Partitioning behaviour of heavy metals in Ashtamudi estuary, India

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Abstract. The pH, salinity, SSC and variations of heavy metals were studied for Ashtamudi estuary during the pre-monsoon period of 2019. Both pH and salinity decreased from the mouth of the estuary, while SSC exhibited a higher value within 4 to 10 Kms from the estuarine mouth. Concentrations of Fe, Cr, Cu, Zn and Ni decreased from the mouth towards the head of the estuary. Among which both Fe and Cr showed higher concentrations within 4 to 10 Kms. Variation of the distribution coefficients (K_d) of trace metals with pH, salinity and suspended sediments indicated lower values for Fe, Cr and Zn at the locations 2 and 3. As the dissolved concentrations of Fe and Cr showed higher values at locations with higher SSC, adsorption and desorption studies were performed using sediments at those locations. Adsorption studies on Fe indicated higher adsorption at higher salinity values, while for Cr, the adsorption decreased with salinity. Kinetic adsorption and desorption studies for Fe and Cr indicated that the adsorption rates of Fe and Cr approached equilibrium after 2 hours and 1.5 hours respectively, while the desorption rates did not exhibit an equilibrium within the experiment duration. The results of kinetic sorption and desorption studies conducted for Fe and Cr exhibiting higher rate of adsorption for Fe and lower rate of adsorption for Cr at higher salinities, were in agreement with the higher K_d values of Fe and lower K_d values of Cr obtained from the field analysis.

1. Introduction

Heavy metals are one of the major pollutants present in estuarine environment that can have sources consisting of both natural and anthropogenic origins. When the metals are released to the estuaries, they may tend to get transported [4],[11],[8]. The heavy metals have long lasting detrimental effects on environment and are dangerous for living organisms [2],[13],[14]. The heavy metals may undergo flocculation and get partitioned to adsorbed form and get removed from the water column. Removal of heavy metals are reported to be more during high tide periods and during estuarine mixing [3]. The distribution of heavy metals in their particulate and dissolved form is defined by the partition coefficient or distribution coefficient. Metal partitioning can also be influenced by the aquatic life and fishing activities [5]. It has been reported that the distribution coefficient varies directly with salinity and particle size, and inversely with dissolved organic carbon [6].
Salinity, pH and suspended sediments concentration play a major role in the partitioning of heavy metals in the estuarine environment. Many studies reported that the partitioning rate increases with salinity [11] while others reported higher partitioning at lower salinity reaches [3]. The variation of partition coefficient with pH reported in literatures is highly contradictory. Enhanced partitioning of metals were observed at higher pH [3], [7] while [3] reported that pH do not have any influence on partitioning. The heavy metals in the estuaries combine with the suspended sediments at suitable conditions. A negative correlation was observed between acid soluble heavy metals and SPM [18]. Many investigations have been carried out on the metal concentrations of Ashtamudi estuary till date. Ashtamudi Lake is subjected to severe pollution by domestic sewage, agricultural activity and industrial wastes [9]. The study conducted in the vattakayal of Ashtamudi estuary concluded that the concentration of heavy metals in the Vattakkayal exceeds the WHO maximum standard permissible limits [10]. Even though many studies have been reported on the higher concentrations of heavy metals in the Ashtamudi estuary, the variation of distribution coefficients of these metals have not been considered. Hence the present study aims to determine the distribution coefficients of Fe, Cr, Zn, Cu and Ni in the Ashtamudi estuary and its behavior with respect to salinity, pH and SSC. Adsorption and desorption behavior of selected metals such as Fe and Cr has also been studied.

2. Material and methods

2.1 Study area
Ashtamudi Estuary, ramsar site is located in the southern part of Kerala. The Ashtamudi Estuary is the second largest in Kerala, located between the latitudes of 8°31′–9°02′N and 76°31′–76°41′E respectively. The estuary drains into the Arabian Sea through a 200 m wide mouth that serves as a permanent connection. This is one of the biggest fish-landing centres of the southwest coast in the country. The Ashtamudi estuary has a length of 16 km with an area of 54 km². Figure 1(a) represent the location map of Ashtamudi estuary and figure 1 (b) shows the sampling locations.

3. Methodology

3.1 Field data collection and analysis
The distance of each station from the mouth of the estuary is given in the table 1. Water samples were collected from marked locations (figure 1(b)) from Ashtamudi estuary during the pre-monsoon in March 2019. The collected samples were stored in acid washed polyethylene containers after preserving with 2 mL concentrated nitric acid. Three samples were collected, one
for determining total heavy metal concentration, second one for determining dissolved heavy metal concentration after filtering through whatman filter paper and the third one for determining the water quality parameters, pH and salinity were determined using water quality analyser as quick as possible while SSC using gravimetric methods. The heavy metal concentrations (total concentrations and dissolved concentrations) were determined using Atomic Absorption Spectroscopy (AAS- PerkinElmer- USA) at the Department of Mining and Geology, Thiruvananthapuram). Distribution coefficients (Kd) were calculated from adsorbed and dissolved concentrations of heavy metals.

Table 1. Latitude, longitude and the distance of each station from the estuarine mouth

| Station | Latitude   | Longitude  | Distance from estuary mouth (km) |
|---------|------------|------------|----------------------------------|
| 1       | 8°56’8.43 | 76°32’35.49| 0                                |
| 2       | 8°57’9.3  | 76°33’55.37| 3.08                             |
| 3       | 8°58’9.53 | 76°34’59.51| 5.77                             |
| 4       | 8°59’31.41| 76°35’2.75 | 7.71                             |
| 5       | 9°0’4.37  | 76°35’52.02| 9.44                             |
| 6       | 9°0’5.45  | 76°36’39.84| 10.45                            |
| 7       | 9°0’6.57  | 76°37’16   | 11.28                            |
| 8       | 9°0’18.44 | 76°37’43.15| 12.15                            |

3.2 Adsorption and desorption experiments
Batch experiments: Experiments were conducted in a rotary shaker at 100 rpm for 30 minutes. Experiments were carried out for samples with 20 mg/L of Fe and 20 mg/L of Cr (VI) for various salinity, pH, and 1g/L suspended sediment concentration. Initial and final concentrations of the metals were determined as per APHA standard methods in a UV/Visible spectrophotometer.

Kinetic experiments: Kinetic sorption experiments were done for 20 mg/L of Fe at pH 7 for salinity ranges of 0, 10, 20 and 25 g/L at 1g/L SSC and 20 mg/L Cr at pH 7 for different salinities of 0, 10, 20, 25 g/L at 1 g/L suspended sediment concentration. Kinetic sorption experiments were done for 3 hours for Cr(VI) and 10 hours for Fe to understand the adsorption kinetics of chromium and iron. The desorption tests form etals were done with 1g/L suspended sediments in water, shaked for 6 hours in the rotary shaker at 100 rpm. The suspended sediments then filtered through whatman filter paper were transfered to distilled water and developed to 100 mL volume in a conical flask. These samples were then placed in a rotary shaker for studying the desorption at different salinities of 0, 10, 20 and 25 for Fe and 0, 15 and 30 for Cr. The samples were taken at 10, 20, 30 and 60 minutes to study the desorption kinetics. Since distilled water is free from any ions, the Fe and Cr ions in the suspended sediments get desorbed to the distilled water, from the absorbance of which the concentration of desorbed metal ion can be determined.

4. Results and discussion

4.1 Variations of salinity, pH, SSC, settling velocity and dissolved trace metals
Statistical parameters of salinity, pH, SSC and dissolved trace metals (Fe, Cr, Cu, Zn and Ni) are shown in the table 2. Maximum salinity was observed for location 1, which constitutes the mouth of the estuary, while the minimum was obtained at the head of the estuary, region with no salt intrusion. Higher pH was observed at the mouth of the estuary while the final station was marked with lower pH. A higher SSC of 0.06 g/L was obtained within 4 to 10 Kms and a minimum was obtained at the final location. The possible estuarine turbidity maxima may coincide within the region of 4 to 10 Kms from the estuarine mouth due to the higher SSC at that region. The Fe and Cr (VI) were found to be exceeding the permissible limit according to USEPA standards. The
maximum dissolved concentrations of Fe and Cr also falls within the region of higher SSC.

Table 2. Statistical parameters of salinity, pH, SSC, settling velocity and trace metals in Ashtamudi estuary

|                | Salinity (g/l) | SSC (g/l) | pH  | Fe (mg/l) | Cr (mg/l) | Cu (mg/l) | Zn (mg/l) | Ni (mg/l) |
|----------------|----------------|-----------|-----|-----------|-----------|-----------|-----------|-----------|
| No.of locations | 8              |           |     |           |           |           |           |           |
| Min            | 9.65           | 0.0039    | 6.92| 0.262     | 0.486     | 0.035     | 0.116     | 0.218     |
| Max            | 24.3           | 0.0599    | 7.54| 0.605     | 0.753     | 0.088     | 0.217     | 0.318     |
| Average        | 15.88          | 0.0218    | 7.239| 0.521     | 0.644     | 0.058     | 0.16      | 0.265     |
| STDDev         | 5.77           | 0.0239    | 0.24| 0.115     | 0.112     | 0.018     | 0.033     | 0.029     |
| USEPAstd*      | 6.5-8.5        | 0.1       | 0.1 | 1         | 5         | 0.2       |           |           |

4.2 Spatial variation of trace metals

The total, dissolved and adsorbed concentrations of trace metals (Fe, Cr, Cu, Zn and Ni) are represented in the figure 2. Adsorbed concentrations of Fe and Cr showed lesser values at 2nd and 3rd locations compared to the other locations. Cu showed higher adsorbed concentrations at 3rd and 4th locations and lower adsorbed concentration at the final location. Both Zn and Ni exhibited higher dissolved concentrations at all locations.
4.3 Distribution coefficients of trace metals

The distribution coefficients of Fe, Cr, Zn, Cu and Ni are shown in the figure 3. Higher $K_d$ values were obtained for Fe at higher salinities and Cr exhibited lower $K_d$ values at higher salinities. Cu exhibited a higher $K_d$ value at the 3rd location. Zn showed higher $K_d$ values at lower salinities. But the $K_d$ of Ni decreased towards upstream river.

4.4 Variation of partition coefficient ($K_d$) with pH, salinity and Suspended sediment concentration

4.4.1 Variation of $K_d$ with pH. The variation of the distribution coefficients of trace metals for different pHs are shown in figure 4. The variation of distribution coefficient with pH shows a positive relation for Fe, Cu, Ni and a negative trend for Cr and Zn. Maximum leaching amount for Ni is observed in the lower pH, which can be explained by that the solid surfaces are positively charged and metal sorption is not steady. Release amounts of metals increases as the pH increases, which is due to the release of organometallic complexes. With pH decreasing in water, the competition between H$^+$ and the dissolved metals for ligands (e.g., OH$^-$, Cl$^-$, S$^{2-}$, and phosphates) becomes more and more significant. The adsorption abilities and bio availabilities of the metals subsequently decrease and then increase the mobility of heavy metal.
Moreover, H\(^+\) (or H\(_3\)O\(^+\) ) occupies more adsorption sites at lower pH values, which results in soluble and carbonate-bound heavy metals precipitated more easily at higher pH values. Both of these processes result in faster heavy metal release rate with lower pH. Lower distribution coefficients were observed for both Fe and Cr within 4 to 10 Kms, indicating lower adsorption at these locations.

![Variation of K\(_d\) with pH for heavy metals](image1.png)

**Figure 4.** Variation of K\(_d\) with pH for heavy metals. (a) Fe (b) Cr (c) Ni (d) Cu (e) Zn

### 4.4.2 Variation of K\(_d\) with salinity.

Variation of partition coefficients with salinity are given in the figure 5. Distribution coefficients of Cu, Ni, and Fe shows positive trend with salinity and Cr and Zn shows negative trend. Formation of Fe (III) hydroxides from Fe (II) through oxidation causes the precipitation of Fe. At higher salinity reaches, suspended sediments are coagulated and are removed from water column. The formation of flocs of suspended sediments leads to higher removal rate of oxyhydroxides from water column. This is why K\(_d\) increases with salinity.
4.4.3 Variation of $K_d$ with SSC. The variations of $K_d$ with SSC are represented in the figure 6. Distribution coefficients for Fe, Cr, Cu, Zn, Ni decrease with suspended sediment concentration. Due to complexation by chloride the desorption of the metal occurs from the resuspended sediments and as a result the concentration of heavy metal adsorbed decreases and thus $K_d$ decreases.
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5. Adsorption and desorption of Fe and Cr
On analyzing the concentration of heavy metals in Ashtamudi estuary, the concentration of Fe and Cr exceeded the permissible limit set by USEPA standards. Further studies on the distribution coefficients demonstrated higher adsorption for Fe and lower adsorption for Cr at the location of possibly recognized turbidity maxima. Hence, inorder to understand the adsorption and desorption of Fe and Cr, laboratory experiments were conducted using the sediments collected from locations within 4 to 10 Kms from the estuarine mouth. Figure 7 represents the variation in the adsorption of Fe and Cr with salinity and figure 8 represents the desorption of Fe and Cr with salinity.

Figure 6. Variation of $K_d$ with SSC for Heavy metals (a) Fe (b) Cr (c) Ni (d) Cu (e) Zn.

Figure 7. Variation of the percentage sorption of (a) Fe (b) Cr with salinity
Adsorption of Fe showed an increase with the salinity which is attributed to the presence of more active sites in the metal to get adsorbed with the suspended sediments. Adsorption of Cr showed a considerable decrease with the salinity, which may be due to the floc formation of suspended sediments with the chlorides present in the solution. Desorption patterns of both Fe and Cr were in agreement with the concept of adsorption indicating lesser desorption for Fe and higher desorption for Cr with salinity.

**5.1 Kinetic sorption studies on Fe and Cr.**

Kinetic sorption studies for Fe and Cr are shown in figure 9. Both adsorption kinetics and desorption kinetics are studied for Fe and Cr.

**Figure 8.** Variation of percentage desorption of (a) Fe (b) Cr with salinity

**Figure 9.** a) adsorption kinetics of Fe (b) Adsorption kinetics of Cr (c) Desorption kinetics of Fe (d) Desorption kinetics of Cr
Kinetic adsorption studies represented in figure 8(a), indicated that, the amount of Fe in the solution decreased with time and attained equilibrium after 2 hours, resulting in no further adsorption of Fe. Adsorption of Cr increased with time and showed a slight decrease before attaining equilibrium at 1.5 hours. An equilibrium in adsorption of Fe and Cr occurs due to the non-availability of active sites to cause adsorption of these metals. Fe is observed to be desorbing gradually, indicating its higher adsorption with suspended sediments at higher salinities, as represented by the higher K_d values at higher salinities. Desorption of Cr at 0g/L salinity reached equilibrium within lesser time and started increasing the desorption, while the desorption of Cr at 25g/L salinity decreased with time and was about to approach equilibrium. The results indicate that at higher salinities Cr exhibit higher desorption and at no or lower salinities Cr exhibits lower desorption, which is in agreement with the results of K_d values of Cr at different salinities.

6. Conclusions

Maximum value of salinity and pH were observed at the mouth of the estuary due to the higher salt intrusion at that region. SSC exhibited higher values within 4 to 10 kms from the estuarine mouth. So the region may be possibly recognized as the estuarine turbidity maxima. The total, dissolved and adsorbed concentrations of Fe, Cr, Zn ,Cu and Ni for different locations were determined. Fe and Cr were found to be exceeding the permissible limit set by USEPA. The distribution coefficients of each metals were determined to understand the variation of K_d with salinity, pH and SSC for different locations. Distribution coefficients of Fe, Cu and Ni showed a positive relation with pH and salinity while for Cr and Zn S showed a negative relationship. For all the five heavy metals, K_d decreased with SSC. Fe and Cr showed higher dissolved concentrations at the region of turbidity maxima. Hence adsorption and desorption studies on Fe and Cr were conducted with the sediments collected from within 4 to 10 Kms from the estuarine mouth to study their partitioning behavior at those locations. Results of adsorption studies of Fe indicated higher adsorption at higher salinities and for Cr adsorption results indicated lower desorption at higher salinities. Both the results were in agreement with the results of distribution coefficients obtained from the field analysis, that were found to be increasing for Fe and decreasing for Cr at higher salinities.

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