the post-monsoon, Fe, Cu and Zn showed a peak value at intermediate salinity, which is located at mid-estuary. Nevertheless, peak concentration of Cd was located at highest salinity reaches. On the contrary, during the pre-monsoon, salinity maximum zone, occurred at mid-estuary, where the salinity was higher than that at the mouth and the peak concentration of trace metals occurred at this maximum salinity reaches. Thus, the peak concentration of trace metals was always at mid-estuary irrespective of the location of salinity maximum zone. During the pre-monsoon, as the salinity was maximum at the mid-estuary, the metal salinity plot was an increasing function of salinity. Thus, the geographical location of peak concentration of trace metals is the same for all the metals, while the peak salinity is different. Hence during the pre-monsoon, the concentration of trace metals was an increasing function of salinity, while during the post-monsoon, the concentration of trace metals increased to a peak and further decreased. Seasonal variations of trace metal concentration were observed in other estuaries as well [24, 25, 21].

The peak concentration of Cd at high salinity reaches shows the input from particulate phase which is caused due to complexation by chlorides. This phenomenon has been reported elsewhere [26]. The mobilization of Cd is enhanced by the chlorocomplexes formed at high salinity levels in estuaries. Thus, the peak concentration of Cd was at the high salinity reaches, irrespective of the geographical position of the estuary. This may lead to the bioavailability of Cd to aquatic life as they are introduced into the water column. Nevertheless, Fe, Cu and Zn showed peak concentrations at the turbidity maxima and occurred at the same geographical location during both the seasons.
3.4 Metal SSC plots

The general appearance of metal-SSC plots during the post-monsoon was repeated during the pre-monsoon (Fig 5). The concentration of trace metals was an increasing function of SSC. The variation of all the trace metals with SSC was much appreciable during the post-monsoon. During the pre-monsoon, Fe and Cd increased with increase in SSC, while the increase in Cu and Zn with SSC was marginal. As the concentration of Cu and Zn was comparatively less during the pre-monsoon, this variation was not felt. The peak concentration of all the trace metals was observed at the turbidity maximum zone, which caused a positive variation of trace metals with SSC; higher the SSC, higher the trace metal concentration. This implies that the resuspension of the bed sediments may have contributed to the trace metals in the water column [15]. Peak concentration of trace metals at the turbidity maximum zone has been reported for other estuaries [22, 23, 10, 19].

A strong positive correlation was observed between Fe, Cd and Cu with SSC during the post-monsoon and the pre-monsoon. These positive correlations show the influence of resuspension of bed sediments on the trace metal concentrations. Zn was positively correlated with SSC during the post-monsoon while there correlation was not significant (P≤0.05) during the pre-monsoon. This may have caused due to the complexation of Zn by chloride causing the desorption of the metal from resuspended sediments during the post-monsoon. The salinity was at its peak during the pre-monsoon and the high salinity levels may have caused the adsorption of Zn on the SSC resulting in less concentration in the water column.
Figure 5 Variation of trace metals with suspended sediment concentration

Table 2. Summary of two factor analysis of variance of trace metals

| Source of variation | d.f | Fe  | Cd  | Cu  | Zn  |
|---------------------|-----|-----|-----|-----|-----|
| Seasons             |     | MS  | F   | P   | MS  | F   | P   | MS  | F   | P   |
| Seasons             | 1   | 167.51 | 6.52 | *   | 0.01 | 10.38 | *   | 0.01 | 12.79 | **  | 0.94 | 6.01 | *   |
| Stations            | 6   | 26.94 | 0.6  | ns  | 0.001 | 0.43  | ns  | 0.001 | 0.55  | ns   | 0.14 | 0.51 | ns  |

Note: d.f: degree of freedom; MS: mean squares; F: F-ratio Test; * indicates significance at P ≤ 0.05; ** indicates significance at P ≤ 0.005; ns indicates not significant

Table 3 Correlation matrix for salinity, SSC and dissolved metal concentration

|                  | Salinity | SSC  | Fe   | Cd   | Cu   | Zn   |
|------------------|----------|------|------|------|------|------|
| **Post monsoon** |          |      |      |      |      |      |
| Salinity         | 1.00     |      |      |      |      |      |
| SSC              | **0.73** | 1.00 |      |      |      |      |
| Fe               | **0.60** | **0.77** | 1.00 |      |      |      |
| Cd               | **0.93** | **0.66** | 0.51 | 1.00 |      |      |
| Cu               | **0.94** | **0.91** | **0.78** | **0.86** | 1.00 |      |
| Zn               | 0.35     | 0.81 | 0.45 | 0.39 | 0.58 | 1.00 |
| **Pre monsoon**  |          |      |      |      |      |      |
| Salinity         | 1.00     |      |      |      |      |      |
| SSC              | **0.74** | 1.00 |      |      |      |      |
| Fe               | **0.80** | **0.89** | 1.00 |      |      |      |
| Cd               | **0.85** | **0.87** | **0.91** | 1.00 |      |      |
| Cu               | **0.91** | **0.86** | **0.97** | **0.93** | 1.00 |      |
| Zn               | 0.54     | -0.01 | 0.23 | 0.41 | 0.34 | 1.00 |

Note: Bold values are significant (p≤0.05)

The ratio of Zn to Cd is often considered as an indicator of anthropogenic pollution in estuarine and coastal waters [27, 28]. The Zn: Cd ratio ranged between 10 and 277 during the post-monsoon (Table 1). Nevertheless, the range was between 1 and 21 during the pre-monsoon. The elemental Zn:Cd ratio ranges between 5 and 10 for oceanic waters [28] and between 600 and 900 for continental rocks. Thus
it is evident that the influence of oceanic water is more in the Muthupet estuary, especially during the pre-monsoon. This is because the river flow is absent during the pre-monsoon. On the other hand the Zn:Cd ratio occurs between the intervals of continental rocks and oceanic waters, closer to oceanic range during the post-monsoon, which highlights that anthropogenic input of Zn into the estuary is secondary. Hence it can be concluded that major process controlling the concentration of Zn in the estuarine water is resuspension of bed sediments.

3.5 Partition coefficient
Partition coefficient or distribution coefficient (Kd) gives information on the effect of reactions taking place between dissolved and adsorbed phases of an element. A higher Kd implies that the element has a higher affinity to get transported in the solid phase. Thus, the knowledge of Kd is significant in impact assessment studies [29]. Fig. 6 shows the variation of Kd with salinity during the post-monsoon and the pre-monsoon for all the metals. The Kd values of Fe were increasing with salinity during both the seasons; a higher Kd value occurred during the pre-monsoon than during the post-monsoon. This shows that Fe is associated with the solid phase ie with suspended sediments during the pre-monsoon. Thus, the behavior of suspended sediments determines the behavior of Fe during pre-monsoon. Earlier studies have reported that the suspended sediments are transported in the upstream river side during pre-monsoon, [17] hence is the case of Fe, thereby inferring that Fe is retained within the estuary. The seasonal variation in the Kd values of Fe is marginal.

There is a general consensus that Kd values has minimal effect due to salinity at regions of salinity greater than 20 [30]. This appears to hold good for Cd, Cu and Zn (Fig. 6). An increase in Kd values has been observed with salinity at a salinity range of 0-20 for Fe, Cu and Zn. Nevertheless, the Kd of Cd was a decreasing function of salinity. Similar observations were made in Port Jackson estuary [10]. Kd values of Zn did not show any influence with salinity.

The Kd of Fe showed a significant dependence on salinity wherein salinity was a direct function of Kd. The formation of Fe(III) hydroxides from Fe(II) through oxidation causes the precipitation of Fe. At higher salinity reaches, the suspended sediments are coagulated and are removed from the water column. The formation of flocs of suspended sediments leads to higher removal rate of oxyhydroxides from the water column. This can be the explained as the reason for higher Kd values with increased salinity in the estuary.

The partitioning of Cd was observed to be dependent on salinity on a marginal scale. A more dependency of Kd on salinity was observed during the post-monsoon than during the pre-monsoon. These seasonal variations in the partitioning of Cd were not much significant. At higher salinity reaches, Cd is complexed by chlorides. These chlorocomplexes are desorbed from the bed sediments and are incorporated into the water column. This leads to the partitioning of Cd from adsorbed phase to dissolved phase thereby showing a reduction in Kd values with increase in salinity. This is clearly depicted in the plot of Kd of Cd vs salinity (Fig 6) where an increase in dissolved Cd with salinity was observed. Mobilization of Cd into the water column at higher salinity reaches have been reported by [10, 31, 15].

The general tendency of Kd was to increase with SSC, a higher dependency being observed for Fe and Cd during the pre-monsoon (Fig. 7). The variation of Kd with Cu and Zn was not much significant. The trend of Kd of Cu during the post-monsoon was to initially increase and then to decrease with SSC. Some of the earlier studies have reported the decline of Kd with an increase in SSC [10, 32]. The Kd was observed to be an increasing function of pH for all the trace metals in the order Cu, Fe, Zn while a decrease in Kd values of Cd with pH was evident. At higher pH, desorption and dissolution of Cd from bed sediments has been reported [31]. This has been due to the enhancement in the formation of chloro complexes of Cd at alkaline ranges.
4. Conclusions
Seasonal variations in the trace metal concentration were observed during the study. The peak values of metal concentration of Fe, Cu and Zn occurred at mid-estuary irrespective of the salinity values, but the behavior of Cd was different from other metals. The complexation of Cd by chlorides have enhanced desorption of Cd from the bed sediments, thereby releasing into the water column at high salinity reaches. Thus, the bioavailability of Cd was higher at high salinity reaches. The geographical location of peak salinity and peak metal concentration did not coincide for all the metals, but the location of turbidity maxima and peak metal concentration was identified to be the same. Thus, the major controlling process of trace metal concentration in the Muthupet estuary is resuspension of bed sediments. The analysis of partition coefficient revealed that salinity plays a major role in the partitioning of metals between aqueous phase and solid phase. The dependency of partition coefficient
of Fe, Cu and Zn with salinity was direct while it was inverse in the case of Cd. Thus, the behavior of Cd is quite different from other metals due to the fact that formation of chlorocomplexes of Cd is the major mobilization factor affecting desorption of Cd from the bed sediments.

Acknowledgement
The project is part of the research project funded by Kerala State Council of Science, Technology & Environment through Best Paper Award Research grant.

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