

Distribution and nature of sedimentary organic matter in a tropical estuary: An indicator of human intervention on environment

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Abstract

Sediment texture controls spatial distribution of sedimentary organic matter (SOM) in Vembanad Lake. Influences of marine derived organic matter (OM) on SOM decreased inner-wards in the northern part of the lake. However, SOM from the southern part of the lake was dominated by terrestrial OM. Marine derived OM showed highest affinity for clay-sized fraction ($<2\mu\text{m}$) of the sediment in the northern part of the lake. However, aged and humified soil derived OM dominated the clay-sized fractions from southern part. Alteration of sediment texture resulted in changed SOM distribution pattern in the lake after the bund construction. Human intervention and changes in land use pattern also identified to influence SOM content in the southern part of the lake.

Key words: Vembanad Lake; Source of sedimentary organic matter; Anthropogenic influence; Hydrodynamic change and texture; Land use pattern; Sediment size fractions

1. Introduction

Coastal and estuarine sediments act as sink for organic matter (OM). The burial of OM in marine sediments represents the major link between the pool of carbon in hydrosphere, biosphere and lithosphere (Rullkotter, 2006). Though estuaries and coastal sediments cover only a fraction (~10%) of the total marine environment, ~ 90% of the total OM is buried here (Hedges and Keil, 1995) and act as a major sinks for atmospheric CO₂ (Budge and Parrish, 1998).

The estuaries are the transition zones between river and ocean. The depositional characters of estuaries such as shallow water depth, high sedimentation rate and in-situ biological production favor OM preservation (Ittekkot et al. 1992). In addition to in-situ production (OM_{marine}), estuaries also receive huge amount of terrestrial OM (OM_{terr}; fresh C3 and C4 plants remains and soil OM) through river discharge and surface runoff from watershed areas (Hedges et al. 1997). Anthropogenic input aided by sewage and sludge discharge, waste treatment plant and altered land use planning etc. also play significant role in sedimentary OM (SOM) budget (Pradhan et al. 2014).

Most of the Indian estuaries are dominated by river borne OM_{terr} supply during southwest monsoon, which decrease substantially during non-monsoon season and dominated by in-situ autochthonous OM (Pradhan et al. 2014). The OM_{terr} being composed mainly of lignin rich compound is more refractory and undergoes less mineralization. It has greater potential of being preserved in sediments (Rullkotter, 2006). However, few Indian estuaries (Dey et al. 2013; Samanta et al. 2015) have also been reported to act as the net source of CO₂ to atmosphere due to extensive heterotrophic bacterial decomposition of transported OM_{terr}. Thus, quantification of source of SOM in sediment can provide better understanding of SOM dynamics in estuaries and coastal lagoons and their role in global biogeochemical cycling.

It has been reported that SOM content can be useful in reconstructing past environmental conditions, evaluate histories of climate change, and assess impacts of humans on local ecosystems (Zillén et al. 2008). However, not much study has been carried out to understand the impact of human activity on SOM from tropical estuarine system. This is the first attempt to understand and characterize the distribution of SOM across a tropical estuary and use this information to understand human-induced changes in local and regional environmental systems.

Vembanad Lake, the longest estuary in India, was selected as the study area. Few studies have been carried out in the northern part of the lake investigating the source and nature of SOM (Saraladevi et al. 1992; Verma et al. 2002; Reddy 2003; Priju and Narayana 2007; Selvam et al. 2012; Gireeshkumar et al.

2013; Shivaprasad et al. 2013). Only couple of reports have described the SOM distribution in the southern part of the Vembanad Lake (Veerayya and Murty 1974; Verma and Subramanian 2002). However, no effort has been made to understand the source and distribution of SOM across the lake.

A bund was built in the year 1974 near Thannirmukkam to prevent intrusion of saline water into the southern part of the lake. Building of this bund has been reported to change the hydrodynamics of the area. An assessment of changes has been reported to take place over the last four decades (Kumar et al. 2014). In addition to the shrinkage both in terms of geographic size as well as volume by siltation, the sluggish nature in the southern part of the lake led to eutrophication and the proliferation of water hyacinths. However their impact on SOM distribution has not been well documented. Thus, an attempt was made to understand the distribution pattern of SOM and characterize them on the basis of their sources in the estuary. This information was further compared with the published literature to understand the impacts of human activities on SOM distribution in the longest and largest lake of India.

2. Materials and methods

2.1. Study area

The Vembanad Lake, situated in Kerala, is the longest and largest brackish-water lake of India. It is located between 09°30' -10°13'N and 76°10' -76°30'E, stretching 90 km and covering an area of nearly 260 sq km (Verma and Subramanian 2002). The width of the lake varies from 500 m to 4 km and the depth between 1.5 and 6 m (Murty and Veerayya, 1973). 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 semi-diurnal tides (Nath et al., 2000; Revichandran et al., 2011). However, a 1.5 km long bund built at Thannirmukkam in the year 1974-75 to prevent the salt water intrusion divided the whole lake into two parts, viz., north and south. The bund remains closed during summer time (December to March months). Thus, the northern part is brackish and southern part of the lake is freshwater dominated (Nath et al., 2000). Four major rivers (Manimala, Meenachil, Achankovil and Pamba) discharge fresh water in the southern part of the lake, whereas several rivers (Periyar, Pullo, Chalakudi, Muvattupuzha, Ittupuzha and Kari) discharge in the northern part of the lake.

The surface salinity at location close to the bar mouth opening to the sea ranges from fresh-water condition (during S-W monsoon, June to September) to 34‰ (during inter-monsoon, October to May) (Verma and Subramanian 2002). The average salinity of southern part of the lake reduced from 23 ‰ to 2.8 ‰ due to building of Thannirmukkam bund. Average value of dissolved oxygen (DO) at surface

during pre-monsoon time remains high at ~ 5 mg/l and pH varies from 5.86 to 8.91 (Nasir, 2010). Sediments undergo periodic anoxia ($Eh \approx -242$ to -160 mV) below an oxygenated water column (Gireeshkumar, 2013). Very high concentration of Chlorophyll-a was reported from Cochin estuary due to additional input of nutrients due to anthropogenic activity. The fresh water discharge through the rivers is maximum during monsoon ($1346 \text{ m}^3\text{s}^{-1}$) and totaling to $22.41 \times 10^3 \text{ Mm}^3 \text{ yr}^{-1}$ (Revichandran et al., 2011). Very high sedimentation rate ($\sim 0.5 \text{ cm.yr}^{-1}$) is reported from this lake (Nasir, 2010) due to deposition of huge amount of sediment brought by rivers ($3,29,106 \text{ t.yr}^{-1}$, Thomson 2002). Southern part of the lake is reclaimed for agricultural practice and has been intensely cultivated, whereas the northern part of the lake is mostly urbanized. Twenty five stations covering most part of the lake (**Fig. 1**) were selected for this study. Sediment sampling was carried out using Van Veen grab during the month of March-April, 2012 (the bund was closed during the sampling time). Top layer from the sediment-water interface was transferred to plastic bags, sealed and preserved in frozen condition until further analysis.

2.2. *Sediment texture and size separation*

Oven dried bulk sediments were sieved using $63 \mu\text{m}$ mesh size. The sediment retained on $63 \mu\text{m}$ sieve was oven dried. The lithogenic fraction (carbonate and OM free) of silt and clay sized sediments ($< 63 \mu\text{m}$ fraction) were further analyzed for texture with a laser particle size analyzer (Malvern Mastersizer 2000; Ramaswamy and Rao, 2006).

Sediments were separated into 4 size fractions viz., clay ($< 2 \mu\text{m}$), finer silt ($2-25 \mu\text{m}$), coarser silt ($25-63 \mu\text{m}$) and sand fraction ($> 63 \mu\text{m}$) to investigate the composition and source of OM present associated with each size fraction. Sediments were wet sieved through $63 \mu\text{m}$ sieve to separate sand ($> 63 \mu\text{m}$) and silt+clay fraction ($< 63 \mu\text{m}$). All the clay-sized sediment ($< 2 \mu\text{m}$) was separated from the $< 63 \mu\text{m}$ fraction following standard pipette analyses technique (Folk, 1980) by repeated collections. The remaining suspension consisting of particle size $2-63 \mu\text{m}$ was again sieved through $25 \mu\text{m}$ sieves for separating particles of $2-25$ and $25-63 \mu\text{m}$ size. All the samples were dried in hot air oven at 35°C , ground in agate mortar and stored in plastic vials until further analysis.

2.3. *OC and TN determination*

Both bulk and size fractionated samples were analyzed for total carbon (TC), total inorganic carbon (TIC), and total nitrogen (TN) contents. TC and TN in sediments were determined using Flash 2000 CHN-elemental analyzer (Thermo Fisher Scientific Incorporation). Precision of the analysis was within $\pm 5\%$. Soil NC ($0.37\% \text{ N}$ and $3.5\% \text{ C}$) was used as certified reference material. TIC was determined by

coulometry (UIC coulometrics). Calcium carbonate (12% C) was used as standard material. Relative standard deviation of the analysis was within $\pm 2\%$. Total organic carbon (OC) was derived from deducting TIC from TC.

2.4. *Stable isotopes of C and N in organic matter*

Subsamples of sediments for $\delta^{13}\text{C}_{\text{org}}$ contents were acidified with HCl (10%) to remove carbonates (Schubert and Nielsen, 2000). The dried and grounded samples were then used for carbon isotope analysis. Untreated samples were used for N isotope analysis. Analysis was performed with the Thermo Finnigan Flash 1112 elemental analyzer, linked with a Thermo Finnigan Delta V plus IRMS at CSIR-NIO. Calibration was carried out using IAEA grade standards Sucrose ($\delta^{13}\text{C} = -10.449\text{‰}$) and Ammonium Sulphate ($\delta^{15}\text{N} = 20.3\text{‰}$) for stable isotope analyses of carbon and nitrogen respectively. Stable isotopic ratio of OC and TN were represented using delta notation relative to standard as,

$$\delta^{15}\text{N or } \delta^{13}\text{C}_{\text{org}}(\text{‰}) = \frac{(R_{\text{sample}} - R_{\text{standard}})}{R_{\text{standard}}} \times 1000$$

where R represents $^{13}\text{C}/^{12}\text{C}$ for C isotopes and $^{15}\text{N}/^{14}\text{N}$ for N isotopes, the standard is PDB for $\delta^{13}\text{C}_{\text{org}}$, and atmospheric N_2 was used as standard for $\delta^{15}\text{N}$. The overall analytical precision for replicate samples was within $\pm 0.2\text{‰}$ for $\delta^{13}\text{C}_{\text{org}}$ and $\pm 0.1\text{‰}$ for $\delta^{15}\text{N}$.

2.5. *Determination of major elements*

The dried and finely ground sediments were analyzed using X-ray Fluorescence Spectrometer (XRF, PANalytical AXIOS) to determine Al and Si concentration in sediments. The accuracy of the analyses, determined using the USGS geochemical reference material QLO-1B, is ± 0.44 and 0.71% for Al and Si respectively. The detailed procedure of sediment preparation is described elsewhere (Kurian et al., 2013).

2.6. *Mixing calculations using end-member values: Quantifying OM contribution from different sources*

The relative contribution of OM from fresh water phytoplankton, terrestrial C3 plants, marine OM ($\text{OM}_{\text{marine}}$) and soil OM (OM_{soil}) was calculated by using 4 end member mixing model following isotope mass balance equation of

$$\delta^{13}\text{C}_{\text{org(Sample)}} = f(\delta^{13}\text{C}_{\text{org}})_{\text{C3}} + f(\delta^{13}\text{C}_{\text{org}})_{\text{OMsoil}} + f(\delta^{13}\text{C}_{\text{org}})_{\text{OMmarine}} + f(\delta^{13}\text{C}_{\text{org}})_{\text{freshwater phytoplankton}} \quad (1)$$

$$\text{and } f_{\text{C3}} + f_{\text{SOM}} + f_{\text{MOM}} + f_{\text{freshwater phytoplankton}} = 1 \quad (2)$$

It is important to note that most of the drainage basin has been found to be dominated only by C3 plants (supporting materials, Fig 1). Thus, terrestrial C4 end-member was not considered during the source contribution calculation.

IsoSource (v 1.3) package was used for calculating the relative contribution from each source (Philips and Gregg 2001). The $\delta^{13}\text{C}_{\text{org}}$ values of -29.1, -25.9, -20 and -31.5 ‰ were considered as end-member values for terrestrial C3 plant, OM_{soil} , $\text{OM}_{\text{marine}}$ and freshwater phytoplankton respectively from literature (Pradhan et al. 2014; Sarma et al. 2014) in this study.

3. Results and Discussion

3.1. Particle size distribution of sediments from Vembanad Lake:

Table 1 shows the variation of surface sediment texture in the Vembanad Lake. The texture of the studied sediment was found to be highly variable across the lake. Similar observation has been reported by Renjith and Chandramohanakumar (2007). They have identified hydrodynamics of Vembanad Lake as the controlling factor for such textural variation. Station-wise distribution of silt-clay fraction is shown in **Fig. 2a**. Finer sediments were found to dominate in both north and southern part of the lake with a distinct coarsening on either side of the bund. The finer sediment dominated most of the southern part of the lake was probably due to the lithology of the drainage basin (Veerayya and Murty 1974; Laluraj et al. 2008) and the influence of agricultural practices near the lake. Veerayya and Murty (1974) have found that high currents prevent finer particles deposition near the western bank of the lake. Finer sediments were found to dominate at the middle of the estuary. It is well known that flocculation of suspended particulate matter dominates at the middle of an estuary due to mixing of freshwater with sea water and was probably responsible for the high finer particles content (Veerayya and Murty 1974; Laluraj et al. 2008).

Al/Si ratio was found to strongly correlate with sediment texture, implying influence of hydrodynamic sorting on sediment texture (**Table 1**). Al/Si ratio, which is also an index of surface area (Galy et al., 2007) was found to vary (**Fig. 2b**) similarly with sediment texture as coarser particles have lesser surface to volume ratio than the finer ones. Coarser particles were found to dominate in either side of the bund. The prevailing depositional environment which flushes away finer particles towards the northern side of the lake was probably responsible for higher coarser particles content in the sediments.

3.2. *Distribution of OC and TN in surface sediments:*

Table 1 shows the distribution of OC, TN content in the studied sediments. The OC concentrations in the sediments varied from 0.25 to 4.49 % (wt. %) with an average of 2.05 %. Higher OC content (avg. 2.21 %) was found in the sediment collected from the southern part of the lake compared to northern part (avg. 1.80 %). Thomson (2002) has reported that this lake receives enormous amount of lithogenic material (3,29,106 t.yr⁻¹), from the adjacent watershed, leading to clastic dilution which may lower the OC concentration in this tropical eutrophic lake (Verma et al. 2002; John et al. 2009).

TN concentration in sediments ranged from 0.02 to 0.39 % (with an avg. of ~ 0.17 %) and were closer to the values reported in literature (Verma and Subramanian 2002; Gireeshkumar et al. 2013). It is interesting to note that though the sedimentary OC content varied significantly between northern and southern part of the lake, not much variation was found in TN content of the sediments (with an avg. 0.16 and 0.17 % in north and south respectively). Strong positive correlation between OC and TN (**Fig. 3**; $R^2=0.95$, $p<0.001$, $n=25$) suggest that most of the TN was associated with OC and can be considered as a measure of organic nitrogen (Paropkari et al. 1987; Liu et al. 2006; Kurian et al. 2013; Gireeshkumar et al. 2013). The OC determined in the studied sediments were further considered as a good representative of sedimentary organic matter (SOM).

3.3. *Source and nature of SOM in Vembanad Lake*

C:N_{molar} ratio, $\delta^{13}\text{C}_{\text{org}}$ and $\delta^{15}\text{N}$ were used to understand the sources of SOM in Vembanad Lake. It is well documented that non-vascular marine phytoplankton is enriched in $\delta^{13}\text{C}_{\text{org}}$ (ranging from -22 to -19 ‰), $\delta^{15}\text{N}$ (ranging from 6-9‰) and nitrogen (C:N_{molar} ratio of 5-6) (Bordovskiy 1965a; b; Currin et al., 1995; Cifuentes and Eldridge 1998; Jia and Peng 2003; Gearing 2013.). The terrestrial higher vascular plants (C3 and C4) has been reported to contain less amount of nitrogen with C:N_{molar} ratio varying from >12-14 and $\delta^{15}\text{N}$ of 1.8 to 3.5‰ (Bordovskiy 1965b; Prahel et al. 1994; Thornton and McManus, 1994). The $\delta^{13}\text{C}_{\text{org}}$ ratio of terrestrial higher C3 plants have been reported to vary from -30 to -23 ‰, whereas C4 plants have a $\delta^{13}\text{C}_{\text{org}}$ of -17 to -9‰ (Smith and Epstein 1971; O'Lery 1988; Pancost and Boot 2004). The C:N_{molar} ratio in SOM was found to be 10.77 near the Cochin bar mouth which gradually increased to 15.70 near the Thannirmukkam bund (**Fig. 4a**). The ratio varied from 12.44 to 17.12 in the sediments from southern part of the lake. However, there was no spatial trend observed. Lower C:N_{molar} ratio of 10.77 near Cochin bar mouth clearly indicates dominance of in-situ marine phytoplankton production, whereas higher C:N_{molar} ratio of 15.70 near bund indicates terrestrial dominance. Gradual increase of

marine influence towards bar mouth is reflected by decreasing C:N_{molar} ratio (Chakraborty et. al. 2015b and references therein). The higher C:N_{molar} ratio from southern part of the lake (ranging from 12.44 to 17.12; avg. 14.76) indicates the dominance of OM_{terr}. Very similar values have been reported in SOM collected from other lakes dominated by OM_{terr} input (Meyers and Ishiwatari 1993; Meyers and Lallier-Vergès 1999). Source of OM from studied sediments were further confirmed using $\delta^{13}\text{C}_{\text{org}}$ and $\delta^{15}\text{N}$.

A wide range of $\delta^{13}\text{C}_{\text{org}}$ was observed in SOM collected across the Vembanad Lake (-20.13 to -27.19 ‰, Table 1). Table 1 indicates that there was contribution of OM from different sources (**Fig 4b**). The enriched $\delta^{13}\text{C}_{\text{org}}$ value (-20.13 ‰) indicates marine derived OM in sediments near the Cochin bar-mouth (see also Gireeshkumar et. al. 2013) which became increasingly lighter (-26.81‰) near the Thannirmukkam bund. Lighter $\delta^{13}\text{C}_{\text{org}}$ values (ranging from -24.96 to -27.19 ‰; avg. -25.99 ‰) in the southern part of the lake indicate terrestrial in nature. However, the most common and intensively cultivated crop in this area is rice (**SM Fig. 1**), which comes under C3 type of vegetation. Also, measured sedimentary $\delta^{13}\text{C}_{\text{org}}$ values are too depleted to consider C4 vegetation as a potential contributor to SOM. Thus, C3 type vegetation and OM_{soil} were the most possible sources of SOM in the southern part of the lake. A scatter with a significant spread in C:N_{molar} ratio against $\delta^{13}\text{C}_{\text{org}}$ (**Fig. 5**) in sediments from southern part of the lake suggests that there was contribution of OM_{terr} from different sources (with range of C:N_{molar} ratio).

The $\delta^{15}\text{N}$ values in the studied sediments were found to vary from 0.97 to 9.85 ‰ (**Table 1**) in the northern part of the lake. An enriching trend of $\delta^{15}\text{N}$ values was observed towards the sea. The $\delta^{15}\text{N}$ values in the sediments collected from the southern part of the lake were found to vary from ~1.07 to 7.24‰ with no spatial trend. The large variation in $\delta^{15}\text{N}$ values in sediments from the northern part of the lake (0.97 to 9.85 ‰) suggests that there was an admixture of marine and terrestrial OM. A strong positive relation of $\delta^{15}\text{N}$ with $\delta^{13}\text{C}_{\text{org}}$ ($r=0.93$, $p<0.001$, **SM Table 1**) suggests that the source signatures are not altered (Kurian et al., 2013 and references therein). Enriched values of $\delta^{15}\text{N}$ towards the northern part of the lake were mainly due to increasing marine influence. The lower $\delta^{15}\text{N}$ values were found in the sediments collected close to the Thannirmukkam Bund and near river mouth which are dominated by terrestrial input. Though the OM in sediments from southern part of the lake is predominantly contributed from terrestrial sources, the $\delta^{15}\text{N}$ values were relatively higher ($\delta^{15}\text{N} \sim 1.07$ to 7.24 ‰, avg. 4.69 ‰), possibly because of the presence of OM_{soil} (~5‰, Cohen 2003; Pradhan et al. 2014). OM_{soil} was estimated to be ~ 32% of total SOM in south (discussed later). Surface run off from the extensively

cultivated areas in the watershed also probably introduced huge amount of OM_{soil} to the southern part of the lake.

3.4. *Textural control on SOM distribution:*

Sediment texture is considered to play a major role in controlling SOM concentration (Chakraborty et al, 2012; 2014, 2015a, 2015b, 2015c) . A significant positive correlation ($R^2=0.88$, $p<0.001$, $n=25$) was observed between the OC and silt + clay (finer fraction) content in the studied sediments (**Fig. 6a**). This study indicates that texture of sediments, controlled by hydrodynamics, primarily control SOM distribution in the Vembanad Lake. The finer fractions which have higher surface area and similar hydraulic equivalence to organic particles leads to increased adsorption of SOM on them (Hedges and Keil 1995; Cotano and Villate 2006; Ramaswamy et al. 2008). Degree of correlation between OC and finer particles was different in two areas; much stronger in the northern part of the lake ($R^2=0.95$, $p<0.001$, $n=10$) compared to southern part ($R^2=0.83$, $p<0.001$, $n=15$) (**Fig. 6b and 6c**). This may be due to different biochemical reactivity of OM_{terr} and OM_{marine} toward the finer particles of the sediments (Bordovskiy, 1965a). It was found that the OM_{marine} was more labile and reactive than OM_{terr} and were readily adsorbed on the finer sediment particles. The similar observation has also been reported in literatures (Paropkari et al. 1987; Hedges and Keil 1995; Hedges et al. 1997). TN in sediment was also found to show strong positive correlation with finer particles ($r=0.92$, $n=25$, $p<0.001$) along the study area (**SM Table 1**). Nitrogen being reactive was probably readily adsorbed on the finer lithogenic particles and showed a strong positive correlation.

3.5. *Relative content and source of SOM in different size fractions*

To study the nature of SOM in different size fractions and their influence on bulk sediments, we carried out OC, TN, $\delta^{13}C_{org}$ and $\delta^{15}N$ analysis in different size fractions of the studied sediments. Relative content of OC and $\delta^{13}C_{org}$ in different size fractions are plotted in **Fig. 7a and b respectively**.

Clay-sized fraction: Clay fraction ($<2 \mu m$) was found to have highest concentration of OC, TN and most enriched in $\delta^{13}C_{org}$ and $\delta^{15}N$ (**SM Table 2**). It was found that 50% of the total OC and 60 % of TN was contributed from this fraction. It contributes the highest OC and TN to the bulk concentration. Clay fraction being of smallest size provides more surface area for adsorption of OC (e.g., Hedges and Keil 1995; Bergamaschi et al. 1997). Strong positive and linear correlation ($R^2=0.84$, $p<0.001$) between OC and TN in this size fraction (**Fig. 8**) indicates organic origin of nitrogen. Clay fraction in the northern part of the lake showed significant variation in $\delta^{13}C_{org}$ and C:N_{molar} (ranging from ≈ -20 to -25 ‰ and \approx

7 to 16 respectively). Enriched $\delta^{13}\text{C}_{\text{org}}$ value of -20 to -21‰ with low C:N_{molar} (\approx 7-8) might be due to presence of nitrogen rich marine phytoplankton produced OM. The OM_{marine} is more reactive and has affinity for adsorption on finer particles (Bird et al., 2003). The OM in this fraction from southern part of the lake was also rich in nitrogen (N:C_{molar} \approx 0.07 to 0.10, avg. 0.08) as well as in $\delta^{15}\text{N}$ (5.5 to 7 ‰, avg. 6.18 ‰), but depleted in $\delta^{13}\text{C}_{\text{org}}$ (-25 to -26 ‰, avg. -25.8 ‰), which may indicate the presence of aged and humified OM_{soil} (Prahl et al. 1994; Hedges et al. 1997; Cohen 2003). Very similar observation has been reported for OM_{soil} from west coast of India ($\delta^{13}\text{C}_{\text{org}}$ and N:C_{molar} ratio \sim -25.9 ‰ and 0.08 respectively - Pradhan et al. 2014). Support for OM_{soil} comes from a discrimination plot of $\delta^{13}\text{C}_{\text{org}}$ versus N/C_{molar} ratio of <2 μm fraction (**Fig 9**; in the fields defined by Keil et al. 1994), which shows that the data of sediments from southern part of the lake distinctly fall in the field of OM_{soil}. However, the nature of SOM gradually changed towards northern part of the lake from OM_{soil} to OM_{marine}. This observation suggests that there was increased OM_{marine} input towards the stations close to barmouth. The presence of OM_{soil} in bulk sediments from southern part and its gradual absence in northern region seems to be related to the land use pattern. Most of the watershed area near northern part of the lake is largely devoid of agricultural practice in contrast to intensely cultivated southern region.

Fine silt fraction (2-25 μm) contributed lesser OC (Fig. 9a), TN (\approx 32 and 40 ‰, respectively) and exhibited lighter $\delta^{13}\text{C}_{\text{org}}$ and $\delta^{15}\text{N}$ (**SM Table 2**) than clay fraction (<2 μm). In this fraction however, a larger spread in TN at higher OC concentration was noticed (**Fig. 10**), possibly because of the contribution of OM from various sources. Both the finer silt and clay fractions in the southern part of the lake had lighter $\delta^{13}\text{C}_{\text{org}}$, whereas, the finer silts in the northern part of the lake was distinctly depleted than clays. Thus, the depletion of $\delta^{13}\text{C}_{\text{org}}$ with elevated C:N_{molar} ratio and lower $\delta^{15}\text{N}$ over clay-size especially in the northern part, may indicate higher contribution of OM_{terr} in this fraction.

Coarser silt (25-63 μm) contributed only \sim 18% to the bulk sedimentary OC concentration. This fraction was also depleted in $\delta^{13}\text{C}_{\text{org}}$ and $\delta^{15}\text{N}$ (-24 to -27 ‰ 0.88 to 4.7 ‰ respectively; **SM Table 2**). This fraction could host coarse woody OM_{terr} which is isotopically lighter (e.g., Harmon 1972), and thus OM in this fraction of the studied sediment was mainly from terrestrial origin. The OC concentration was below the detection level in sand fraction (> 63 μm), thus they did not contribute to the sedimentary OC pool.

From the above discussion it is clear that the finer clay fraction ($<2 \mu\text{m}$) hosted highest amount of OC (~50%). However, importantly significant amount of OC was found in the finer and coarser silt fractions as well. Hence their role in sedimentary OC cycling in coastal environments cannot be ignored.

3.6. End-member mixing – Quantifying the terrestrial OM component

The end-member mixing model was used to quantify the OM contribution from different sources on the total OM of the studied sediment. The model showed that there was significant variation in the proportion of OM contribution from different sources into the studied sediments from north and southern parts of the lake. Two significant differences are clearly discernable; sediments collected from the northern part of the lake was rich in marine organic matter (as discussed earlier) whereas, the sediments collected from the southern part of the lake had higher terrestrial carbon dominated by OM_{soil} . In the northern area, the contribution from $\text{OM}_{\text{marine}}$ varied from ~19% near Thannirmukkam bund to ~98% at northern most part (**Fig. 11**). Conversely, the contribution of OM_{terr} was very low (combined OM_{soil} and OM_{C3} was $< 2\%$) near the opening to the sea, but with a significant increase at the bund (OM_{soil} ~34% and OM_{C3} derived ~22%). Higher OM_{soil} than OM_{C3} is possibly because it is bound to clay fraction must have been transported from south. Fresh OM_{C3} is mostly bound to coarser fraction. The $\text{OM}_{\text{fresh water phytoplankton}}$ has contributed very little to SOM pool and varied from negligible at north to a maximum of ~21% near bund.

The terrestrial component ($\text{OM}_{\text{soil}} + \text{OM}_{\text{C3}}$) varied from 47 % to 60 % in the southern part of the lake. The contribution from both OM_{soil} and OM_{C3} source were nearly uniform in the south (~32 % and 22 % respectively). Though very high chlorophyll-a concentration and thick growth of macrophytes has been reported from this lake (Nasir, 2010), by far their contribution was least in studied sediments.

3.7. Historical changes: human influence on sedimentary OM distribution

Sediment texture of Vembanad Lake was studied extensively earlier by Veerayya and Murty (1974). They carried out sampling prior to the construction of Thannirmukkam bund. This bund has been reported to influence the biodiversity of the area (Arun 2006; Balachandran 2007). We compared our textural and OC data with published values before construction (i.e. prior to 1974) of bund to study the change in post bunding (after 1974) depositional environment and OC distribution if any. The OC concentrations were converted to SOM concentrations (using van Bemmelen factor of 1.724) to enable compare with the OM values reported by Murty and Veerayya (1973).

Before the construction, a large area in the southern part of the lake has been reported to dominate with silty sand. Sediments in the north- western part of the lake, mainly at the mouths of rivers has been reported to be sandy (Murty and Veerayya 1973; see **Fig. 12a** for comparison). The present study showed a significant shift in relative proportion of sand, slit and clay with time in many parts of the lake. While sandy sediments still prevail at the river mouths in the north of the lake (**Fig. 12b**). More sandy areas were added on either side of Thannirmukkam bund which were earlier flooded by silty sand probably due to amplification of tidal components (Joseph et al., 2009). Lower energy environment away from bund and increased agricultural activity (and soil erosion) in areas surrounding southern part of the lake have led to the deposition of finer particles. The increase in finer fraction (**Fig. 12c**) has a direct bearing on accumulation and preservation of sedimentary OM content.

Before construction of the bund, sediments from the southern part of the lake has been reported to contain comparatively lower SOM (data of Murty and Veerayya, 1973). Decomposition of SOM in presence of high dissolved O₂ and high temperature has been reported to be responsible for lesser concentrations of SOM in the southern part of the lake (Murty and Veerayya, 1973). An increase in SOM concentration (maximum of 3% increase) was found in the southern part of the lake in the intervening forty years period (**Fig. 13a and b**). Bunding has led to deposition of finer particles in the southern part resulting in higher SOM concentration. Not only siltation, additional input of nutrients have led to development of eutrophication of water body (Martin et al., 2010) and reducing conditions (Nath et al. 2000) as against high dissolved oxygen levels reported before (Murty and Veerayya 1973 and references therein). Increased runoff from agricultural field resulted in deposition of significant amount of OM_{soil} (as discussed earlier) in sediments which has better preservation efficiency. Thus all these anthropogenic activities have led to the increased SOM content in the southern part of the lake.

4. Conclusions

This study suggests that particle size distribution of sediment controlled the spatial distribution of SOM in Vembanad Lake. Influences of marine derived OM (OM_{marine}) on SOM decreased inner-wards in the northern part of the lake. However, SOM from the southern part of the lake was dominated by terrestrial OM (OM_{terr}). Contribution of OM from different sources to the different size fractions of the sediment indicates that adsorption of OM_{marine} in clay-sized fraction (<2 μm) of sediment from northern part led to enriched δ¹³C_{org}. Whereas, aged and humified OM_{soil} dominated the clay-sized fractions from southern part. The coarser fractions (sizes 2-25 and 25-63 μm) had lighter δ¹³C_{org} and δ¹⁵N was because of the

presence of coarse woody material. Importantly, the study showed that the non-clay size fraction also hosts a significant fraction (42-50%) of total organic carbon content in the sediments.

An attempt was made to understand the impact of Thannirmukam bund construction in controlling sediment texture across the lake (construction of bund is expected to alter the hydrodynamics in this area). Change in SOM distribution pattern in Vembanad Lake was observed by comparing after the bund construction. Alteration of texture resulted in changed SOM distribution pattern. Human intervention and land use pattern changes have resulted in higher SOM content in the sediments from southern part of the lake. Lake reclamation and intensified increased agricultural activity has led to an increase in soil erosion and deposition of finer particles rich in OM_{soil} (in south), which had a better preservation efficiency.

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Figure Captions:

Fig. 1: Map showing location of sampling stations from Vembanad Lake

Fig. 2: Spatial distribution pattern of, a) Silt+Clay (finer fraction) and b) Al/Si representing surface area.

Fig. 3: The OC vs. TN from Vembanad Lake. Strong correlation ($R^2=0.95$, $p<0.001$) between them indicates organic origin of nitrogen.

Fig. 4: Spatial variation of a) C:N_{molar} ratio and b) $\delta^{13}\text{C}_{\text{org}}$ from south to north of the lake. Gradual enrichment of $\delta^{13}\text{C}_{\text{org}}$ and lowering of C:N_{molar} ratio towards north indicates increasing dominance of marine OM.

Fig. 5: Variation of C:N_{molar} ratio against $\delta^{13}\text{C}_{\text{org}}$. Significant spread in C:N_{molar} at depleted $\delta^{13}\text{C}_{\text{org}}$ may indicate dominance of terrestrial OM (which is possibly originated from a mixture of variable $\delta^{13}\text{C}_{\text{org}}$ and C:N_{molar} ratio).

Fig. 6: Variation of OC against silt+clay fraction. Stronger correlation for sediments from northern side may be due to dominance of reactive marine OM in sediments in that area.

Fig. 7a: Organic carbon accumulation (%) in different size fractions of sediments. Though the fine clay fraction (<2 μm) had hosted highest proportion of OC, the accumulation was significant in non-clay fraction also.

Fig. 7b: The $\delta^{13}\text{C}_{\text{org}}$ variation in different size fractions of sediments. Distinct size-related changes are seen in northern sediments with finer fractions have enriched isotopic values indicating accumulation of OM from different source in different size fractions. Sediments from southern part on the other hand show uniform $\delta^{13}\text{C}_{\text{org}}$ values in all the size fractions, indicating accumulation of isotopically lighter terrestrial OM.

Fig. 8: Variation in TN with OC in <2 μm and 2-25 μm size fraction respectively. A strong positive relation is seen indicating a dominant organic source of nitrogen.

Fig. 9: The N:C_{molar} ratio versus $\delta^{13}\text{C}_{\text{org}}$ in <2 micron size fraction. Base map was adopted from Keil et al. (1994). It clearly indicates presence of soil OM in sediments from southern part.

Fig. 10: Variation in TN with OC in <2 μm and 2-25 μm size fraction respectively. A strong positive relation is seen indicating a dominant organic source of nitrogen.

Fig. 11: Relative proportion of OM from different sources using 4- end member mixing calculation of $\delta^{13}\text{C}_{\text{org}}$. Marine OM was dominant source in northern part of the lake whereas soil OM and C3 plant produced OM are dominant in southern part of the lake.

Fig. 12: Historical change in sediment texture from the study area. a) Texture reported by Murty and Veerayya (1973) of sediments collected before the construction of bund; b) and c) sand and clay distribution from the present study. A clear change in coarser as well as finer particles in areas near bund as well as southern part of the lake with time is visible.

Fig. 13: Historical change in SOM from the study area. a) OM concentration reported by Murty and Veerayya (1973) of sediments collected before the construction of bund; and b) OM distribution from the present study. The OM concentration has increased substantially (maximum of 3%) in sediments in south influenced by human induced textural changes, increased agricultural activity, bottom oxygenation changes

Table 1: Sampling location, water depth, sediment texture, TIC, TOC, TN, C:N_{molar}, $\delta^{13}\text{C}_{\text{org}}$, $\delta^{15}\text{N}$, and Al/Si ratio in the surface sediments of Vembanad Lake

Sample	Longitude (°E)	Latitude (°E)	Depth (m)	TIC (%)	TOC (%)	TN (%)	C:N _{molar}	$\delta^{13}\text{C}_{\text{org}}$ (‰)	$\delta^{15}\text{N}$ (‰)	Clay (%)	+ Silt	Sand (%)	Al/Si
North of Thannirmukkam bund													
S-1	76.3010	9.9140	5	0.20	3.62	0.39	10.77	-20.13	9.85	87.57		12.43	0.48
S-2	76.3022	9.8920	2	0.02	2.58	0.22	13.52	-22.07	7.06	71.33		28.67	0.37
S-3	76.3320	9.8790	4	0.02	1.61	0.14	13.07	-22.11	6.75	22.59		77.41	0.23
S-4	76.3395	9.8810	2	0.07	3.55	0.33	12.55	-21.29	7.04	99.35		0.65	0.49
S-5	76.3453	9.8410	2.5	0.04	0.96	0.08	13.48	-24.69	3.60	29.07		70.93	0.18
S-6	76.3705	9.8160	4	0.02	0.25	0.02	14.75	-25.29	2.86	3.65		96.35	-
S-7	76.3777	9.7430	6	0.05	0.99	0.08	15.27	-25.27	4.12	19.29		80.71	0.13
S-8	76.3761	9.7030	4	0.06	1.83	0.14	15.70	-26.81	2.06	42.72		57.28	-
S-9	76.3954	9.6910	5	0.04	2.09	0.16	15.31	-20.13	0.97	58.73		41.27	0.26
S-10	76.3958	9.6820	3	0.03	0.48	0.04	12.64	-22.07	2.48	11.98		88.02	-
South of Thannirmukkam bund													
S-11	76.3923	9.6670	1.5	0.03	0.89	0.07	14.77	-26.69	1.07	1.24		98.76	0.06
S-12	76.3875	9.6510	1.5	0.02	0.37	0.03	12.44	-26.56	1.85	4.30		95.70	-
S-13	76.3816	9.6400	2	0.02	1.53	0.13	13.37	-26.02	4.12	37.12		62.88	0.14
S-14	76.3920	9.6230	2	0.02	1.04	0.08	14.43	-25.69	3.80	24.67		75.33	-
S-15	76.4164	9.6241	1.5	0.03	2.68	0.19	16.88	-25.50	5.51	73.18		26.82	0.30
S-16	76.4203	9.6044	3	0.02	4.49	0.34	15.28	-25.57	6.11	91.09		8.91	-
S-17	76.3978	9.6037	4	0.02	2.05	0.14	17.12	-26.04	4.21	44.55		55.45	-
S-18	76.3765	9.6066	3	0.03	0.93	0.08	14.48	-25.57	4.37	21.88		78.12	0.09
S-19	76.3732	9.5860	3	0.03	1.80	0.14	15.18	-25.40	3.47	72.65		27.35	-
S-20	76.3924	9.5826	1.5	0.02	3.09	0.26	13.59	-24.96	6.06	87.49		12.51	-
S-21	76.4155	9.5820	2	0.02	1.78	0.13	15.40	-26.54	7.24	33.19		66.81	-
S-22	76.4119	9.5627	1.5	0.01	2.51	0.18	16.09	-26.53	5.67	42.28		57.72	0.24
S-23	76.3895	9.5622	3	0.01	3.67	0.31	13.85	-27.19	6.59	95.21		4.79	0.40
S-24	76.3648	9.5636	2	0.01	2.60	0.20	14.93	-25.76	6.08	77.19		22.81	0.29
S-25	76.3684	9.5396	2	0.023	3.79	0.33	13.52	-25.85	4.24	91.05		8.95	0.47

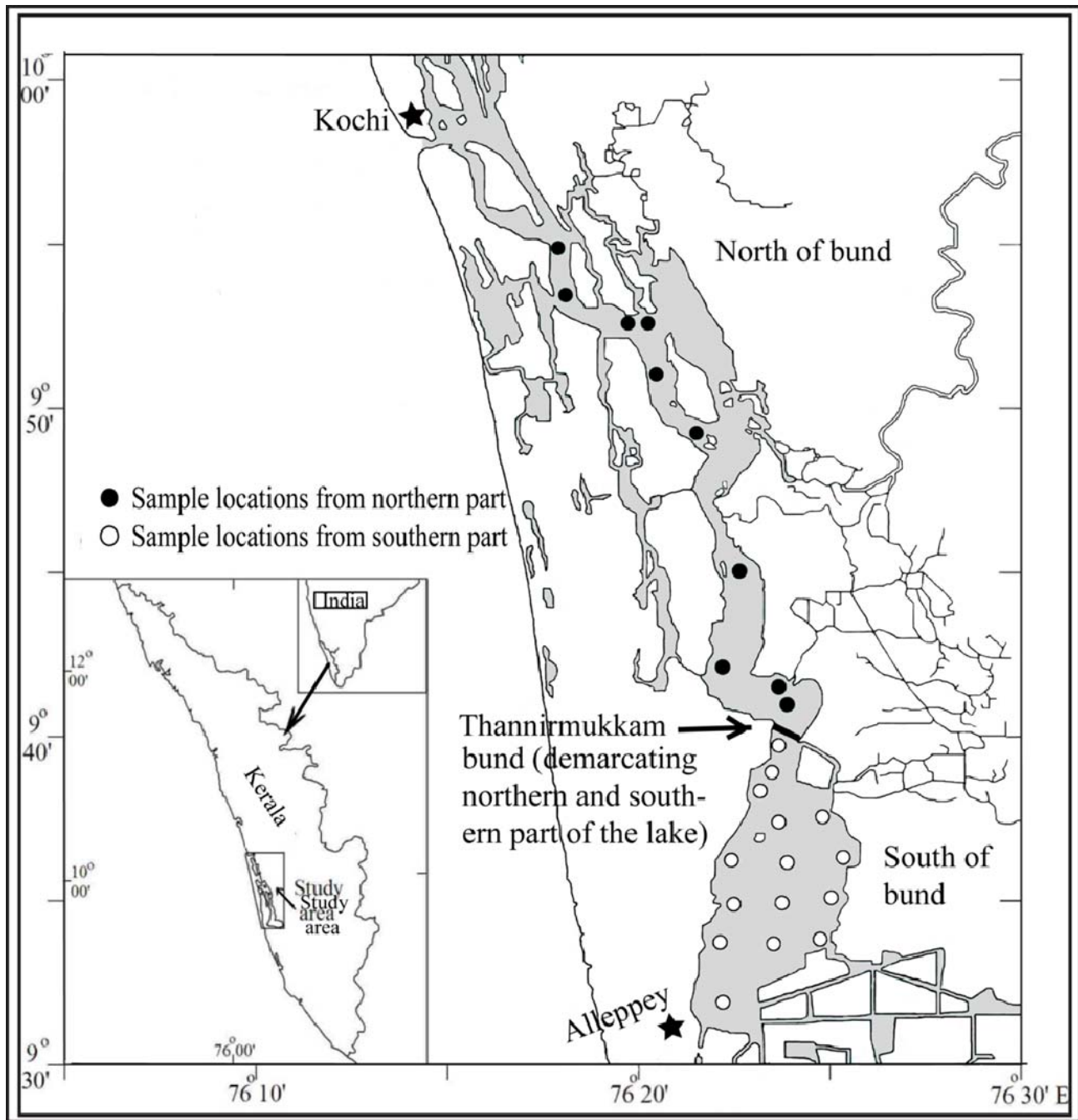


Fig. 1

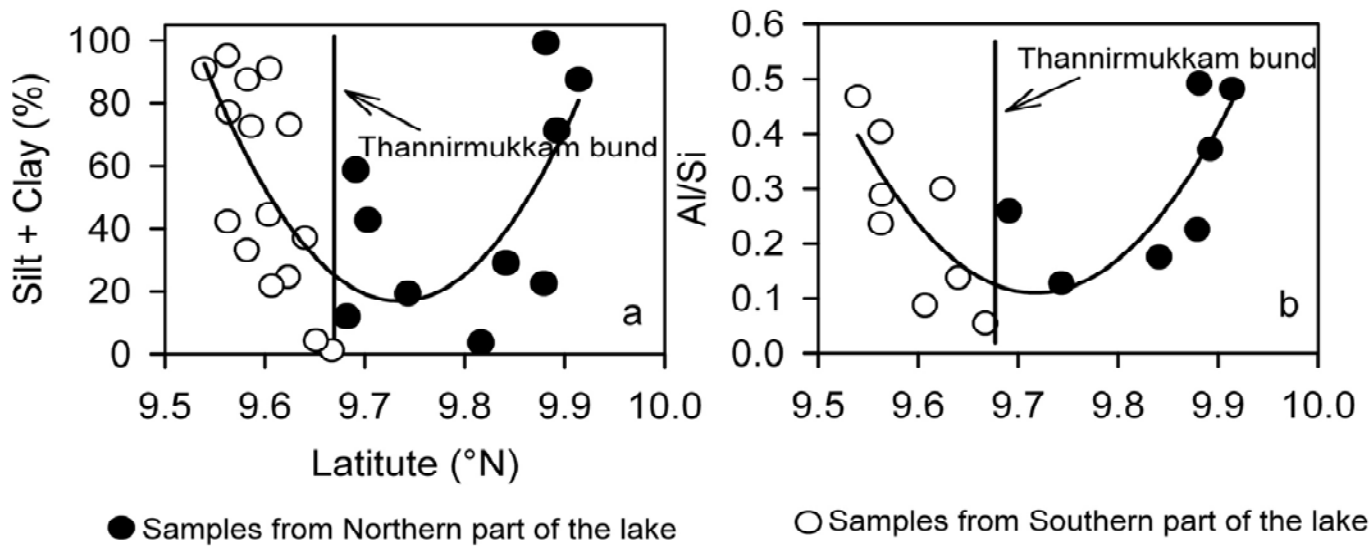


Fig. 2

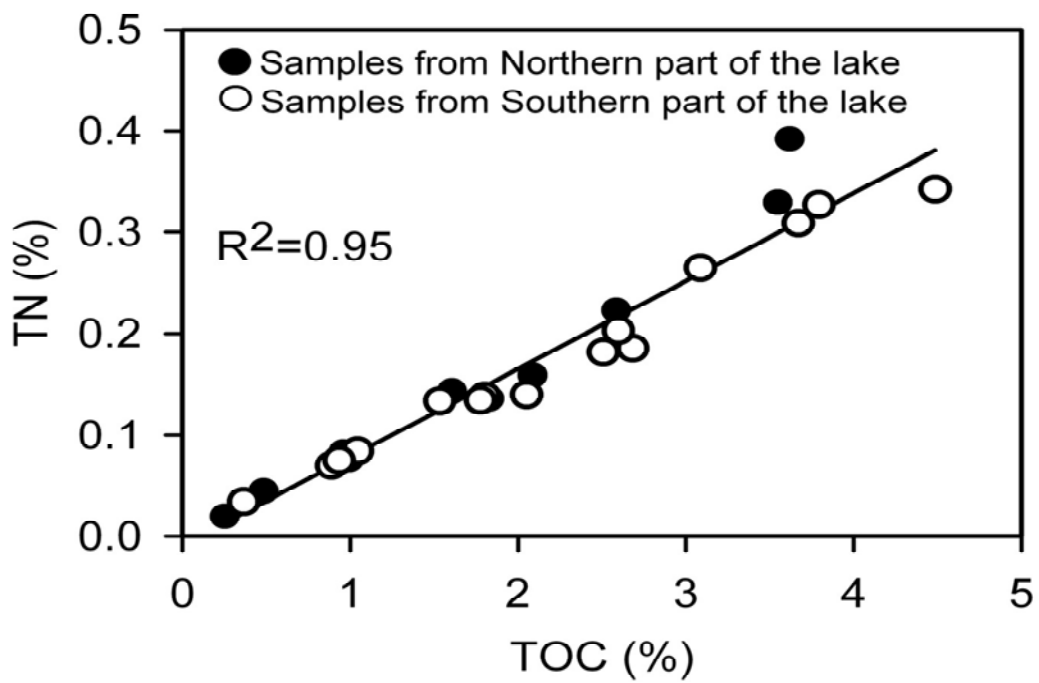


Fig. 3

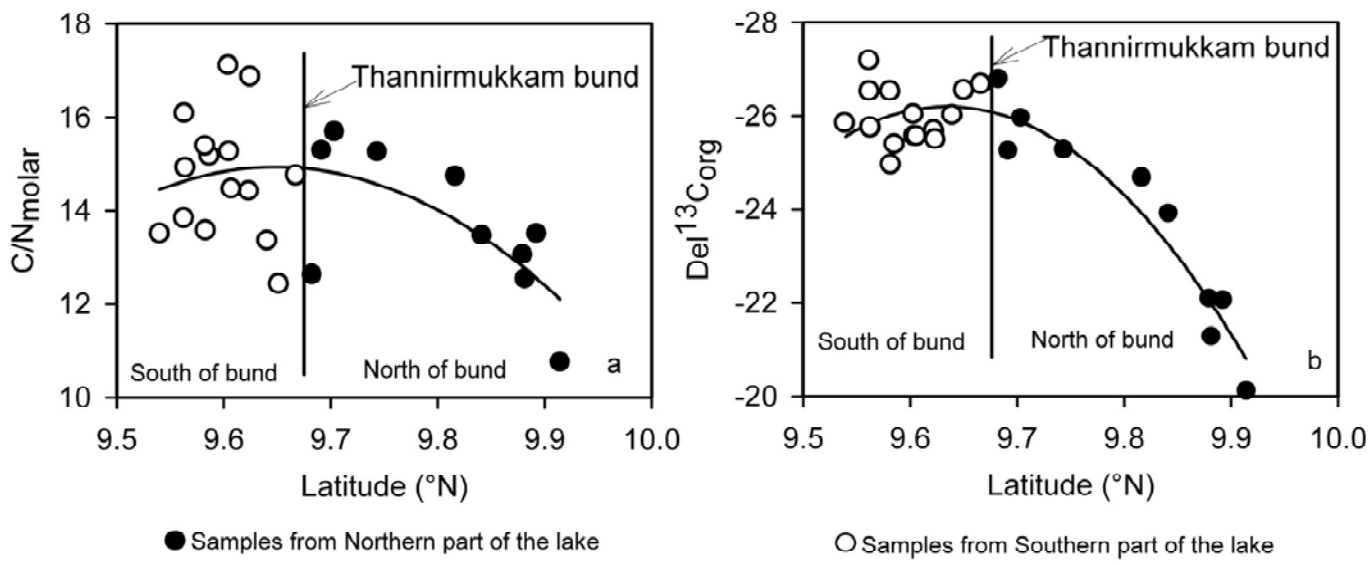


Fig. 4

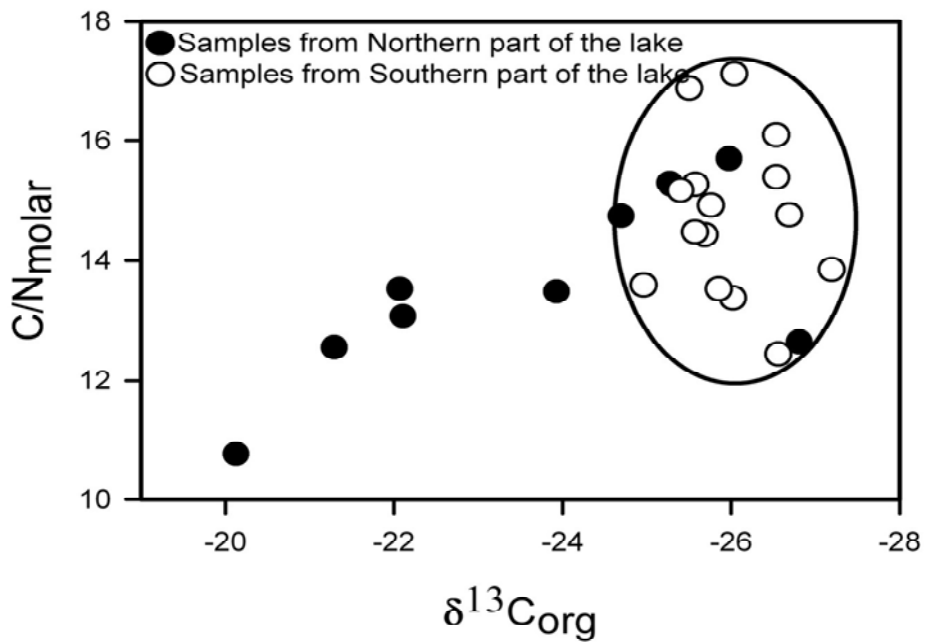


Fig. 5

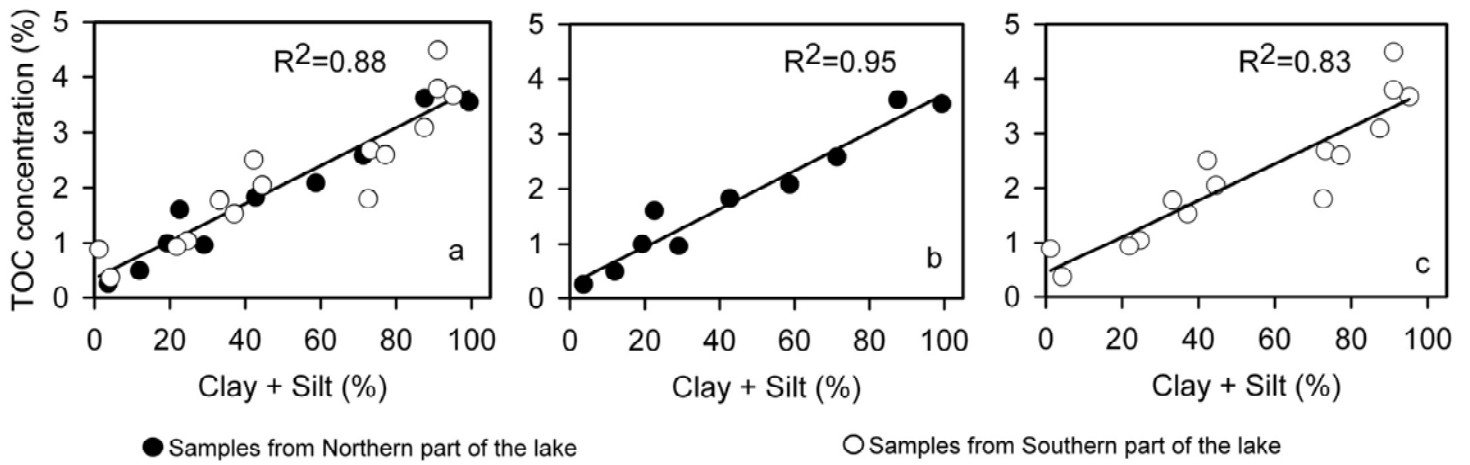


Fig. 6

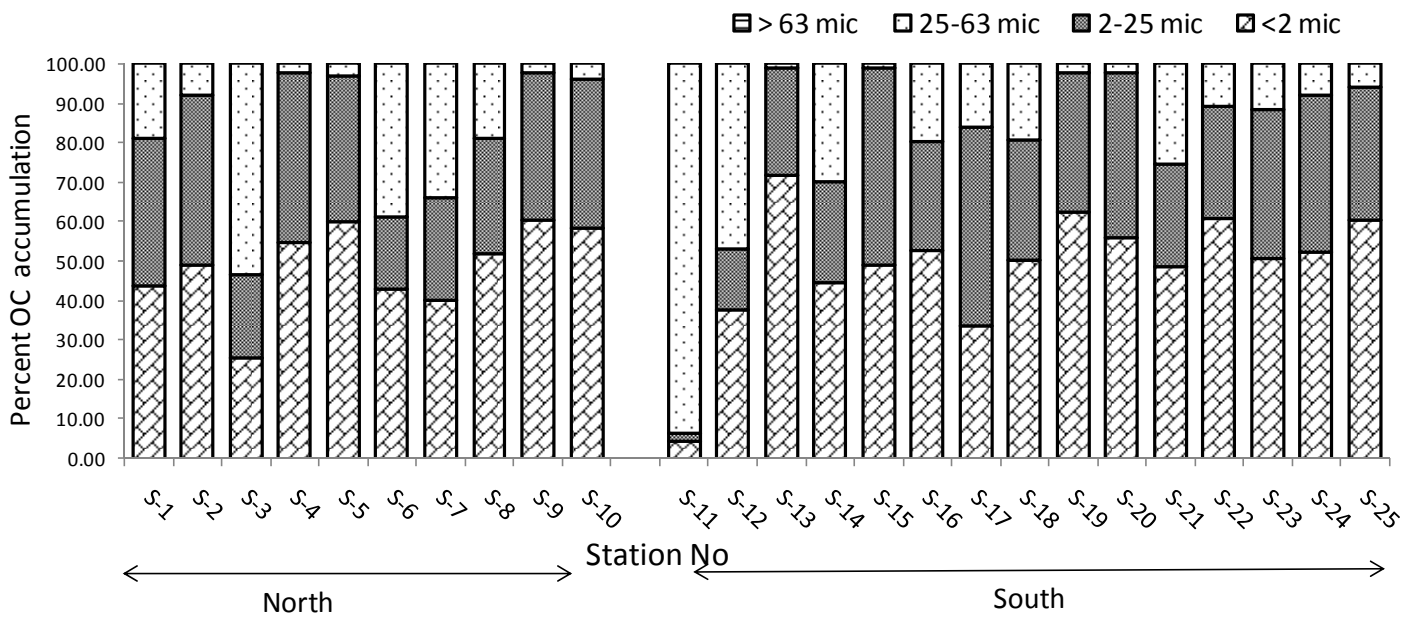


Fig. 7a

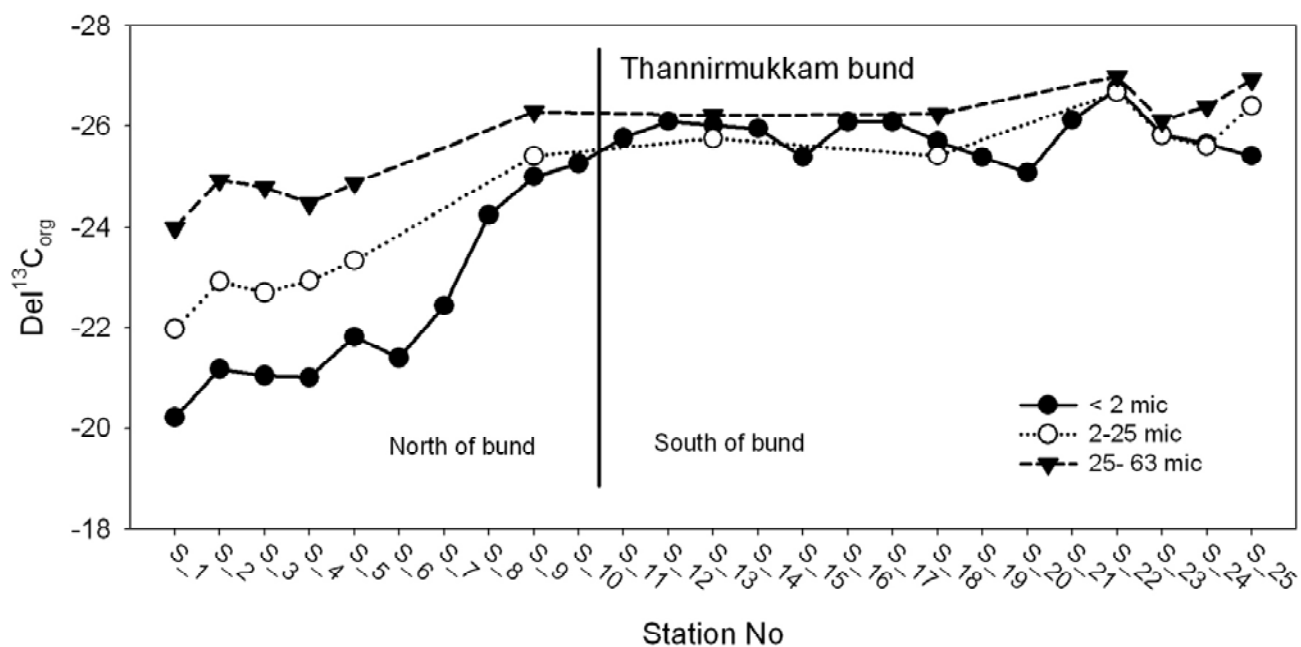


Fig. 7b

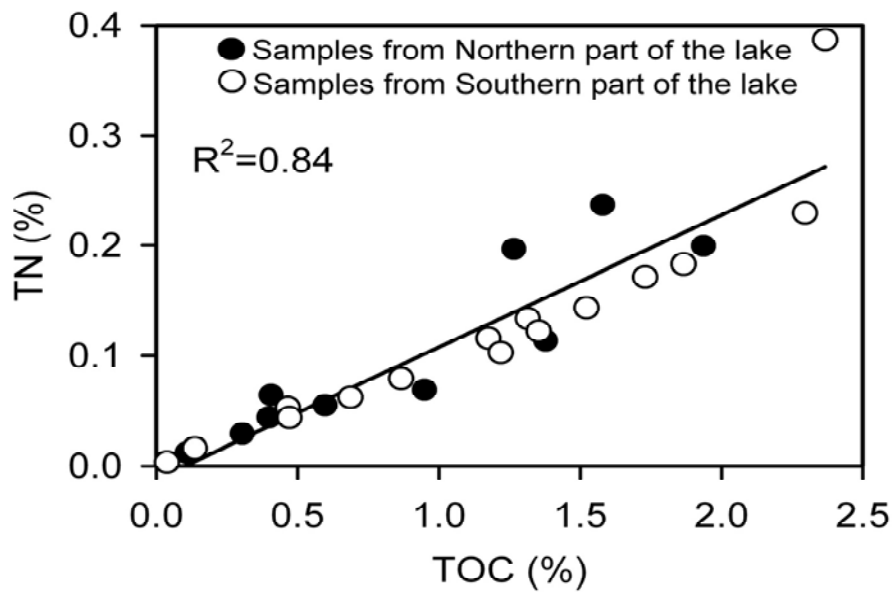


Fig. 8

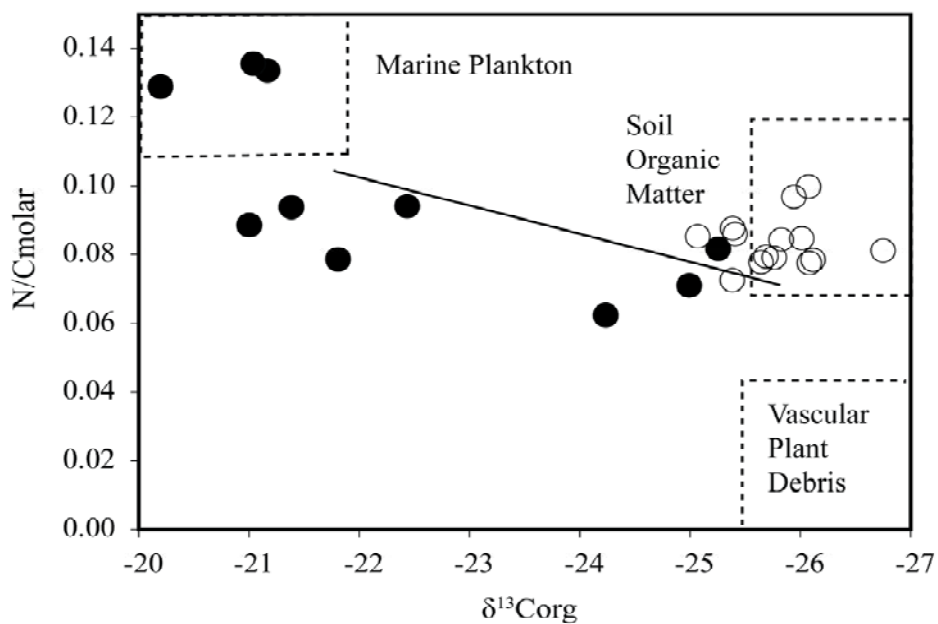


Fig. 9

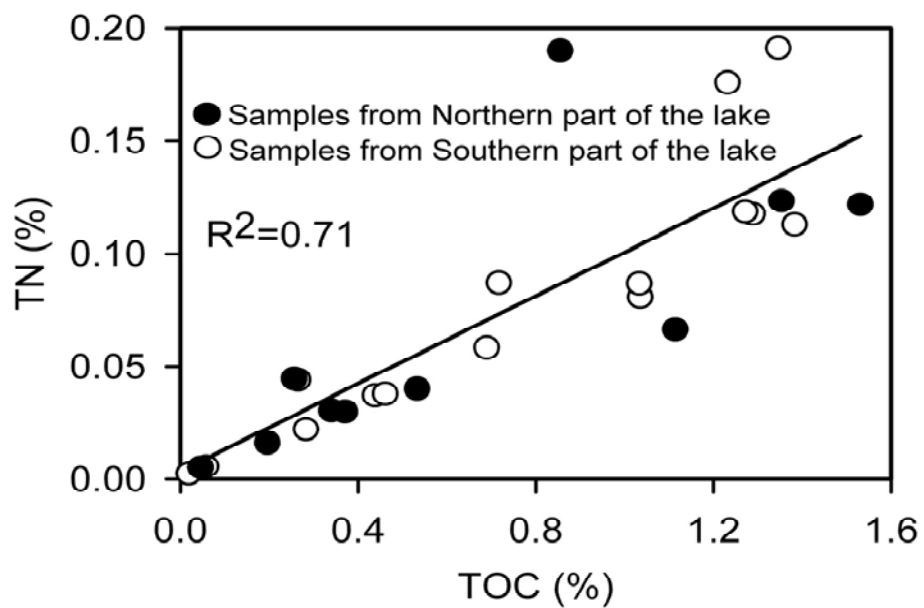


Fig. 10

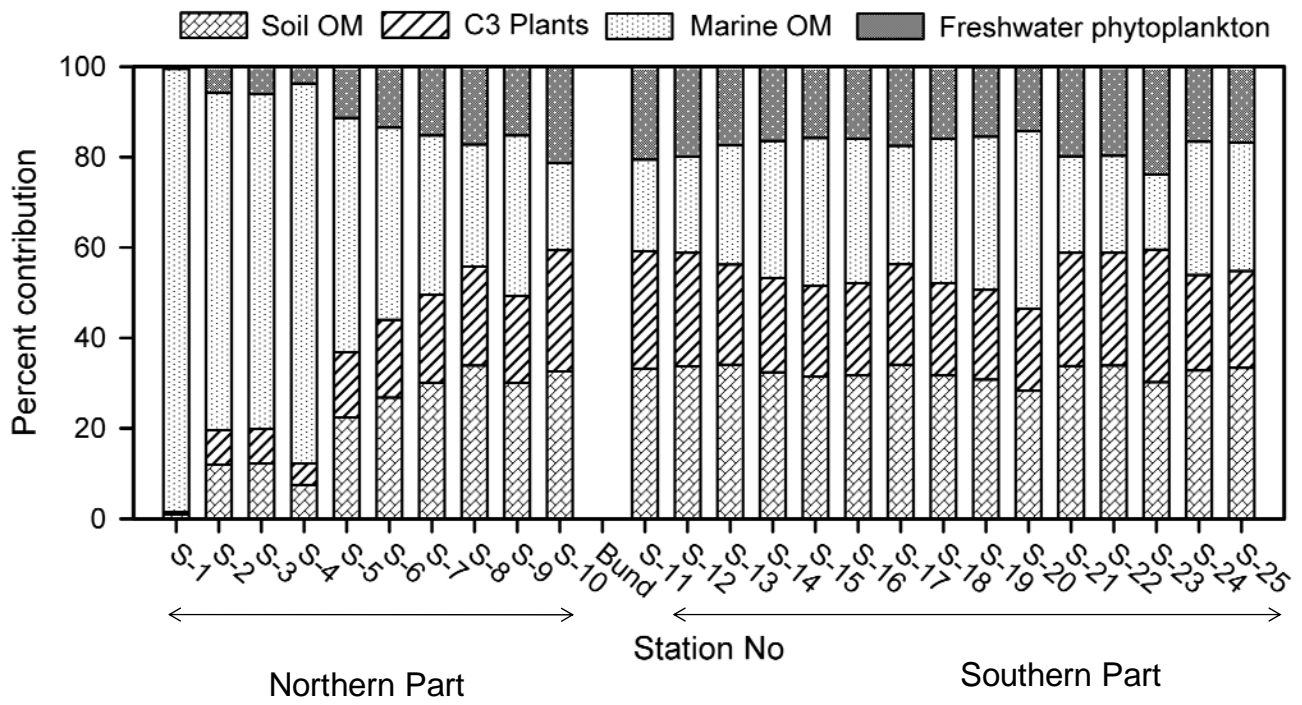


Fig. 11

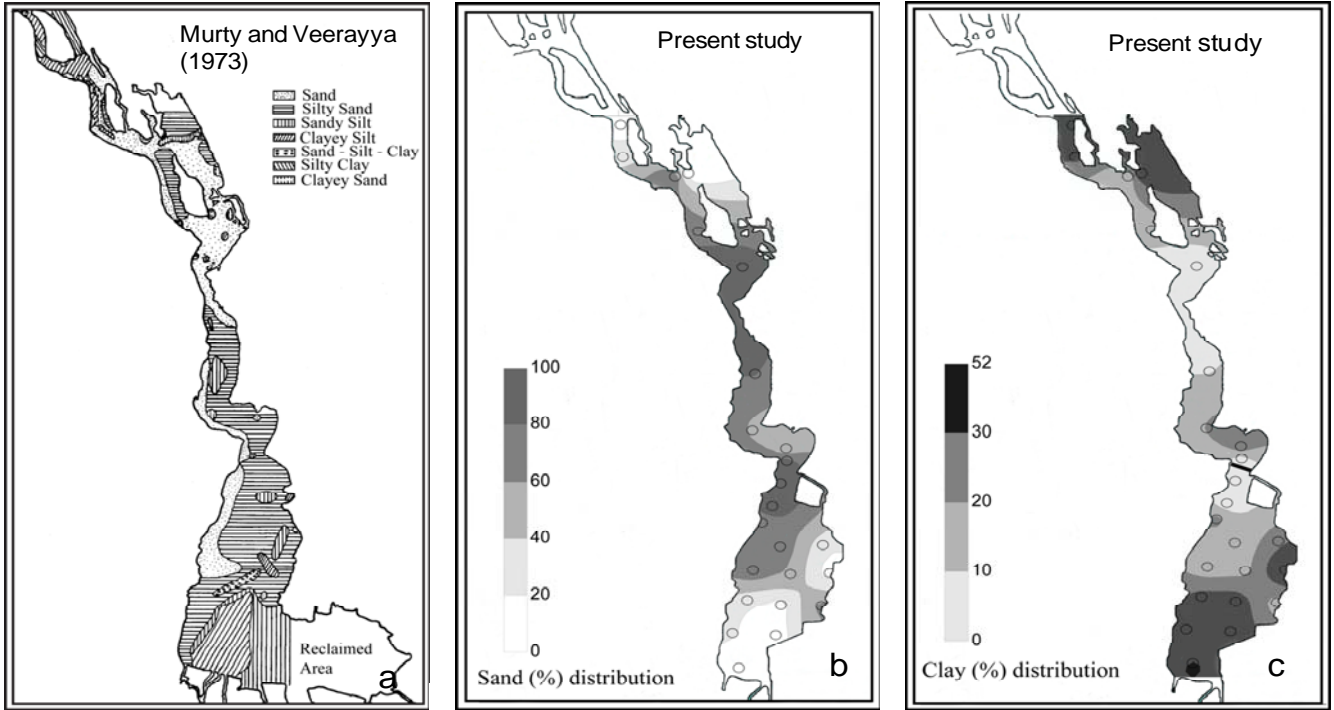


Fig. 12

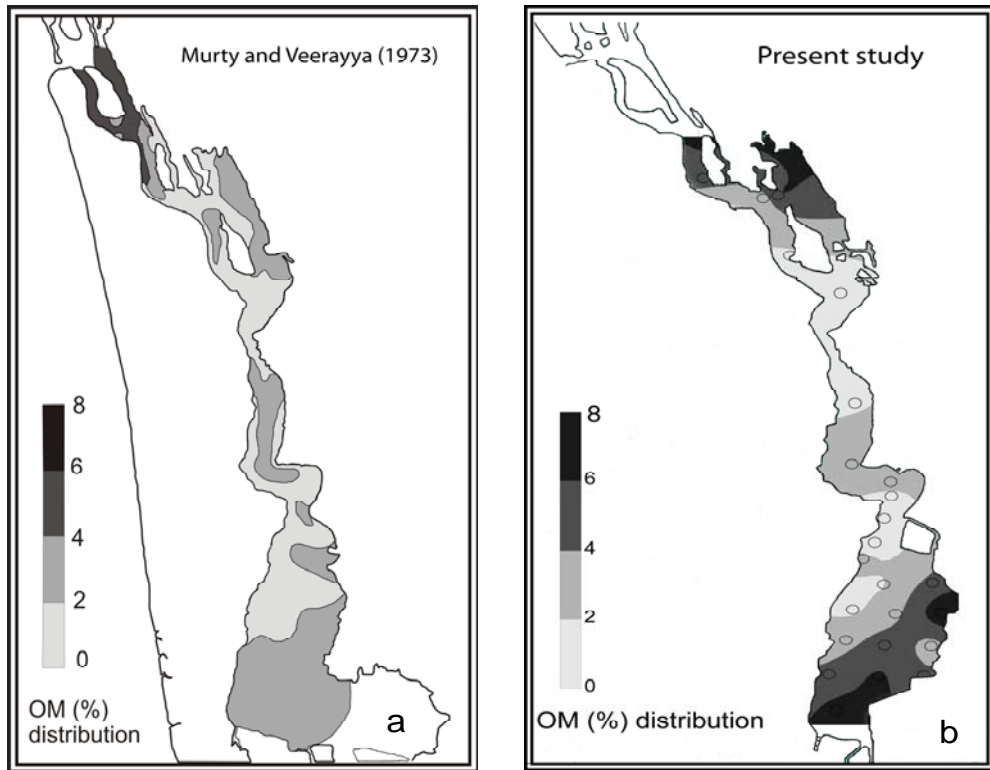


Fig. 13

Supporting materials:



SM Fig. 1: Vegetation map of Kerala showing dominance of C3 plants surrounding Vembanad Lake (source: <http://www.mapsofindia.com/maps/kerala/keralaagriculture.htm>)

SM Table 1: Pearson correlation among different parameters from a) Total- all 25 stations, b) stations only from north of Thannirmukkam Bund (10 stations) and c) stations only from south of Thannirmukkam Bund (15 stations)

a) Total

	<i>N (%)</i>	<i>TOC (%)</i>	<i>C/Nmolar</i>	<i>Del13C</i>	<i>Del15N</i>	<i>Silt+Clay (%)</i>	<i>Sand (%)</i>	<i>Si (%)</i>	<i>Al (%)</i>	<i>Al/Si</i>
<i>N (%)</i>	1.00									
<i>TOC (%)</i>	0.97	1.00								
<i>C/Nmolar</i>	-0.26	-0.05	1.00							
<i>Del13C</i>	0.42	0.27	-0.54	1.00						
<i>Del15N</i>	0.70	0.64	-0.28	0.57	1.00					
<i>Silt+Clay (%)</i>	0.92	0.94	-0.08	0.31	0.59	1.00				
<i>Sand (%)</i>	-0.92	-0.94	0.09	-0.31	-0.59	-1.00	1.00			
<i>Si (%)</i>	-0.92	-0.95	0.33	-0.41	-0.66	-0.95	0.95	1.00		
<i>Al (%)</i>	0.91	0.92	-0.40	0.47	0.64	0.93	-0.93	-0.99	1.00	
<i>Al/Si</i>	0.96	0.95	-0.46	0.48	0.65	0.94	-0.94	-0.98	0.98	1.00

b) North

	<i>N (%)</i>	<i>TOC (%)</i>	<i>C/Nmolar</i>	<i>Del13C</i>	<i>Del15N</i>	<i>Silt+Clay (%)</i>	<i>Sand (%)</i>	<i>Si (%)</i>	<i>Al (%)</i>	<i>Al/Si</i>
<i>N (%)</i>	1.00									
<i>TOC (%)</i>	0.98	1.00								
<i>C/Nmolar</i>	-0.63	-0.49	1.00							
<i>Del13C</i>	0.83	0.77	-0.70	1.00						
<i>Del15N</i>	0.78	0.69	-0.78	0.93	1.00					
<i>Silt+Clay (%)</i>	0.94	0.97	-0.44	0.69	0.59	1.00				
<i>Sand (%)</i>	-0.94	-0.97	0.44	-0.70	-0.59	-1.00	1.00			
<i>Si (%)</i>	-0.96	-0.99	0.70	-0.80	-0.64	-0.97	0.97	1.00		
<i>Al (%)</i>	0.94	0.97	-0.71	0.82	0.65	0.94	-0.94	-0.99	1.00	
<i>Al/Si</i>	0.97	0.99	-0.74	0.83	0.69	0.96	-0.96	-1.00	0.98	1.00

c) South

	<i>N (%)</i>	<i>TOC (%)</i>	<i>C/Nmolar</i>	<i>Del13C</i>	<i>Del15N</i>	<i>Silt+Clay (%)</i>	<i>Sand (%)</i>	<i>Si (%)</i>	<i>Al (%)</i>	<i>Al/Si</i>
<i>N (%)</i>	1.00									
<i>TOC (%)</i>	0.99	1.00								
<i>C/Nmolar</i>	0.01	0.16	1.00							
<i>Del13C</i>	0.14	0.16	0.11	1.00						
<i>Del15N</i>	0.62	0.66	0.28	0.10	1.00					
<i>Silt+Clay (%)</i>	0.91	0.91	0.09	0.34	0.64	1.00				
<i>Sand (%)</i>	-0.91	-0.91	-0.09	-0.34	-0.64	-1.00	1.00			
<i>Si (%)</i>	-0.94	-0.98	-0.07	0.05	-0.74	-0.96	0.96	1.00		
<i>Al (%)</i>	0.96	0.98	-0.04	-0.02	0.70	0.97	-0.97	-0.99	1.00	
<i>Al/Si</i>	0.98	0.99	-0.09	-0.08	0.61	0.96	-0.96	-0.97	0.99	1.00

SM Table 2: The $\delta^{13}\text{C}_{\text{org}}$ and $\delta^{15}\text{N}$ variation in different sediment size fraction from Vembanad Lake

Sample	< 2 μm		2-25 μm		25-63 μm	
	$\delta^{13}\text{C}_{\text{org}}$	$\delta^{15}\text{N}$	$\delta^{13}\text{C}_{\text{org}}$	$\delta^{15}\text{N}$	$\delta^{13}\text{C}_{\text{org}}$	$\delta^{15}\text{N}$
North of bund						
S-1	-20.21	4.88	-21.97	6.77	-23.99	4.74
S-2	-21.18	5.71	-22.91	5.93	-24.93	1.66
S-3	-21.05	4.06	-22.69	6.42	-24.79	2.59
S-4	-21.01	4.96	-22.93	4.36	-24.46	2.74
S-5	-21.82	3.33	-23.33	2.55	-24.88	1.20
S-6	-21.39	5.21	-	-	-	-
S-7	-22.44	2.64	-	-	-	-
S-8	-24.24	5.43	-	-	-	-
S-9	-25.00	4.85	-25.42	2.77	-26.29	0.88
S-10	-25.26	6.34				
South of bund						
S-11	-25.77	5.59	-	-	-	-
S-12	-26.10	6.30	-	-	-	-
S-13	-26.02	5.66	-25.76	3.53	-26.22	4.11
S-14	-25.95	6.26	-	-	-	-
S-15	-25.40	6.55	-	-	-	-
S-16	-26.09	6.89	-	-	-	-
S-17	-26.09	6.01	-	-	-	-
S-18	-25.70	6.22	-25.42	2.38	-26.25	2.64
S-19	-25.39	5.12	-	-	-	-
S-20	-25.08	6.58	-	-	-	-
S-21	-26.12	7.04	-	-	-	-
S-22	-26.76	6.12	-26.68	4.91	-27.00	1.61
S-23	-25.83	5.76	-25.82	4.83	-26.11	2.21
S-24	-25.65	6.53	-25.61	4.45	-26.39	1.53
S-25	-25.42	6.18	-26.41	4.11	-26.94	1.29