Role of hydrographical parameters and total organic carbon on mercury allocation along the riverine transect of Beypore, south-west coast of India

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Distribution of total mercury (THg) was carried out in the sediments of Beypore estuary. The THg concentration in surface sediments varied from 0.03 ppm to 0.17 ppm. The pollution index approach using contamination factor (CF) revealed that the sampling stations are moderately contaminated with respect to mercury. Further, the effects of hydrographical parameters (pH, salinity, dissolved oxygen) and total organic carbon (TOC) of the sediment were studied over the spatial distribution of mercury (Hg). Correlation analysis unveiled THg exhibited significant positive correlations with TOC (R=0.91) and salinity (R=0.744). However significant inverse correlation was observed between pH and Hg (R =-0.93). The C: N ratios suggest that the organic matter is labile in nature. Total organic carbon was found to control the distribution of Hg. It is the first base line study in this estuary.

[Keywords: pH; Salinity; Dissolved oxygen; Total organic carbon; Mercury; Beypore estuary]

Introduction

Mercury (Hg) is regarded as a global pollutant and an extremely toxic metal occurring naturally in air, water and soil¹⁻². The element Hg occurs naturally from countless sources⁴⁻⁶ and its toxicity is well established³. Numerous studies pertaining to Hg in coastal and estuarine sediments have unveiled the fact that organic matter is a key variable which influences distribution of Hg in aquatic environments⁷⁻¹³. Total organic carbon (TOC) is found to exhibit excellent correlations with Hg circulation in sediments⁸⁻¹⁰. It is cited that primary driver of sediment diagenesis in freshwater and marine sediments is organic carbon (OC) flux¹⁴. The stability of Hg-OC complexes depends on several factors: 1) nature and composition of organic matter; 2) Hg concentrations; and 3) pH, ionic strength and redox condition of the medium¹⁵⁻¹⁷.

Organic carbon transported to the sediment can be of two types namely, autochthonous and allochthonous carbon¹⁸. Autochthonous carbon, which is typically considered the more labile of the two types of carbon, is produced at or near the site of consumption. Organic carbon produced outside the system of interest is considered allochthonous organic carbon¹⁸. Since organic carbon in fluvial systems can be degraded during transport by microbial and macrobriotic processes, allochthonous carbon (produced elsewhere) tends to be more refractory¹⁹. Both the magnitude and type of organic carbon play major roles in controlling the rates of sediment diagenesis. Carbon and nitrogen in aquatic ecosystems are governed by the amalgamation of terrestrial and autochthonous organic matter²⁰⁻²⁴. It is found that freshly formed organic matter from mainly planktonic organisms has a C/N ratio of 6 to 9²⁶⁻²⁸. Salinity is regarded as a key factor in understanding speciation of Hg in estuarine sediments²⁶⁻³⁰. Earlier studies have observed that salinity intrusion brings high turbidity, which can also alter the Hg distribution³¹. Further increasing association of Hg with sediments has also been reported via “salt out” effects in estuary¹⁶, ³², ³³. pH is also considered as an important factor in unveiling the mobility of Hg in sediments³⁴,³⁵.

The present study encompasses the effect of physico-chemical parameters and total organic carbon on the spatial distribution of Hg concentration in Beypore estuary. The literature shows that very few data banks are available in this estuary. Studies regarding physico chemical parameters, tidal influence, nitrogen fluxes and trace metal chemistry have been undertaken in this estuary²⁶⁻²⁹. The potent pollution source identified was Gwalior rayon factory, a popular paper and pulp industry that changed the face of river Chaliyar. Paper pulp factory
requires caustic soda (NaOH) for bleaching process and in the production of NaOH, Hg cathode is widely employed. Further Hg finds use as biocides in paper industry as well as in certain antifouling paints. Presently, data literature available regarding the distribution of Hg is sparse. Literature studies reveal that Hg enrichment in river water was high (2.810 ppm) when compared to permissible limits (0.002 ppm). In this aspect, the study was undertaken to assess the concentration of Hg in the surface sediments of Beypore and its relation with environmental parameters.

Materials and Methods

Description of the study area

The Chaliyar River is one of the largest river basins and it flows through the Arabian Sea through Beypore estuary (11°18’ N and 75°48’ E) situated near Calicut (South-west coast of India). The River originates from the Ilambalari hills in Gudalur Taluk of Nilgiri district in Tamil Nadu at an elevation of 2066 m above sea level. The Chaliyar river flows through Nilambur, Mampad, Edavana, Areacode, Vazhakkad and Feroke before it joins the Arabian Sea through Beypore estuary. Eight samples comprising bottom water and surface sediment samples were collected from the study region starting from the bar mouth where the river opens into the sea (up to 14 km from the bar mouth each station separated at a distance of 1.75 km). The sampling was done in the pre-monsoon time (February-March) of 2015. Sediments were collected by van veen grab and niskin sampler was used to collect the bottom water, for further hydrographical analysis. The water samples were collected in triplicate from each station and average value is reported. The sediments collected were transferred to plastic vials, sealed and frozen until analysis. The map of the sampling site is given in Fig. 1.

Analytical methodology

The pH of the sample was analyzed by pH meter, dissolved oxygen by Winkler method and salinity by Mohr Knusden method. All the parameters were measured according to standard protocols. Elemental carbon, nitrogen and sulphur were measured using CHNS analyser (Elementar Vario EL

Fig. 1 — Location map of sampling sites
III) and the values are reported in percentage. Total organic carbon was measured using TOC analyser (Skalar Model: 2CA16910, primacs mcs analyzer). Total mercury was measured using direct Hg analyser (Teledyne Leeman, Hydra II, detection limit ≤ 0.2 ng). In brief, 0.1 to 0.5 g of homogenized sample is weighed in a nickel boat, which serves as the sample holder. The sample holder is directly fed into the instrument, which is calibrated using standard prior to analysis. The instrument employs the technique of sample combustion (thermal decomposition), Hg concentration via gold amalgamation and detection by cold vapour atomic absorption. High purity oxygen gas is used for initial oxidation.

Contamination factor

The level of contamination in a sediment sample by a metal is usually assessed in terms of contamination factor\textsuperscript{44}, expressed as

\[ CF = \frac{C_s}{C_b} \]

Where \( C_s \) is the concentration of the metal under consideration and \( C_b \) is the background concentration of the respective metal. If \( CF \leq 1 \), it refers to low contamination, \( 1 < CF \leq 3 \) means moderate contamination, \( 3 < CF \leq 6 \) implies considerable contamination, and \( CF > 6 \) indicates very high contamination.

The metal enrichment in a particular region is generally estimated using shale average, crustal abundances as reference baselines. But this criteria omits the local lithology and sediment properties. However, data regarding regional background concentration for mercury in Beypore estuary is limited except that of Nair (1994)\textsuperscript{40}, where concentration in Hg sediment was reported to be between 0.05-2.0 ppm. The present contamination factor (CF) reported in this paper was calculated based on shale average proposed by Turekian and Wedepohl (1961)\textsuperscript{45}.

Results and Discussion

Total mercury concentration (THg)

The Hg concentration in sediments ranges from 0.03 to 0.17 ppm (Table 1) with a mean value of 0.09 ppm. This might be due to anthropogenic contamination since multifaceted activities such as transportation, fishery harbour, boat yards, and discharge of CFL lamps are taking place widely at the mouth of the estuary as well as near the vicinity. The world shale average value is 0.08 ppm\textsuperscript{45} and pollution index using CF showed the presence of moderate contamination (Table 1). Previous data on Hg distribution in Beypore estuary showed that concentration of Hg varied from 0.5 ppm to 2 ppm in the river side related to industrial areas\textsuperscript{40}. The scan of the Beypore estuary reveals that several changes have been introduced therein after within these two decades. The closing down of factory and the construction of the regulator bridge to prevent salt water intrusion might have influenced the Hg dynamics. The industrial unit (Gwalior rayon factory) was located approximately 3.5 km from the regulator bridge. The low concentration observed for Hg might be attributed to fewer reasons such as firstly the important pollution source; the paper pulp industry has been closed there by reducing its exact point source. Secondly surface sediment samples were

<table>
<thead>
<tr>
<th>Stations</th>
<th>Lat &amp; Long</th>
<th>pH</th>
<th>Salinity (ppt)</th>
<th>DO (mg/L)</th>
<th>TN (%)</th>
<th>TOC (%)</th>
<th>TS (%)</th>
<th>Hg(ppm)</th>
<th>CF</th>
<th>C/N</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>11°09'31.9&quot;N 75°48'04.9&quot;E</td>
<td>7.11±0.01</td>
<td>22.3±0.55</td>
<td>2.79±0.03</td>
<td>0.29</td>
<td>1.33</td>
<td>0.21</td>
<td>0.17</td>
<td>2.08</td>
<td>4.5</td>
</tr>
<tr>
<td>2</td>
<td>11°10'38.6&quot;N 75°48'46&quot;E</td>
<td>7.53±0.005</td>
<td>15.56±0.80</td>
<td>3.76±0.04</td>
<td>0.24</td>
<td>1.12</td>
<td>0.28</td>
<td>0.1</td>
<td>1.26</td>
<td>4.6</td>
</tr>
<tr>
<td>3</td>
<td>11°10'48.6&quot;N 75°49'36.4&quot;E</td>
<td>7.41±0.01</td>
<td>12.14±0.98</td>
<td>4.28±0.03</td>
<td>0.21</td>
<td>0.98</td>
<td>0.14</td>
<td>0.1</td>
<td>1.25</td>
<td>4.6</td>
</tr>
<tr>
<td>4</td>
<td>11°11'39.2&quot;N 75°50'07.9&quot;E</td>
<td>7.89±0.01</td>
<td>4.88±0.28</td>
<td>5.74±0.08</td>
<td>0.15</td>
<td>0.62</td>
<td>0.1</td>
<td>0.09</td>
<td>1.1</td>
<td>4.1</td>
</tr>
<tr>
<td>5</td>
<td>11°12'26.8&quot;N 75°52'15.2&quot;E</td>
<td>8.09±0.01</td>
<td>3.58±0.488</td>
<td>4.77±0.08</td>
<td>0.06</td>
<td>0.33</td>
<td>0.04</td>
<td>0.03</td>
<td>0.4</td>
<td>5.5</td>
</tr>
<tr>
<td>6</td>
<td>11°13'34.4&quot;N 75°52'52&quot;E</td>
<td>7.88±0.01</td>
<td>2.78±0.22</td>
<td>5.22±0.10</td>
<td>0.08</td>
<td>0.56</td>
<td>0.1</td>
<td>0.08</td>
<td>1.01</td>
<td>7</td>
</tr>
<tr>
<td>7</td>
<td>11°15'47.8&quot;N 75°58'04.7&quot;E</td>
<td>8.02±0.01</td>
<td>1.35±0.08</td>
<td>4.79±0.07</td>
<td>0.03</td>
<td>0.21</td>
<td>0</td>
<td>0.03</td>
<td>0.41</td>
<td>6.5</td>
</tr>
<tr>
<td>8</td>
<td>11°14'34.1&quot;N 75°55'19.3&quot;E</td>
<td>7.47±0.005</td>
<td>1.06±0.07</td>
<td>5.91±0.04</td>
<td>0.31</td>
<td>1.2</td>
<td>0.05</td>
<td>0.11</td>
<td>1.37</td>
<td>3.8</td>
</tr>
</tbody>
</table>
analysed for Hg contamination. The sedimentations occurring throughout must have suppressed the Hg deep inside, urging the need of a core sediment study. Third in monsoon seasons, where heavy flushing occurs, Hg might have flowed into the sea.

**Effect of hydrographical parameters of bottom water column with Hg distribution**

The distribution of pH, salinity and dissolved oxygen of the water column lying over the sediments with the THg distribution is depicted (Table 1). The pH of the water column remains alkaline throughout with an average value of 7.67±0.34 in Beypore estuary. Data anthologies regarding the effect of pH on the mobility of Hg are diverse. Some authors reported that at low pH Hg gets released from sediments, whereas others claimed that at low pH Hg gets adsorbed into the sediments. However prevailing of acidic conditions favour Hg methylation at the water column and at the sediment water interface. Low pH conditions cause microbial activity enhancing leading to Hg methylation. The present study confines to alkaline pH in the sampling sites discarding the presence of Hg methylation. At alkaline pH, a greater amount of Hg is transformed to elemental Hg minimising the formation of methyl Hg. Similar citations are reported elsewhere.

The salinity ranges from 0.98 ppt to 22.3 ppt and positive correlation (Table 2) were observed with salinity in the Beypore estuary (Pearson Correlation=0.744). It is an established fact that chlorine ions can affect the process of mercury methylation and demethylation. The rate of Hg methylation decreases upon increasing the salt concentration owing to formation of chlorine complexes with Hg. The highest Hg concentration was reported at the bar mouth 0.17 ppm where the salinity was found to be 22.3 ppt and thereby decreasing trend was observed as salinity decreases. Under saline conditions, total dissolved solids at high rate may cause flocculation or coagulation and thereby Hg adsorption increases in sediments. Similar observation was made in Godavari Estuary.

There was no correlation (Table 2) observed for DO and Hg. DO was inversely correlated with salinity. This is evident from the fact that DO was considerably lower at the barmouth (2.82 mg/L) where salinity was maximum. Studies regarding methylation of Hg in sediment have been reported to be more positive in anoxic regions of estuarine and freshwater environments, especially near the redox interface. Methylation is primarily biologically-mediated, and the methylating genes (hgcA and hgcB) have so far only been found in anaerobic microbes. The regression analysis (Fig. 2) showed

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**Table 2 - Pearson correlation table showing relationship of Hg with other parameters**

<table>
<thead>
<tr>
<th></th>
<th>pH</th>
<th>Salinity</th>
<th>DO</th>
<th>TN</th>
<th>TOC</th>
<th>TS</th>
<th>Hg</th>
<th>CN Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Salinity</td>
<td>-0.309</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DO</td>
<td>0.218</td>
<td>.907(**)</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TN</td>
<td>-0.258</td>
<td>0.577</td>
<td>-0.295</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TOC</td>
<td>-0.296</td>
<td>0.687</td>
<td>-0.428</td>
<td>.978(**)</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TS</td>
<td>-0.191</td>
<td>.862(**)</td>
<td>-0.689</td>
<td>0.585</td>
<td>0.7</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hg</td>
<td>-0.93**</td>
<td>.744(*)</td>
<td>-0.48</td>
<td>.866(**)</td>
<td>.914(**)</td>
<td>0.672</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CN Ratio</td>
<td>0.23</td>
<td>-0.357</td>
<td>0.028</td>
<td>-.799(*)</td>
<td>-0.691</td>
<td>-0.353</td>
<td>-0.569</td>
<td>1</td>
</tr>
</tbody>
</table>

** Correlation is significant at the 0.01 level (2-tailed)
* Correlation is significant at the 0.05 level (2-tailed)
that pH of the water column was negatively correlated ($R^2=0.85$), whereas salinity weakly, but positively correlated ($R^2=0.48$) and DO was poorly correlated.

**Effect of total organic carbon (TOC), total nitrogen (TN), total sulphur (TS) on Hg**

Organic matter is considered one of the prime components of bottom sediments and it is generally responsible for binding of metals. It has been showed that organic matter can bind up to 95% of the divalent mercury species. The mobility of mercury in the environment is well mediated by organic matter. The TOC during the study was found to vary from 0.21 to 1.33% with a mean of 0.79% (Table 1) and TN ranges from 0.03 to 0.31% with a mean of 0.17% in the surface bulk sediments of Bey pore estuary. A linearity (Fig. 4) was observed between TOC and TN ($R^2=0.94$) which indicates that the major part of TN was related with TOC and can be considered as organic nitrogen. Similar citations were previously studied. Hence C:N ratios reported here adheres to $C_{\text{org}}/N_{\text{org}}$ ratios.

Correlation analysis (Table 2) and regression analysis (Fig. 3) showed that THg was positively correlated with TOC ($R=0.91$), TN ($R=0.86$) and TS ($R=0.67$). This shows that THg is more associated with TOC and probably depends upon the sources of TOC. Earlier studies by Kainz and Lucotte suggest that TOC can be a significant factor in controlling Hg and organic carbon interaction in sediment. The reduced correlation of THg with nitrogen reveals even though N atoms in organic matter can bind Hg, the bond formed between them is weaker. Similar suppositions were reported. Mercury has great affinity towards sulphur and main sulphur species responsible for binding Hg are groups like thiol (R-SH), disulphide (R-SS-R) and disulphane (R-SSH). The TS content during the sampling period varied from 0 to 0.21% with a mean value of 0.11%. This factor becomes prominent in anoxic conditions. However, during the study, DO concentration varies from 2.87 mg/L to 5.93 mg/L, which concludes oxic conditions prevailed during the sampling time. This statement is further supported by the fact weaker correlations were observed between Hg and TS.

The C:N ratios are useful tools in predicting the source of organic matter. Organic matter with low
C:N ratios (4-10) are considered to be labile where as high C:N ratios suggest they are non-labile. The lability of sedimentary organic matter is known to affect methylation of Hg in sulphate rich sediments. The C: N ratios were found to vary from 3.8 to 7 which suggests that organic matter is labile in nature. This means that Hg binding with the organic matter may shift towards the water column thereby decreasing concentration of Hg in the sediment.

**Conclusion**

The above paper investigated influence of hydrographical parameters of bottom water together with sedimentary parameters on Hg. These parameters are imperative tools, which can unravel the water column status as well as sediment condition. Moderate Hg pollution was found during the sampling period when compared with the previous data where high contamination was reported. The outcome of the study is summarised as follows:

1) The pH of overlying water column was negatively correlated with Hg distribution.
2) Salinity was found to influence Hg deposition, as chloride concentration increases remobilization of particulate matter in water column into sediments through flocculation might have taken place.
3) The concentration of DO throughout the sampling period shows oxic conditions prevailed; however, no correlation was found to exist with Hg.
4) Hg concentration was positively correlated with TOC, ascertaining its influence.
5) The C: N ratios showed that organic matter is labile in nature, which indicates Hg binding to organic matter in sediments can be mobilized into the water column.
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