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Organic matter-A key factor in controlling mercury distribution in estuarine sediment

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ABSTRACT

Organic matter (OM) was found to play an important role in controlling mercury (Hg) distribution and speciation in estuarine sediment of the Vembanad Lake. The sedimentary organic carbon (OC) from the northern part of the lake was influenced mainly by marine in situ biological production. However, the sedimentary OC was mainly of terrestrial origin in the southern part of the lake. The average concentrations of Hg in the sediments were relatively higher in the northern part (ranging from ~6.5–172.0 µg/kg, with an average concentration of 59.6 µg/kg) than the southern part of the lake (ranging from ~6.8–114.0 µg/kg with an average concentration of 49.7 µg/kg). This study suggests that nature and source of sedimentary OC probably control Hg speciation in the Vembanad Lake system. Speciation study of Hg suggests that a major part (55-90 %) of the total Hg was mainly associated with organic phases in the sediment. The variation in concentrations of organic matter bound Hg with the increasing Hg/TOC ratio suggest that more Hg binding sites were available in the sediment from the northern part of the lake but not in the southern part of the lake. Anthropogenic activities were responsible for the higher Hg content in the sediment collected from the northern part of the lake. It is suggested that the strong affinity of sedimentary total nitrogen (TN) for Hg is independent of its source. The sedimentary OM was found to control Hg distribution in different size fraction of the estuarine sediment.

Key words: sedimentary organic matter; Mercury binding ligand; Organic carbon; mercury-sediment interactions; Vembanad Lake; Sediment grain size distribution

1. Introduction

Depending upon the physicochemical conditions, sediments which are ecologically important part of aquatic ecosystems can act both as source and sink for contaminants. Hence, sediments are not only considered as carriers but also potential secondary sources of contaminants in an aquatic ecosystem (Burdige, 2011; Chakraborty et al. 2014; Chakraborty et al. 2012; Knee and Paytan, 2011; Nath et al. 2014; Torres et al. 2013). Sediment contamination (by trace/heavy metals) in coastal areas is a major environmental issue because of their potential toxic effects on biological resources and often, indirectly, on human health (Ernst, 2012; Peña-Fernández et al. 2014; Peng et al. 2009; Chakraborty et al. 2010).

Grain size distribution in sediment significantly influences trace/heavy metals concentrations and their bioavailability in sediment. Some studies have shown that highest concentrations of metals are associated with fine grained sediment particles (Chakraborty et al. 2014a, 2014b). Higher specific surface area of clay-silt particles increases the association of trace/heavy metals with these particles (Thorne and Nickless, 1981; Araújo et al. 1988; Cauwet, 1987). However, it has also been reported that metal concentrations in sediments may not increase with decreasing particle size of sediment. High concentration of metal has been reported in the coarser and larger size fractions (Ramesh et al. 1990; Krumgalz, 1989; Combest, 1991). These exceptions probably demonstrate that metal concentrations in sediment are not controlled exclusively by particle size. There are several other factors (quality and quantity of organic matter, distribution of different mineral phases, metal loading etc.) may also control metal speciation, distribution, accumulation and bioavailability in coastal sediments. It is, therefore, essential to identify the factors that control toxic metals speciation and their bioavailability in coastal/estuarine sediments.

Mercury (Hg) is considered as one of the most toxic metals found in environment and having no known essential biological function (Allen, 1994). Moreover, unlike many heavy metals, Hg participates in a variety of biogeochemical processes with a complex cycle characterized by exchanges between different compartments of ecosphere: atmosphere, hydrosphere, and biosphere. In natural environment, Hg occurs in three redox states (0, +I and +II) and can exist in several different chemical forms. All these forms have different chemical properties and are potentially toxic. The organic Hg compounds, of which methylmercury is the most common, are of special concern because of their high toxicity.

Speciation study of Hg in various matrices has attracted much attention and that reflects by the large number of publication in the recent years (Acquavita et al. 2012; Amos et al. 2014; Bloom and Gill, 1999; Yin et al. 2013; Yu et al. 2012;Lamborg et al. 2014).

A major research and monitoring on mercury (Hg) poisoning have been undertaken mainly in coastal and estuarine sediments in different parts of the world. Mercury speciation in sediment depends on several variables such as pH, total organic carbon (TOC), redox condition, sulphide concentration, and other geochemical factors of the system (Gilmour and Henry, 1992).

It has been reported that TOC in sediment can influence Hg distribution and speciation in the sediment by providing enough strong binding sites in sediment surface (Hammerschmidt and Fitzgerald, 2004; Hammerschmidt et al. 2004; Mason and Lawrence, 1999; Stoichev et al. 2004). OC in sediment may increase reduction processes of Hg^{2+} within the system.

Stability of Hg-OC complexes depend on several factors: 1) nature and composition of organic matter; 2) Hg concentrations; 3) pH, ionic strength and redox condition of the medium. The conditional stability constants for Hg–OC complexes vary over 26 orders of magnitude. Recent studies indicate that the conditional stability constants for mercury binding to strong binding sites are of the order of 10^{22}–10^{28} (Gu et al. 2011; Noh et al. 2013; Randall and Chattopadhyay, 2013).

However, reduction of Hg^{2+} to Hg^0 can be initiated by OC (Alberts et al. 1974; Skogerboe and Wilson, 1981). Mercury reduction by OC is affected by pH, concentrations of dissolved oxygen, and chloride. It has been hypothesized that quinone or seminquinone moieties in organic matter are involved in the transfer of electrons leading to mercury reduction (Alberts et al. 1974).

Significant positive correlation between total Hg and OC contents in estuarine/coastal/open sea sediments has been reported in literature. However, others studies have observed no correlation at all especially in polluted coastal areas (Kehrig et al. 2003; Wu et al. 2013).

The nature of sedimentary OC has been reported to vary from upstream to downstream in an estuary. Particulate and dissolved terrestrial organic carbon has been reported to undergo substantial transformation and biogeochemical processing during fluvial transport as well as during estuarine circulation. Depending on the type of terrestrial source for the organic matter and the length and speed of the fluvial path as well as residence time in the estuary, the majority of this organic matter is highly modified and/or removed along the way towards the ocean. In addition to that, marine OM from in situ biological production also plays an important role in changing the nature of estuarine sedimentary OC from upstream to downstream. However, the changes in Hg complexing capacity of these substantially transformed and marine derived sedimentary OM in estuaries are not known.

Information on fate and transport of Hg in tropical estuarine sediments is limited. The purpose of this study was to determine the impact of TOC and total nitrogen (TN) on the Hg distribution and speciation in surface estuarine sediments, collected from the twenty five geographical locations of the Vembanad Lake , the longest lake in India, from the south west coast of India. The northern part of this lake is well connected with Arabian Sea. Whereas, the southern part of the lake is fluvial dominated and free from brackish water intrusion. An increasing contribution of marine autogenous organic matter towards the seaward side has been reported by Gireeshkumar et al. (2013). Thus, the choice of this area was made in order to understand the variable contribution of marine and terrestrial OM (in sediment) on Hg binding and speciation in different grain size fractions of sediment.

2. Materials and Methods:

2.1. Study area:

The Vembanad Lake, situated in Kerala, is the longest (stretching about 90 km) and largest brackish-water lake of India. It is considered as one of the large tropical estuaries in India (Qasim et al. 1969). It is permanently well connected to Arabian Sea through two openings (at Kochi and Azhikode). Being connected to Arabian Sea, this lake is regularly influenced by mixed semidiurnal tides (Nath et al. 2000). However 1.5 km long Thannirmukam bund is a salt water barrier which prevents salt water intrusion to the southern part of the lake and divides the whole lake in two parts, viz north and south (Figure 1). This bund was constructed in 1974 as per to prevent tidal action, salt water intrusion and to promote agriculture in the low lying area of the southern part of the lake. Thus, northern and southern part of the lake exhibit two different sub-environments as the northern part is brackish and southern part of the lake is freshwater dominated (Nath et al. 2000). Three rivers Manimala, Achankovil and Muvattipuzha discharge fresh water in the southern part of the lake. Surface salinity ranges from fresh-water condition (during Southwest monsoon occur from July through September) to 34‰ (during inter-monsoon) at location near bar mouth (Verma and Subramanian, 2002). Depth in most part of the lake varies between 1.5 to 6 m (Murty and Veerayya, 1973). It receives about 320 cm rainfall during S-W monsoon (Gireeshkumar et al. 2013). Southern part of the lake is reclaimed for agricultural practice. High sedimentation rates (0.5 cm/yr) has been reported (Dinesh Kumar et al. 1994) in the Vembanad Lake. This high sedimentation rate in this lake is due to river discharge (south part) and the resulting tidal influx (north part). Twenty five stations were selected for our study covering most part of the lake (Figure 1). Sampling was done during pre-monsoon time, March-April of 2012. Sediments were collected by Van Veen Grab (Gage, 1975). Top 10-15 cm layer from the sediment-water interface were transferred to plastic bags, sealed and preserved in frozen condition until further analysis.

2.2. Sediment texture:

The frozen sediment samples (bulk) were then dried at 35°C in oven. Texture of the dry sediment was analyzed by (after sieving with 63µm sieve size) laser size particle analyzer (LPSA.). Malvern Mastersizer 2000 was used for size particle analysis. The detailed procedure has been described in the literature by Ramaswamy and Rao (2006). The data were presented as weight percentage (wt %) in this study.

2.3. Size separation:

The bulk sediment samples were separated into four different size fractions (<2 µm, 2-25 µm, 25-63 µm and >63 µm). Adequate amount of sediments were taken (depending upon their texture) and sieved through 63µm sieve. The sediments that have passed through 63µm sieve were transferred to 1000 ml measuring cylinder and the size fraction <2 µm was collected from the suspension following the method developed by Folk (1980). This was repeated several times for complete removal of this fraction. The remaining suspension was sieved through 25 µm sieve for separating it into size fractions viz. 2-25 µm and 25-63 µm. Sample fractions were then dried at 35 °C in oven, homogenized and grinded very finely in agate mortar-pestle and stored in acid cleaned plastic vials.

2.4. Elemental analysis:

Both bulk and size fractionated samples were analyzed for total carbon (TC), total inorganic carbon (TIC), total nitrogen (TN) content. TC and TN in sediments were determined using Flash 2000 CHN-elemental analyzer (Thermo Fisher Scientific Incorporation). Precision of the analysis was within ± 5 %. Soil NC was used as certified reference material. TIC was determined by coulometry (UIC coulometrics). Anhydrated calcium carbonate was used as standard material. Relative standard deviation of the analysis was within ± 2 %. Total organic carbon (TOC) was derived from deducting TIC from TC.

2.5. Sequential extraction method for Hg speciation

The sequential extraction protocols proposed by the European Community Bureau of Reference, usually called the BCR method (Ure et al. 1992) was modified and used to understand the distribution of Hg in the different phases of the coastal sediments. This protocol allows us to determine the sum of ion-exchangeable, water soluble and carbonate/bicarbonate form of Hg (Fr. 1): Hg bound to Fe–Mn oxides i.e., reducible fraction of Hg (Fr. 2); concentrations of Hg associated with organic matter and sulphide, i.e., oxidizable fraction of Hg (Fr. 3) and residual Hg fraction (Fr. 4) in sediment. All the extraction processes were performed in Teflon containers. The reagents used in this study were of analytical grade or better (ultrapure). The protocol has been vividly described in the literature (Chakraborty et al. 2014a). The concentrations of Hg in each extracted solution and in residual fraction were determined by direct mercury analyzer. All the extractions were in triplicate. Two reagent blanks were analyzed for every extraction. In all cases blank results were below the detection limit of the analytical technique (0.0015 ng).

2.6. Determination of Hg in estuarine sediments by Direct Mercury Analyzer:

Mercury was analyzed by Direct Mercury Analyzer (Tri cell DMA-80) from Milestone, Italy. The DMA-80 combines the techniques of thermal decomposition, catalytic conversion, amalgamation, and atomic absorption spectrophotometry. Controlled heating stages are implemented to first dry and then thermally decompose a sample introduced into a quartz tube. A continuous flow of oxygen (99.9 % pure) carries the decomposition products through a catalyst bed where interferences are trapped. All Hg species are reduced to elemental Hg and are then carried along to a gold amalgamator where the Hg is selectively trapped. The system is purged and the amalgamator is subsequently heated which releases all Hg vapours to the single beam, fixed wavelength atomic absorption spectrophotometer. Here, absorbance measured at 253.7 nm is proportional to Hg content in the sample. The Tri-Cell DMA-80 was found to have a dynamic range of 0.0015 – 1200 ng.

3. Results and Discussion

Data of sand, silt, clay, TOC, TN and Hg content in the surface sediments from the Vembanad Lake are reported in **Table 1**. The average concentrations of Hg in the studied sediments were relatively higher in the northern part of the lake (ranging from ~ 6.5–172.0 µg/kg, with an average concentration of 59.6 µg/kg) than the southern part of the lake (ranging from ~ 6.8–114.0 µg/kg with an average concentration of 49.7 µg/kg). The average concentration of Hg in the Vembanad Lake sediments was below or comparable with the Hg concentrations reported in unpolluted coastal sediments from the other parts of the world (Abi-Ghanem et al. 2011; Apeti et al. 2012; Bełdowski and Pempkowiak, 2007; Covelli et al. 2001; Fang and Chen, 2010; Horvat et al. 1999; Leermakers et al. 2001; Orecchio and Polizzotto, 2013). However, high concentration of Hg (ranging 130-170 µg/kg) was found in few stations close to Cochin estuary (Table 1). According to the Canadian sediment quality guidelines for the protection of aquatic life, the interim sediment quality (ISQGs) and probable effect levels (PELs) for Hg in sediment are 130 and 700 µg/kg respectively. The United States environmental protection agency has also suggested that effects range low (ERL) and effects range median (ERM) values for Hg in coastal sediment are 150 and 750 µg/kg. Average Hg concentrations in the sediments from different parts of the Vembanad Lake (except few sediment samples collected from the estuarine sediment in the northern part of the lake) were lower than the concentrations recommended by the United State Environmental Protection Agency and the Canadian Council of Ministers of the Environment for the protection of aquatic life.

The variation of Hg against the (a) silt+clay content (b) TOC and (c) TN concentrations (means of all stations) in the studied sediment are shown in Figure 2. A significant positive correlation coefficient was found between the Hg and the finer particle (silt+clay) content in the bulk sediments (Pearson correlation coefficient (r) =0.87, p <0.001, n= 25). Strong positive correlation between the finer particles (silt+clay), TOC and TN (r=0.94 and 0.92, p<0.001, n=25) (supporting materials, SM Table 1) content in the sediment was also observed. This indicates that there was high sorption and affinity of TOC and TN on the finer particles in the studied sediments (Hedges and Keil, 1995; Paropkari et al., 1987). A strong positive correlation (R^2=0.95 , p<0.001, n=25; SM Fig. 1) was also found between the TOC and TN content in the sediments and probably indicates that a major part of TN was associated with TOC and can be considered as organic nitrogen (Gireeshkumar et al. 2013; Kurian et al. 2013; Paropkari et al. 1987).

This adsorbed TOC and TN in the finer fractions of the sediments might have increased complexation of Hg with the finer particles in the studied sediments and increased the concentration of Hg in the finer fraction of the sediments. A similar observation has also been reported in the literature (Boszke et al. 2004, Thomas, 1972).

A relatively higher positive correlation was found between Hg and TOC and higher average concentration of Hg in the bulk sediments from the northern part of the lake (in presence of less amount of TOC) compared to the sediment from the southern part (with comparatively more TOC) (SM Fig. 2). The reason of such kind of differences can be attributed to the change in the nature of the OM in the sediments from the northern and southern part of the lake (Gireeshkumar et al. 2013; Verma and Subramanian, 2002). However not only TOC, but TN also showed a strong positive correlation with Hg (R^2=0.78, p<0.001, n=25; SM Fig. 3). However no distinct difference was found in the correlation between TN and Hg from north and south part of the lake.

3.1. C/N$_{\text{molar}}$ ratios as source indicators of organic matter provenance in sediment from Vembanad Lake systems

The TOC was found to vary from 0.25 to 4.49 % (Table 1), with a mean of 2.05 % in the surface bulk sediments of the Vembanad Lake. Relatively lower TOC content (mean 1.80 % range: 0.49–3.62 %) was observed in the Northern part of the lake and higher TOC was observed in the sediments (mean 2.22 %; range 0.88–4.49 %) collected from the southern part of the lake.

TN in the bulk sediments was also determined and found to vary from 0.02 to 0.39 % (Table 1), with a mean of 0.17 % in the surface bulk sediments of the Vembanad Lake. Relatively lower TN content (mean 0.16 % range: 0.02–0.39 %) was observed in the northern part of the lake compared to the sediments (mean 0.17 %; range 0.03–0.34 %) collected from the southern part of the lake. The variability of TN against TOC showed straight lines in the studied sediments with a regression of R^2=0.95. The straight line was also found to pass through the origin (SM Fig 1). Thus, the $C:N_{molar}$ ratios reported here is strictly C_{org}/total-N, they can be taken to approximate C_{org}/N_{org} ratios.

Figure 3 shows the latitudinal variation of $C:N_{molar}$ ratio in the studied sediment along the lake. The latitudinal variation of $C:N_{molar}$ indicates that there was a drop in $C:N_{molar}$ ratio in the northern part of the lake sediment compared to the $C:N_{molar}$ratio found in the sediment from southern part of the lake. This decreasing $C:N_{molar}$ ratio indicates that the sedimentary OC in from the northern part of the Vembanad Lake was mainly influenced by marine OM derived from in situ biological production and decreasing contribution from terrestrial OM. Further determination of stable isotopic ratio of OC ($\delta^{13}C_{org}$) in the sediments confirms the increasing influence of marine OM towards the northern part of the lake. The $\delta^{13}C_{org}$ value in the sediments collected from the northern part of the lake was found to vary from -20 to -27 ‰. Whereas the $\delta^{13}C_{org}$ value in the sediments from southern part varied from -25 to -27 ‰. The $\delta^{13}C_{org}$ data are presented as supporting material (see SM Table 2). Similar observation has also been reported by Gireeshkumar et al. (2013). They have reported an increasing trend in $\delta^{13}C_{org}$ towards north, indicating the influence of marine OM in the sedimentary OC. Figure 3 indicates that TOC in the sediments from the southern part of the lake was influenced mainly by terrestrial OM (Verma and Subramanian, 2002). The high Hg content in the sediment from the northern part of the Lake indicate that the TOC (influenced by marine OM) was probably having better Hg complexing capacity than the TOC (mainly influenced by terrestrial OM) in the sediment from the southern part of the lake. However, Hg association of with sediments depends on several processes. It could be linked with absorption processes of Hg by marine organism (e.g., phytoplankton), sulphide content in sediments etc.

The correlation between TN and Hg was comparable in both the parts of the lake. This may indicate that sources of TN may not control their Hg binding capacity within the sediment in the study area. This is because of the fact that Hg (a B-type metal cation, characterized by a ‘‘soft sphere’’ of highly polarisable electrons in its outer shell) shows a pronounced preference for nitrogen over ligands containing oxygen. It is evident from Table 1 that the concentrations of total sulphide (average) content in sediment is comparatively low in the northern part of the lake and indicates that variation of association Hg with sediment is probably dependent on the sources of TOC (SM Fig 6) . Similar observation has been reported by Kainz and Lucotte (2006) that source of TOC can be a potent factor in controlling Hg and OC interaction in sediment.

3.2. Distribution of Hg in different size fraction of the sediment and influence of TOC

The distribution of Hg in four different size fractions (<2 µm, 2-25 µm, 25-63 µm and >63 µm) of the surface sediments from the Vembanad Lake was studied. The purpose of this study was to understand role of TOC on Hg distribution in different size fractions of the studied sediments. The distribution patterns of Hg and TOC in the different grain sizes are plotted (Figure 4).

The variation in concentrations of Hg and TOC in different grain size of the sediments clearly indicates a decrease in concentration with the increasing grain size of the sediment at all the stations. Similar observation has also been reported by Boszke et al. (2004). The maximum Hg concentration was found to associate with the smallest grain size sediment fractions (viz., <2 µm and the 2-25 µm). The concentrations of Hg in the sediment of grain size 25-63 µm was found to be low. Sediments of sand size (>63 µm) had the lowest Hg concentrations.

The variation of Hg content in the clay-sized sediment fraction (<2µm) is plotted against TOC and TN (Figure 5A and 5B respectively). A positive strong correlation was found between Hg and TOC in this size fraction. The correlation becomes much stronger in this grain size of the sediments collected from the northern part (R^2=0.97, p<0.001, n=10) than the sediments collected from the southern part (R^2=0.82, p<0.001, n=15) of the lake.

The northern part showed very strong correlation between TN and Hg (R^2= 0.93, p<0.001, n=10) compared to the moderate correlation (R^2=0.59, p<0.01, n=15) in the south. Strong correlation between TOC and TN (R^2=0.84, p<0.001, n=25, SM Fig: 4) in this fraction indicates that both are of organic in origin and this correlation was similar for both northern and southern part.

Figure 5C indicates that TOC in the size fraction (2-25 µm) of the sediments from the northern part of the lake had a strong affinity for Hg. A strong positive correlation was found between Hg and TOC in this fraction. TOC and TN in this fraction was also strongly correlated (R^2=0.71, p<0.001, n=25, SM Fig. 5). However this relation appeared better in southern part (R^2=0.82, n=25) compared to north (R^2=0.554, n=25). Correlation between Hg and TN (Figure 5D) was moderate to weak in this fraction but was better in south (R^2=0.64) than north (R^2=0.41).

Total organic carbon and Hg content in 25-63 µm and >63 µm fraction was too low compared to the other fractions. No correlation was found between Hg and TOC in both the fractions. Very low OC in these fractions probably decreased the association of Hg in these fractions.

It is well known that the total concentrations of metals in sediments are inadequate to provide better understanding of its speciation and their bioavailability in the system. Further study was carried out to understand Hg-speciation in the sediments by using a sequential extraction protocol. It appears that the various sequential extraction protocols have advantages and disadvantages and there is no ideal protocol for general use. Therefore, the choice of sequential extraction procedure must be related to a definite objective. In this study, BCR sequential extraction protocols were used to fractionate Hg associated with different geochemical phases in the studied sediments.

3.3. **Mercury speciation in estuarine sediments by using a modified BCR sequential extraction protocol**

It was found that major fraction of the total Hg was associated with the TOC (organic phases) in the studied sediments. The concentration of Hg associated with organic phases was found to vary from ~ 55-90 % of the total Hg. The second highest fraction of Hg was found to associate with residual part of the sediments (Fr. 4). Figure 6 shows that the concentration of Hg associated with total organic carbon (TOC) (Fr. 3) gradually increased with the increasing Hg/TOC ratio in the sediments collected from northern part of the lake. However, a steady decrease in Hg association with organic phase was observed with the increasing Hg/TOC ratio in the sediments collected from the southern part of the lake. The increasing [Hg]/[TOC] ratio in the sediments did not increase the concentrations of Hg present in Fr 1 (exchangeable, water soluble and carbonate forms of Hg) and Fr. 2 (Hg associated with Fe/Mn oxide) in the sediments collected from the northern part of the lake. This indicates that sufficient Hg-binding ligands were available within the sedimentary organic phases (marine derived) to form thermodynamically stable Hg complexes. However, increasing $[Hg]_T$/TOC ratio decreased the concentrations of Hg associated with organic phases and indicates the absence of enough Hg-binding sites within the organic phases in the sediment collected from the southern part of the lake.

Relatively high Hg content, low TOC and more association of Hg with the organic phases in the sediment collected from the northern part of the lake indicates that sedimentary OC derived from marine in situ biological production probably had higher Hg-binding capacity than the terrestrial OC. However, it must be taken into account that southern part of the lake is freshwater dominated Thus, one could expect that water discharge increase suspended particulate matter (SPM) in water column and may facilitates exchange reactions between Hg (from estuarine sediment) with SPM of the overlying water column.

Conclusion

This study indicates that OM plays an important role in controlling Hg distribution in estuarine sediments. Nature of TOC and their sources can determine the total Hg content in the sediment and the different size fractions. C:N$_{molar}$ ratios indicate that organic carbon in the sediment from the northern part of the Lake is mainly marine OM derived from in situ biological production while the sediments from the southern part of the lake mainly contained terrestrial OM. This study indicates that marine OM (in sediment) probably has higher affinity for Hg than terrestrial OM. However, interactions of Hg with TN are independent of the source of sedimentary TN. The distribution of Hg in different size fraction of the sediment is also found to be controlled by TOC present in the size fractions of estuarine sediment.

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Captions and legends:

Fig. 1: Map showing the sampling locations from the Vembanad Lake (covering almost entire lake; Kochi in the north and Alleppy in the south). The sampling locations are represented with two different plot symbols; ● (north) and ○ (south)

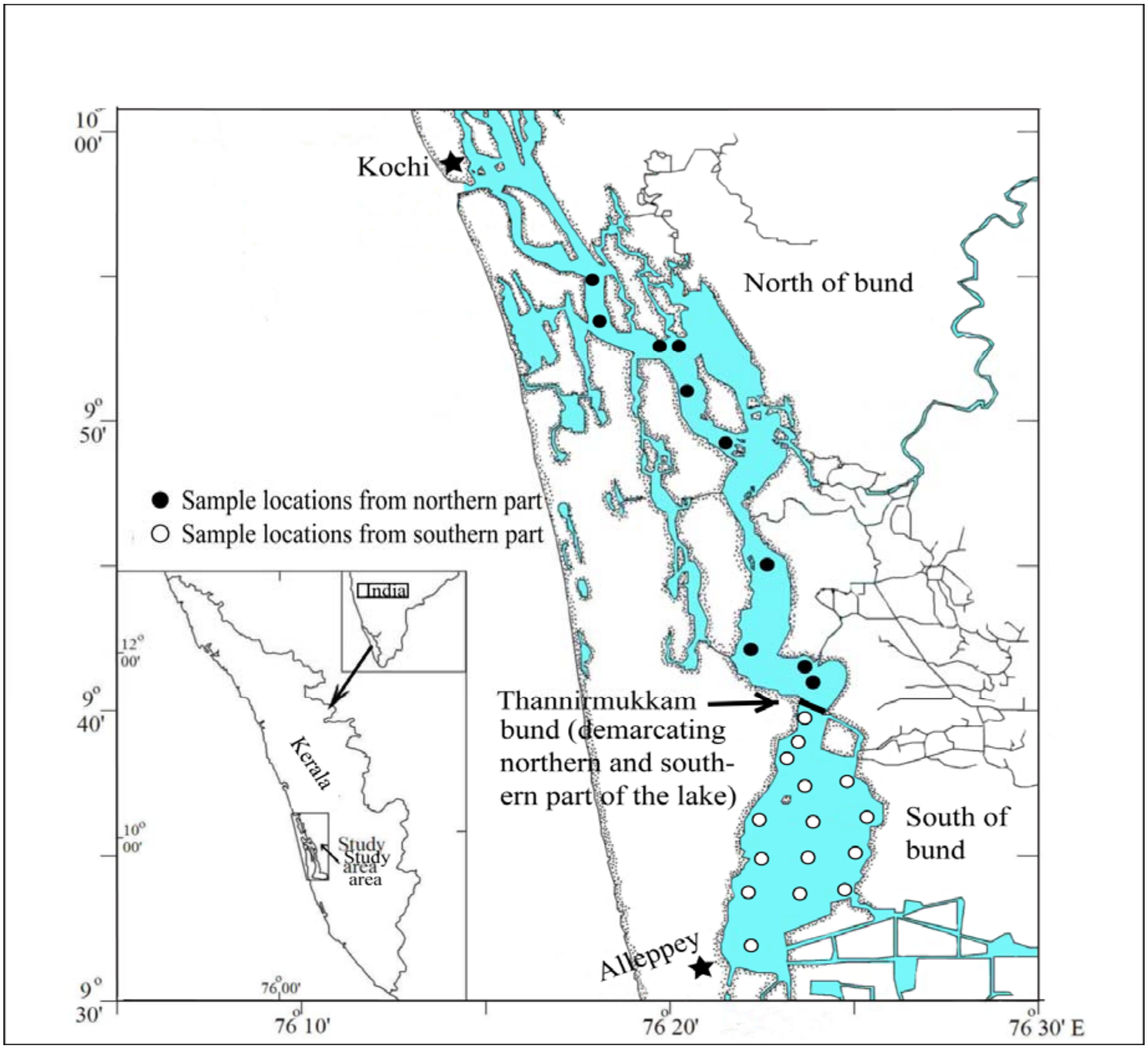
Fig. 2: Variation of Hg concentration in sediments with changing **a**- sediment texture, **b**- total organic carbon and **c**- total nitrogen concentrations. The data obtained from the two sides of the lake are represented with two different plot symbols; ● (north) and ○ (south)

Fig. 3: Latitudinal variation of C:N_{molar} ratio in the lake sediment from south to north of the Vembanad Lake. The data obtained from the two sides of the lake are represented with two different plot symbols; ● (north) and ○ (south)

Fig. 4: Variation in Hg and TOC concentration in different size fraction of the surface sediments.

Fig. 5: (5A)Variation in correlation coefficients between TOC and Hg content (in <2µm fraction of the sediment collected from the north and south part of the lake). **a**- all stations, **b**- stations from north and **c**- stations from south. (5B): Variation in correlation coefficients between nitrogen (TN) on Hg in the sediment (of <2µm size fraction collected from the north and south part of the lake). **a**- all stations, **b**- samples from north and **c**- stations from southern part of the lake. (5C): Correlation between TOC and Hg content in the sediments of 2-25µm size from the north and south part of the lake. (**a**- all stations, **b**- stations from north and **c**- stations from south). (5D): Variation in correlation coefficients between nitrogen (TN) on Hg binding in sediment of 2-25µm size fraction collected from the north and south part. **a**- all stations, **b**- samples from north and **c**- stations from southern part of the lake. The data obtained from the two sides of the lake are represented with two different plot symbols; ● (north) and ○ (south)

Fig. 6: Hg concentration associated with organic phases in the sediment against the varying Hg/TOC ratio in the studied sediments. The data obtained from the two sides of the lake are represented with two different plot symbols; ● (north) and ○ (south)



10° 00'
9° 50'
9° 40'
9° 30'
76° 10'
76° 20'
76° 30' E
Kochi
North of bund
● Sample locations from northern part
○ Sample locations from southern part
Thannirmukkam bund (demarcating northern and southern part of the lake)
South of bund
Alleppey
India
Kerala
12° 00'
10° 00'
76° 00'
Study area

Fig. 1

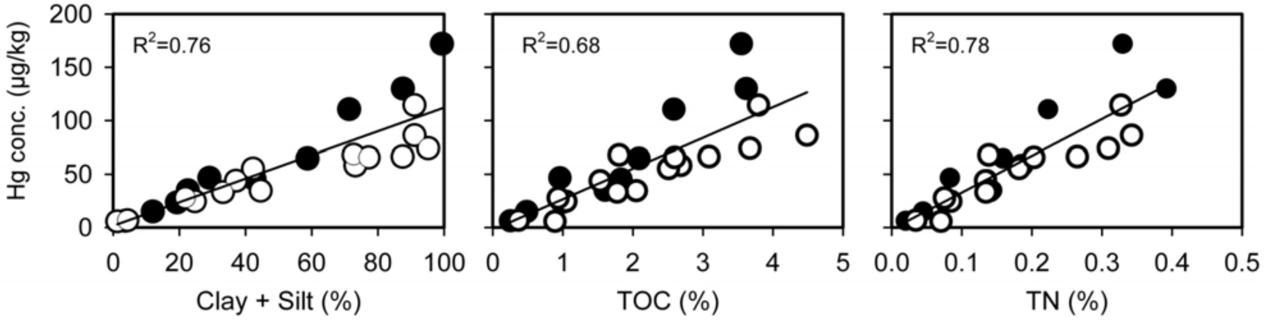

R^2=0.76
R^2=0.68
R^2=0.78
Hg conc. (µg/kg)
200
150
100
50
0
0
20
40
60
80
100
Clay + Silt (%)
0
1
2
3
4
5
TOC (%)
0.0
0.1
0.2
0.3
0.4
0.5
TN (%)

Fig.2

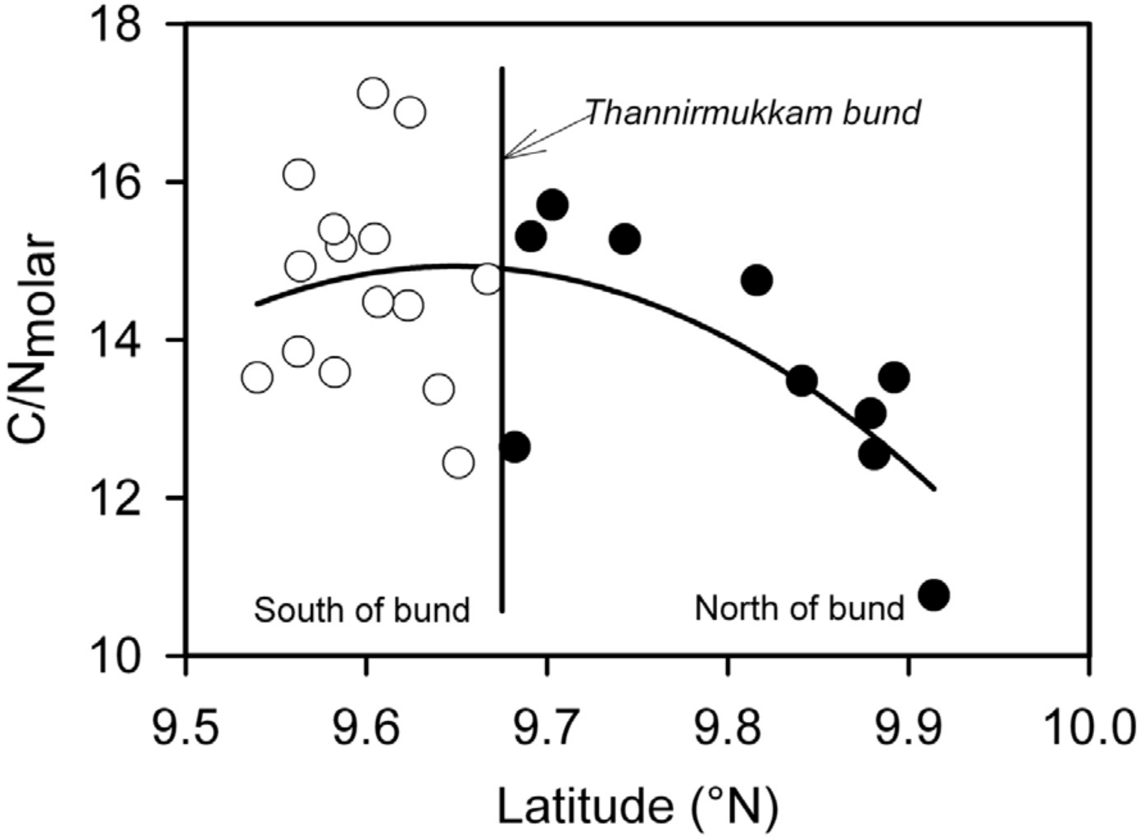

18
16
14
12
10
C/Nmolar
Thannirmukkam bund
South of bund
North of bund
9.5
9.6
9.7
9.8
9.9
10.0
Latitude (°N)

Fig. 3

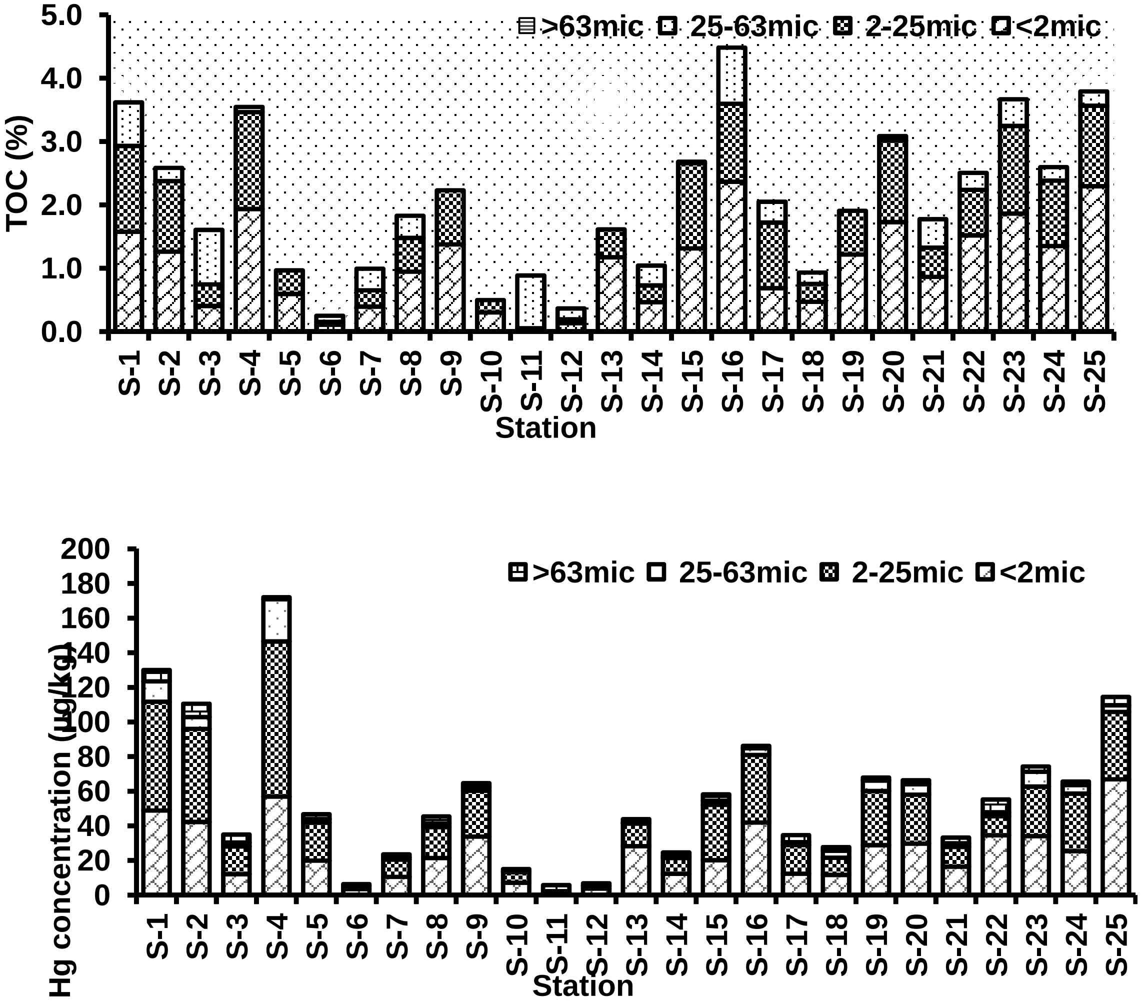

TOC (%)
0.0
1.0
2.0
3.0
4.0
5.0
>63mic
25-63mic
2-25mic
<2mic
S-1
S-2
S-3
S-4
S-5
S-6
S-7
S-8
S-9
S-10
S-11
S-12
S-13
S-14
S-15
S-16
S-17
S-18
S-19
S-20
S-21
S-22
S-23
S-24
S-25
Station
Hg concentration (μg/kg)
0
20
40
60
80
100
120
140
160
180
200
>63mic
25-63mic
2-25mic
<2mic
S-1
S-2
S-3
S-4
S-5
S-6
S-7
S-8
S-9
S-10
S-11
S-12
S-13
S-14
S-15
S-16
S-17
S-18
S-19
S-20
S-21
S-22
S-23
S-24
S-25
Station

Fig. 4

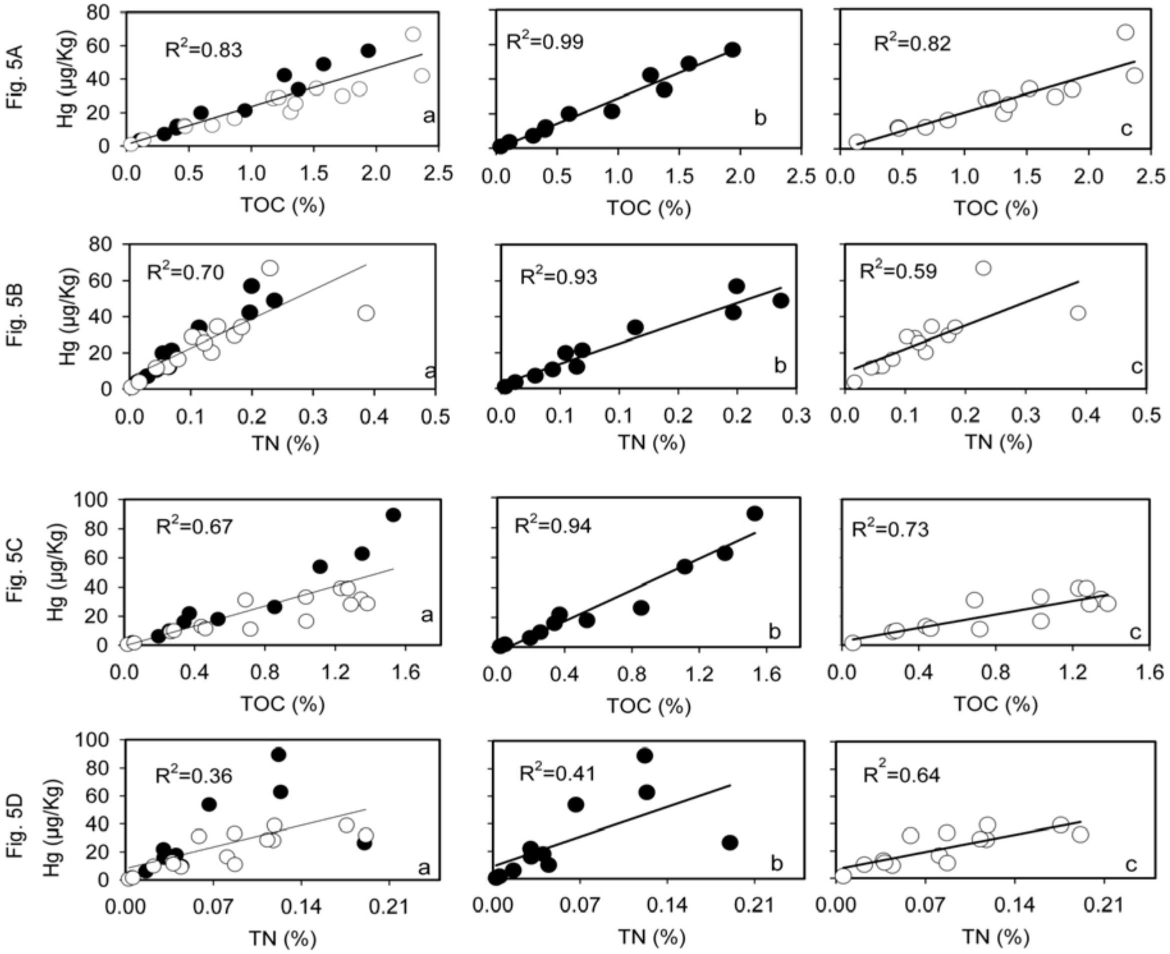


Fig. 5A
Hg (µg/Kg)
R^2=0.83
a
R^2=0.99
b
R^2=0.82
c
TOC (%)
Fig. 5B
R^2=0.70
R^2=0.93
R^2=0.59
TN (%)
Fig. 5C
R^2=0.67
R^2=0.94
R^2=0.73
TOC (%)
Fig. 5D
R^2=0.36
R^2=0.41
R^2=0.64
TN (%)

Fig. 5

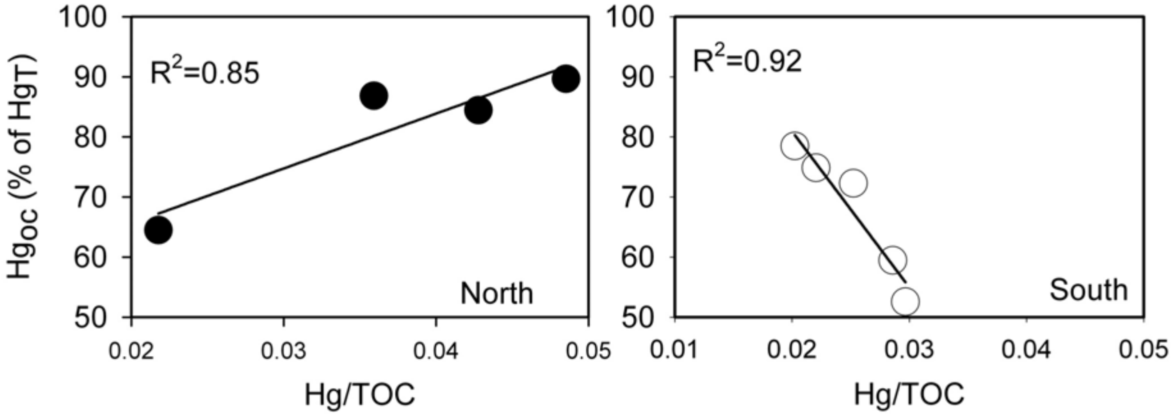

Hg$_{OC}$ (% of HgT)
R^2=0.85
North
R^2=0.92
South
Hg/TOC

Fig. 6

Supporting materials:

Organic matter-A key factor in controlling mercury distribution in estuarine sediment

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Determination of $\partial^{13}C_{oc}$ in sediment samples by Isotope Ratio Mass spectrometer (IRMS):

Subsamples of sediments for $\partial^{13}C_{oc}$ contents were acidified with HCl (10%) to remove carbonates. Traces of HCl were removed by washing the sediments several times with distilled water. The sediments were then used for $\partial^{13}C_{oc}$ analysis. Calibration was carried out using 2, 5-Bis-(5-tetrabutyl-benzoxazol-2-yl) thiopen (BBOT) as a standard. $\partial^{13}C_{oc}$ of OC was performed with the Thermo Finnigan Flash 1112 elemental analyzer, linked with a Thermo Finnigan Delta V plus IRMS. The overall analytical precision for replicate samples was within ±1.6% for OC and ±0.2‰ for $\partial^{13}C_{oc}$. All isotopic compositions are reported as, per-mil (‰) relative to variation (∂) from the PDB standard.

$$\partial^{13}C_{oc} = \left\{ \left({}^{13}C / {}^{12}C \right)_{\text{Sample}} / \left({}^{13}C / {}^{12}C \right)_{\text{PDB}} - 1 \right\} \times 1000$$

Determination of sulfide in sediment samples:

Sediment sample of ~0.2g was taken to a 3-neck round-bottom flask. A volume of 10 mL of dimethylformamide (DMF) was added. The mixture was thoroughly stirred with a magnetic stir bar to secure an efficient mechanical breakup of the sample. Whereas DMF enhances the reactivity of reduced sulfur species, it also allows oxidation to take place at an enhanced rate. To prevent oxidation prior to distillation, extended contact of the sediment- DMF slurry with air avoided. As soon as the sample was mixed with DMF, the reaction flask was connected to the gas line and flushed with N_2 for 10 min. Subsequently, 8 mL 5M HCl was injected through the chemical port followed by the addition of 16 mL 1M $CrCl_2$ solution. The sample is bubbled at a rate of 2 to 5 bubbles per second with N_2 for 2 h and the system was stirred continuously.

Zinc acetate solution was used as sulfide trap. The liberated sulfide was trapped as zinc sulfide in 20 mL of 5% (w/v) ZnAc-solution. Zinc sulfide precipitate was dissolved by adding 2ml of 50% HCl and liberated sulfide was measured on a spectrophotometer at 670nm by Cline method.

Table 1(a)- Pearson Correlation coefficient (includes all the stations, n=25)

	TOC	TN	C:N$_{molar}$	Cay + Silt	Hg
TOC	1.00				
TN	0.97[a]	1.00			
C:N$_{molar}$	-0.05	-0.26	1.00		
Cay + Silt	0.94[a]	0.92[a]	-0.09	1.00	
Hg	0.82[a]	0.88[a]	-0.34[b]	0.87[a]	1.00

a. Correlation is significant at the 0.001 level (p<0.001, two tailed)

b. Correlation is significant at the 0.05 level (p<0.05, two tailed)

Table 1(b)- Pearson Correlation coefficient (for stations in the north, n=10)

	TOC	TN	C:N$_{molar}$	Cay + Silt	Hg
TOC	1.00				
TN	0.98[a]	1.00			
C:N$_{molar}$	-0.49	-0.63b	1.00		
Cay + Silt	0.97[a]	0.94[a]	-0.44	1.00	
Hg	0.95[a]	0.93[a]	-0.54[c]	0.98[a]	1.00

a. Correlation is significant at the 0.001 level (p<0.001, two tailed)

b. Correlation is significant at the 0.025 level (p<0.025, two tailed)

c. Correlation is significant at the 0.05 level (p<0.05, two tailed)

Table 1(c)- Correlation coefficient (for stations in the south, n=15)

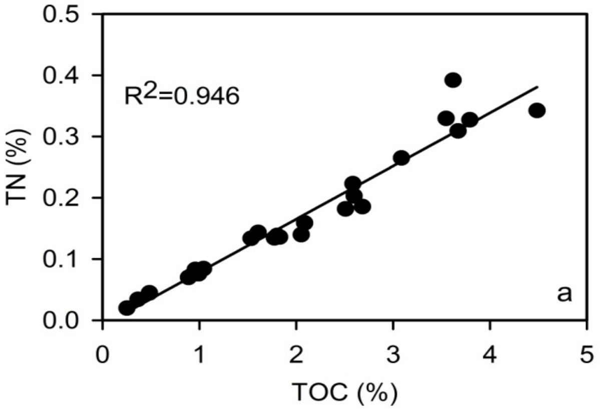
	TOC	TN	C:N$_{molar}$	Cay + Silt	Hg
TOC	1.00				
TN	0.99[a]	1.00			
C:N$_{molar}$	0.16	0.01	1.00		
Cay + Silt	0.91[a]	0.91[a]	0.09[a]	1.00	
Hg	0.90[a]	0.91[a]	0.02	0.93[a]	1.00

a. Correlation is significant at the 0.001 level (p<0.001, two tailed)

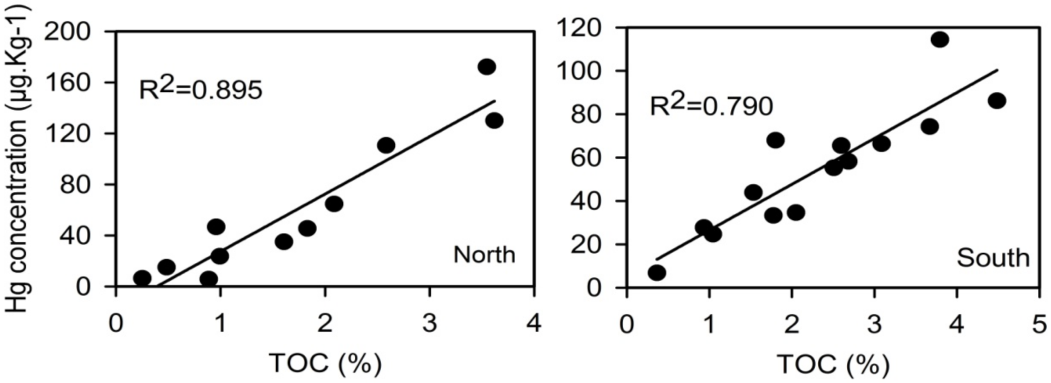
Table 2: Stable isotopic ration of organic carbon ($\delta^{13}C_{org}$, ‰)

Sample	Longitude (°E)	Latitude (°E)	Depth (m)	$\delta^{13}C_{org}$ (‰)
North of Thannirmukkam Bund				
S-1	76.3010	9.9140	5	-20.13
S-2	76.3022	9.8920	2	-22.07
S-3	76.3320	9.8790	4	-22.11
S-4	76.3395	9.8810	2	-21.29
S-6	76.3705	9.8160	4	-24.69
S-7	76.3777	9.7430	6	-25.29
S-9	76.3954	9.6910	5	-25.27
S-10	76.3958	9.6820	3	-26.81
South of Thannirmukkam Bund				
S-11	76.3923	9.6670	1.5	-26.69
S-12	76.3875	9.6510	1.5	-26.56
S-13	76.3816	9.6400	2	-26.02
S-14	76.3920	9.6230	2	-25.69
S-15	76.4164	9.6241	1.5	-25.50
S-16	76.4203	9.6044	3	-25.57
S-17	76.3978	9.6037	4	-26.04
S-18	76.3765	9.6066	3	-25.57
S-19	76.3732	9.5860	3	-25.40
S-20	76.3924	9.5826	1.5	-24.96
S-21	76.4155	9.5820	2	-26.54
S-22	76.4119	9.5627	1.5	-26.53
S-23	76.3895	9.5622	3	-27.19
S-24	76.3648	9.5636	2	-25.76
S-25	76.3684	9.5396	2	-25.85

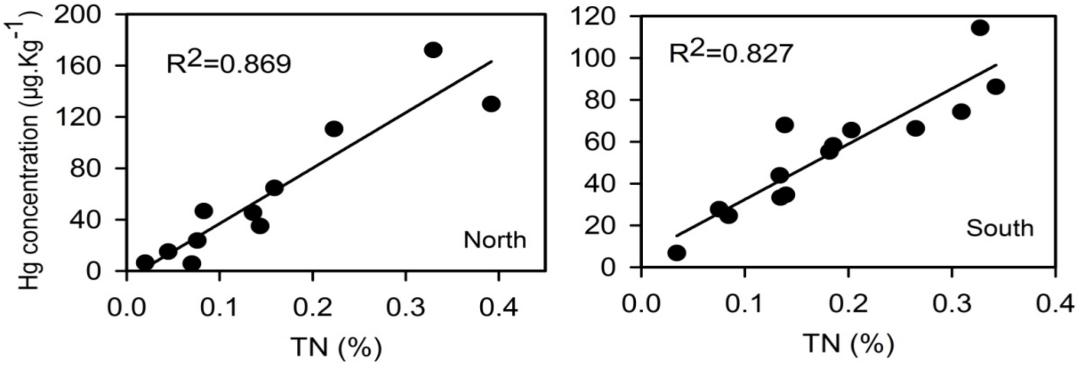
Supporting materials:



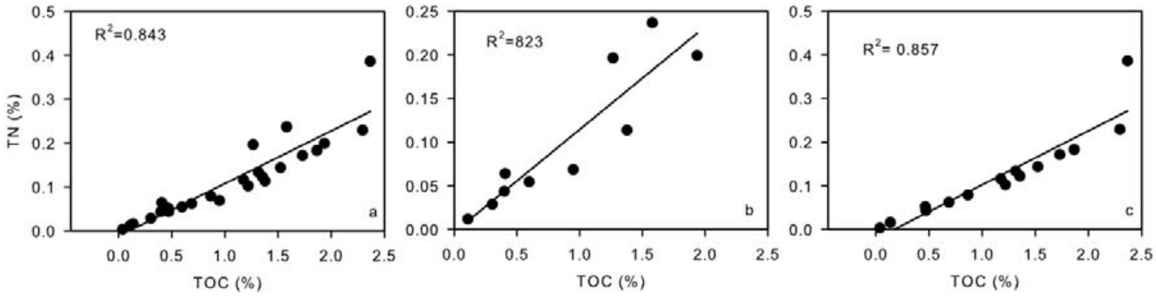
SM Fig 1: Relationship between TOC and TN in sediments from Vembanad Lake.



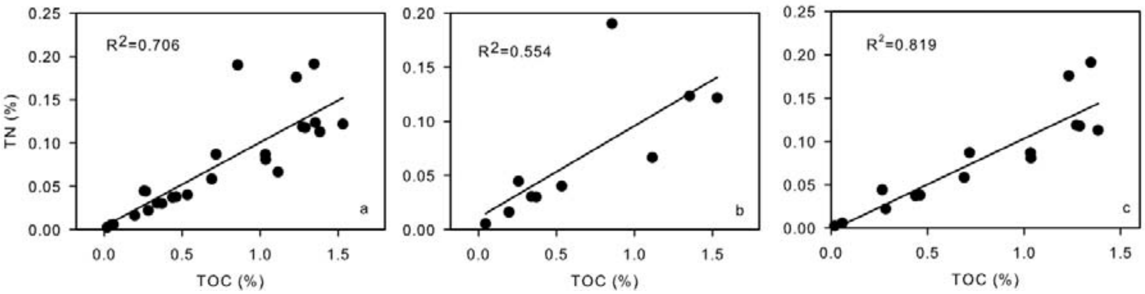
SM Fig. 2: Variation of Hg concentration against varying TOC concentration from northern and southern part of the Lake



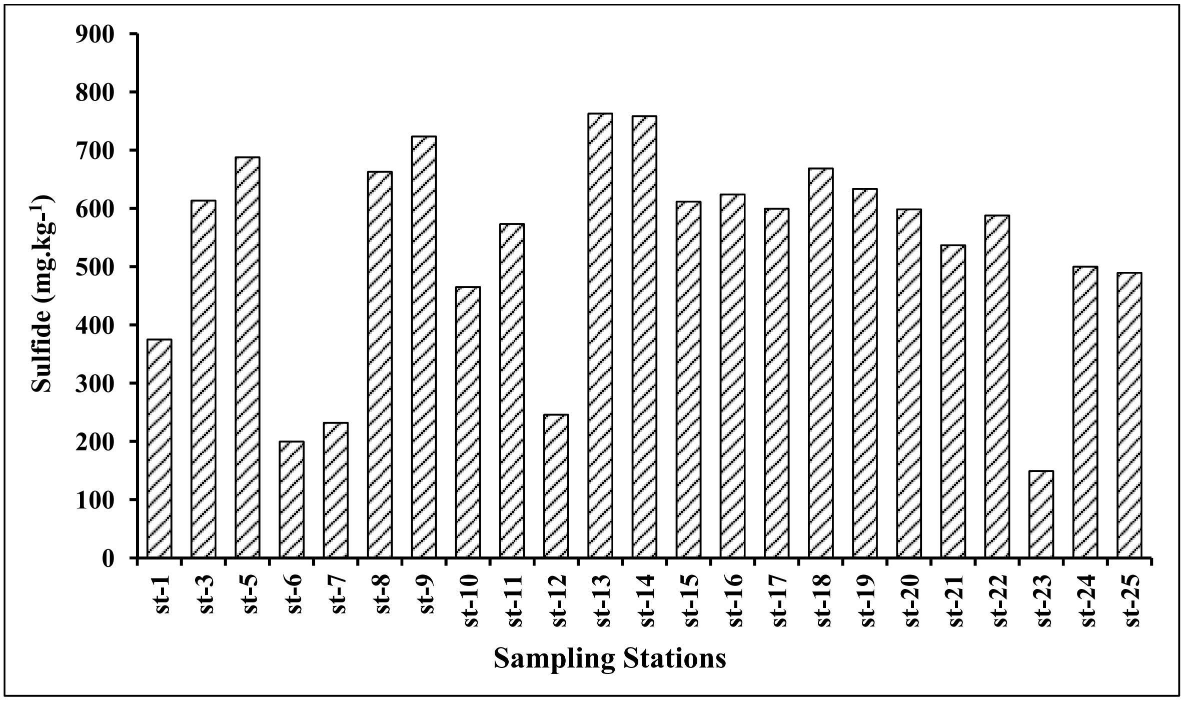
SM Fig. 3: Variation of Hg concentration against varying TN concentration from northern and southern part of the Lake



SM Fig 4: Correlation between TOC and TN in sediment of <2µm size fraction from north and south part of the lake. (a- all stations, b- stations from north and c- stations from south)



SM Fig 5: Correlation between TOC and TN in sediment of 2-25µm size fraction from north and south part of the lake. (a- all stations, b- stations from north and c- stations from south)



SM Fig. 6: Variation of sulfide concentration in surface sediments from the northern and southern part of the Lake