MERCURY IN THE CORE SEDIMENT OF VEMBANAD BACKWATER – AN IMPLICATION TOWARDS ANTHROPOGENIC CONTAMIANTION

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INTRODUCTION

Mercury, a global pollutant (Li et al., 2009), is an extremely toxic trace metal, naturally occurring in air, water and soil (Lin et al., 2007) and is one of the most studied pollutants (Ruiz et al., 2005). Because of its transboundary nature, mercury popping up in places where it was never expected before and it burdens in sediments and other non-biological materials are estimated to have increased up to five times pre-human level; primarily as a result of man's activities (Brim *et al.*, 1994). Earlier studies estimated a global natural mercury emission of 1800-5800 tons/year (Li et al., 2009). The global anthropogenic mercury emission to atmosphere in 2000 was 2190 tons (Pacyna et al., 2006) and 54% of that was contributed by Asian countries (Li et al., 2009). Therefore a lot of studies have been undertaken on mercury contamination in various ecosystems (Mason et al., 2006; Subramanian, 2003; Cizdziel et al., 2003), speciation (Gabriel and Williamson, 2004), bioavailability (Boszke et al., 2007; Bower et al., 2008) and bioaccumulation (Sunderland, 2007).

The presence and behavior of Mercury in aquatic systems are of great interest and importance since it is the only metal which bioaccumulates and magnifies through all the levels of aquatic food chain (Mieiro et al., 2009). Sediments can act as both sink and source of mercury. The accumulated mercury in the sediments can be remobilized or reenter in to the water column through bioturbation or dredging. Hence it is important to study the mercury accumulated in the subsurface sediments, which might have resulted from the past industrial activities.

Tropical regions except Florida Everglades and Amazone basin were less studied when compared with the temperate regions of the earth (Watras *et al.*, 1994; Bowels *et al.*, 2001). A very few studies on mercury pollution have been carried out in Indian ecosystems, especially along the western coast (Mahesh, et al., 2010). Hence it is more significant to study the mercury pollution in the developing countries likes India, which is now become the Hotspots of mercury pollution (Sharma, 2003). Mercury pollution has become a new threat to ecosystems of India (Omana and Mahesh, 2008) as the country has been identified as the biggest consumer of mercury and the quantum of mercury released in to its environment is 220 metric tons from known sources every year (Sharma, 2003; BSCB, 2003). The largest consumer of mercury in India is the chlor-alkali industry (Srivastava, 2002) and they alone contribute 40 % of the total mercury pollution in India. Earlier studies (Ouseph, 1992 & 1996) showed that mercury

contamination was high in Vembanad backwaters mainly due to the production of caustic soda usingy mercury cell process, which was replaced by membrane technology during 2004. But the studies done in elsewhere showed that the mercury concentration will persist in the sediment even if the source is stopped (Li et al., 2009; Karunasagar et al., 2006). Therefore the present study analysed the Total mercury (THg) profiles in core sediments collected from polluted and less polluted region of Vembanad Lake.

MATERIALS AND METHODS

STUDY AREA

Vembanad backwaters, one of the three Ramsar sites of Kerala, having an area of 151,250ha, is the brackish, humid tropical wetland ecosystem (Fig. 1), which is of extraordinary importance for its hydrological function, its biodiversity and the fish population it supports and is well connected with Arabian sea through Cochin estuary (Jayakumar, 2002).

SAMPLING AND ANALYSIS

Two sediment core samples and six surface sediment samples were taken from two distinct sites (Mulavukadu and Kumarakom) of Vembanad lake (Fig. 1) by using gravity corer of 50 cm length and grab sampler respectively. About 250 g of the surface sediment samples were collected and transferred to plastic bags and stored in cool. The core sediments were sub-sampled at 2 cm interval. Sediment samples for THg analysis were dried at 35^{o}C using an oven (KEMI make). The dried samples were subsequently grounded in an agate mortar and sieved to <63 micron fraction. Samples for total mercury analysis (0.1-0.25g) were subjected to hot re-fluxing HNO_3/H_2SO_4 digestion followed by bromine mono-chloride (BrCl) oxidation (USEPA, 2001). Cold Vapour Atomic Fluorescence Spectrometer (CVAFS- Model III, Brooks Rand, USA) was used for the determination of Hg in all the samples. Hg free Nitrogen was used as purging gas while high pure Argon as carrier gas. Cold vapour of elemental mercury formed during the reduction with $SnCl_2/NaBH_4$ was purged with nitrogen and trapped in a gold trap. After 20 minutes of purging, gold trap was taken to trap desorption module where the amalgamated mercury thermally desorbed into the carrier gas stream and detected in CVAFS detector.

Total organic carbon (Walkley and Black method) and pH of the sediment samples were also analysed.

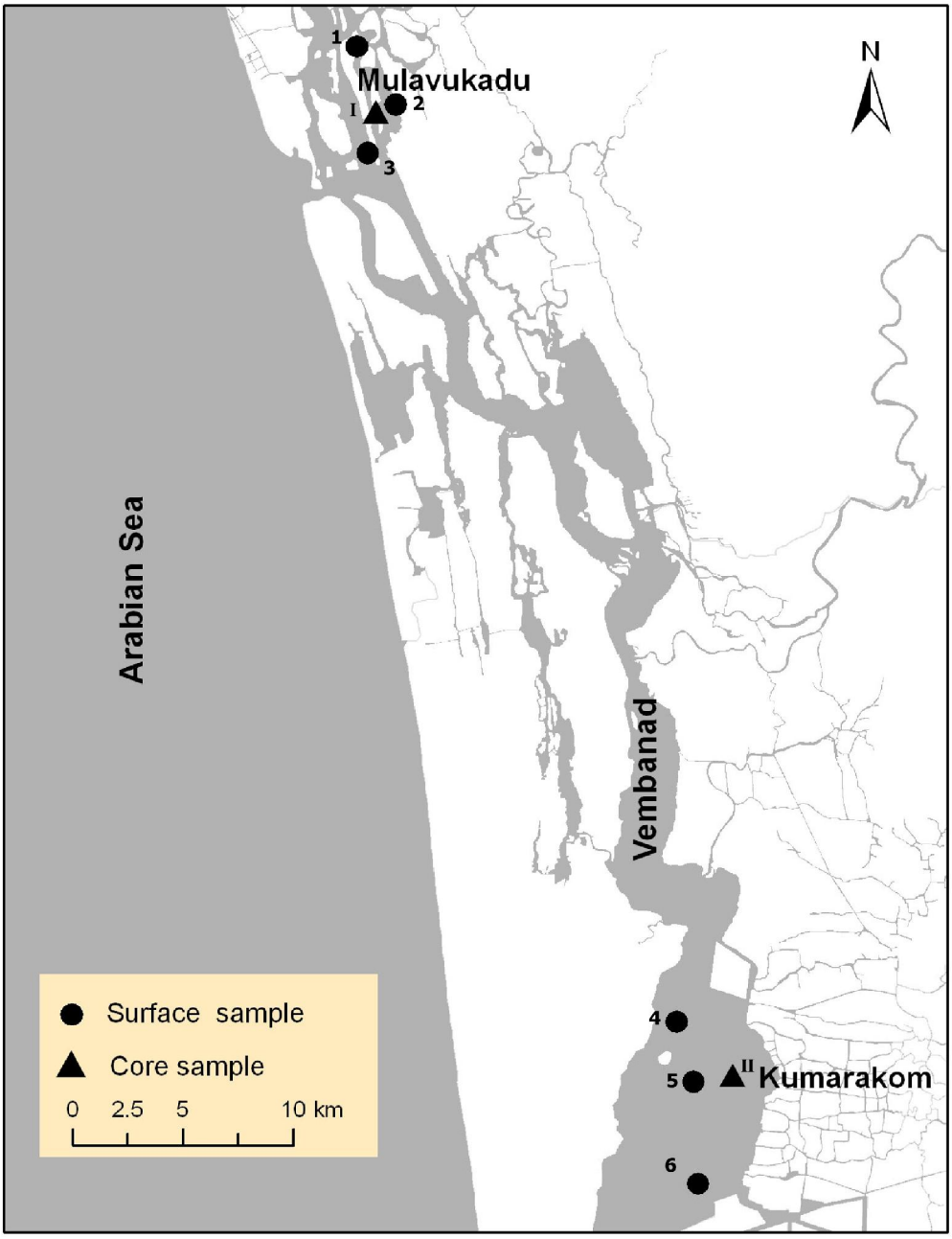

Fig. 1 study area showing sampling locations

RESULTS AND DISCUSSION

The THg concentration in sediments during three seasons were plotted graphically (Fig.2). Mean THg concentration of surface sediments ranged from 61.1 – 2054.3 ng/g during the study period. High THg content was

observed in the sediments collected from the Mulavukadu region and was ranged between 500 – 2730 ng/g with an average value of 1238 ng/g. The high concentration of THg was observed during pre-monsoon season. Kumarakom region showed comparatively lower values (20.9ng/g and 370 ng/g).

The high concentration observed in the Mulavukadu region was a clear indication of anthropogenic contamination. The core collected from Mulavukadu region(Core I) exhibited higher values than the core taken from the Kumarakom region (Core II). The first core showed a high THg content at a depth of 8-12cm. The concentration of THg in the Core 2, which was taken from less polluted Kumarakom region showed 3-4 times lesser than that of first Core.

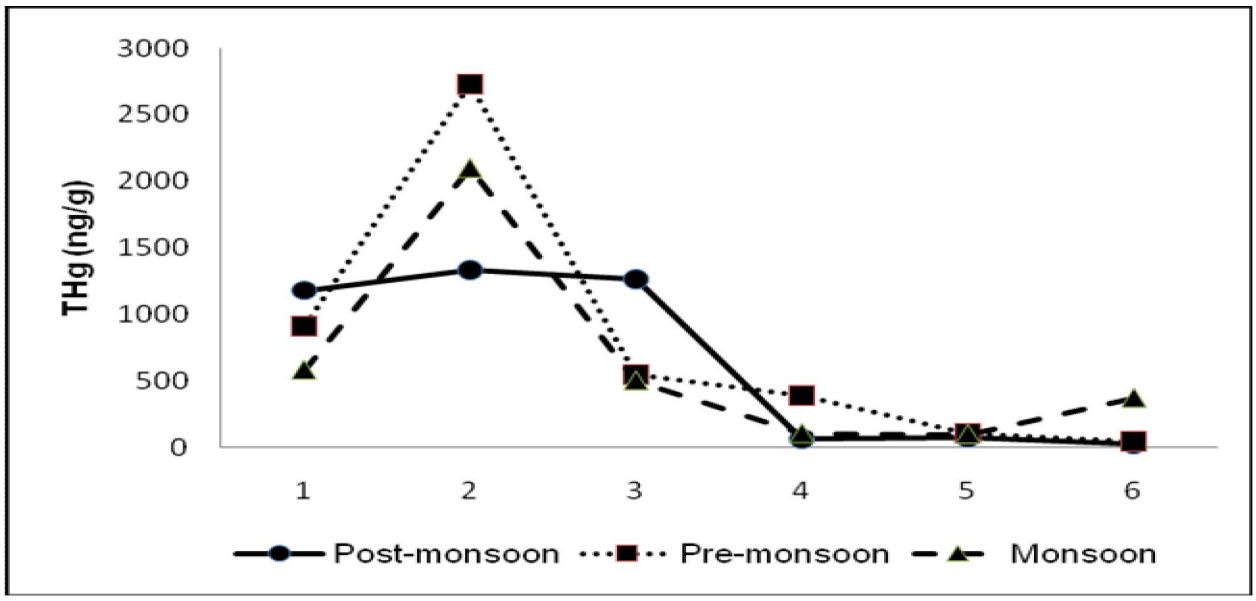

Fig. 2 Mercury concentration in different seasons at Mulavukadu (1-3) and Kumarakom (4-6) regions

The core samples examined showed that THg values were much higher in the subsurface sediment than that of surface sediments. The THg content was reduced to less than half (0.273 µg/g) from the data obtained during the year 1992 (Ouseph, 1992) when the effluent discharge point (EDP) has a maximum of 11.5µg/g.

The changes in the sediment core taken from Mulavukadu region was obviously correlated with the industrialisation of the Cochin area, especially the installation of chlor-alkali plant. The industry had been continuously discharging mercury containing waste in to the Periyar river from the electrolytic process until the technology changed during the year 2004. The decrease towards the surface sediment seen in the core profile can be owed to the same. These low concentrations in the upper few centimetres suggesting recent mercury inputs were substantially diminished in these areas after the closure of the source. In general it can be stated that the subsurface

THg maximum at Mulavukadu corresponds to the historic discharges from chloralkali plant. Similar type of results were observed in earlier works also (Shi *et al*., 2007).It was also interpreted that Kumarakom region was comparatively less polluted than the Mulavukadu region.

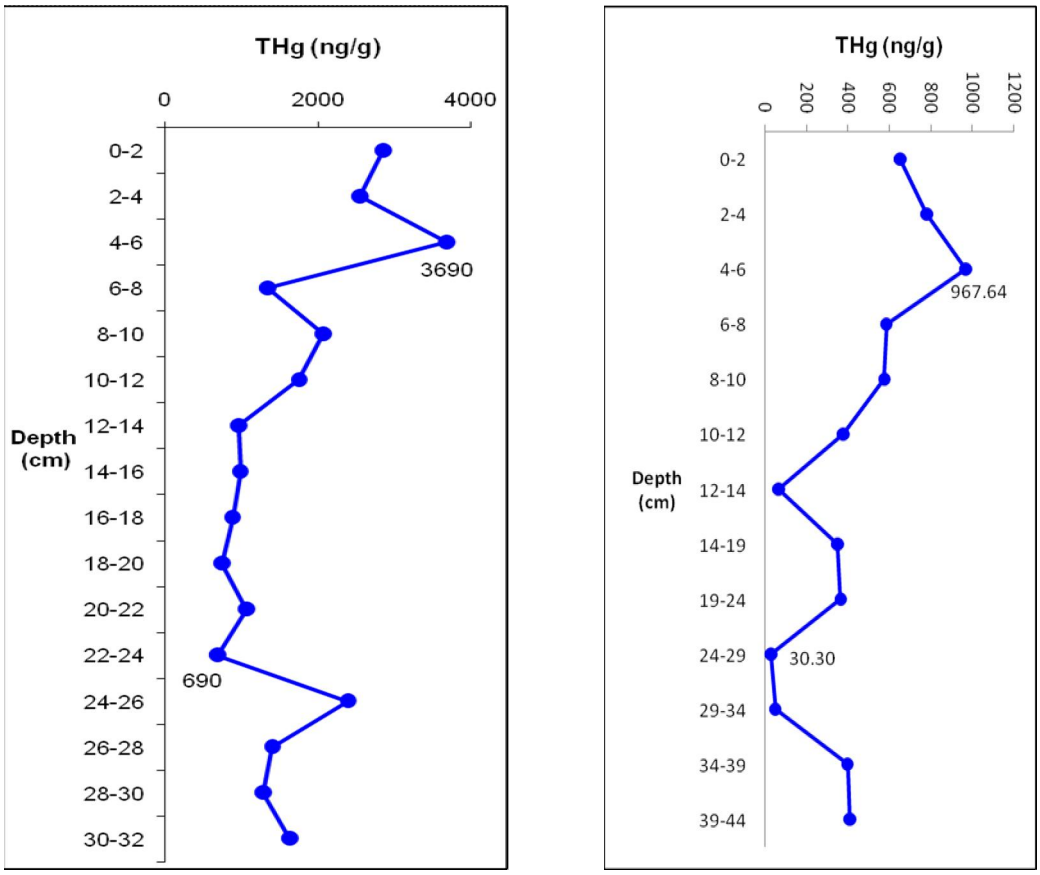

Fig. 3 Mercury pollution profile of Core I and II

The mean concentration observed for THg in this study was 0.69µg/g, which is in between the Threshold Effect Level (TEL - 0.13 µg/g) and Possible Effect Level (PEL - 0.7 µg/g) (Smith *et al.,*1996) . The concentration fall in the range between TEL and PEL will occasionally expected to be associated with adverse biological effects.

The results of pH (4.27-7.31) and organic carbon (1.82%-5.31%) content are given in the Table 1. THg in surface sediments has not showed any significant correlation with pH and organic carbon. However, OC and pH showed a negative correlation with the mercury content at Northern part (Mulavukadu) while it is positively with pH and negatively with OC at Southern part (Kumarakom). Generally mercury adsorption decreases with decrease in pH, since the H^+ ions replacing Hg ions (Gabriel and Williamson, 2004; Panda *et al.,* 1990). But a few studies showed that under low pH conditions, THg and methyl mercury (MHg) would be high in the sediments (Anderson *et al*., 1990; Stein *et al.,* 1996). Panda *et al.* (1990) reported that pH is an important factor regulating the availability of

Hg from sediments. But contradictory reports were also observed in the literature (Jackson *et al.*, 1980). At high pH conditions adsorption of mercury with minerals favoured (Gabriel and Williamson, 2004). Most of the mercury in the sediments was bound with organic materials rather than the inorganic components, where cations displace loosely bound mercury during acidic conditions. In the present study it was observed that the site with high Hg content were having low pH values compared to other regions.

Majority of the THg in aquatic system was found in sediments due to the effective binding with organic carbon bearing particles. This may retard the transfer of mercury to overlying water through interstitial water (Gilmour *et al.*, 1992). Earlier works suggested that high rate of methylation was observed in the presence of organic matter under high anaerobic conditions (Jackson, 1986). Later, Hissler and Probst (2006) found that no clear relationship could be brought in between Hg concentration and organic carbon content in the bottom sediment. Even though, the organic matter can increase mercury methylation by stimulating the heterotrophic bacteria or abiotic methylation by humic substances and there are chances to reduce the availability of mercury for methylation at higher organic matter content (Ullrich *et al.*, 2001). Therefore detailed studies are needed to confirm the effect of geochemical parameters on mercury methylation in Vembanad Lake.

Table 1. pH and OC content of surface sediment

Sample No.	pH			OC%		
	Post-monsoon	Pre-monsoon	Monsoon	Post-monsoon	Pre-monsoon	Monsoon
1	5.96	6.56	6.63	3.03	2.42	2.67
2	5.8	6.34	6.58	2.37	2.13	1.82
3	7.12	7.31	7.1	4.00	5.31	1.91
4	4.94	6.65	6.49	2.15	2.28	1.90
5	4.58	5.49	6.95	3.58	3.84	2.35
6	4.27	4.95	6.93	4.89	4.83	3.97

THg concentrations in the core samples collected from the downstream to the areas affected by industrial pollution indicated a subsurface maximum corresponds to the historic discharge from the Chlor-alkali plant. It can be concluded from the results that after the closure of the highly polluting Hg-cell process in the chlor-alkali industry, the Hg level in the sediments has been reduced to half the level. But at the southern part, comparatively less polluted area of the Lake, the maximum concentration noticed at the <10cm layer of surface sediment. This might be owed to the anthropogenic sources like agricultural runoff, small scale industries and increased fuel burning. The Hg profile in the core sediments indicated an increased concentration in the subsurface sediments,

which may get into the Lake system by remobilisation or resuspension. It will be deleterious for the biota and humans if mercury remobilised from the sediment.

CONCLUSION

The study revealed that the Cochin part of the lake is more contaminated than the southern part. The profile of mercury content in the core sediment showed that the presence of anthropogenic sources of mercury in the Cochin region during the past. Any change in physicochemical characteristics of the water and sediments of Cochin estuary can lead to methylation of mercury to form methyl mercury, which is one among the five most toxic chemicals on Earth. Also any developmental activities in future may remobilise the mercury from the subsurface sediments where the high concentration of mercury is recorded in the core samples. The present study therefore draws a special attention as Cochin is considered as one of the major fish landing centres in India and also a huge population is existing in this region depending directly on the estuary for their livelihood.

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