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## 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 the spatial distribution of sedimentary organic matter (SOM) in the 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 the highest affinity for the clay-sized fraction ( $<2\ \mu\text{m}$ ) of the sediment in the northern part of the lake. However, aged and humified soil-derived OM was predominant in the clay-sized fractions from the southern part. Alteration of sediment texture led to a change in the distribution pattern of SOM in the lake after bund construction. Human intervention and changes in land-use pattern were also found to influence the SOM content in the southern part of the lake.

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### 1. Introduction

Coastal and estuarine sediments act as a sink for organic matter (OM). The burial of OM in marine sediments represents the major link among the pools of carbon present in the hydrosphere, biosphere, and lithosphere (Rullkotter, 2006). Although estuaries and coastal sediments cover only a fraction ( $\sim 10\%$ ) of the total marine environment,  $\sim 90\%$  of the total OM is buried here (Hedges and Keil, 1995), acting as major sinks for atmospheric  $\text{CO}_2$  (Budge and Parrish, 1998).

Estuaries represent the transition zones between river and ocean. The depositional characteristics of estuaries such as shallow water depth, high sedimentation rate, and in situ biological production favor the preservation of OM (Ittekkot et al., 1992). In addition to in situ production ( $\text{OM}_{\text{marine}}$ ), estuaries also receive large amounts of terrestrial OM ( $\text{OM}_{\text{terr}}$ ; fresh C3 and C4 plant 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 plants and altered land-use planning also play a significant role in the sedimentary organic matter (SOM) budget (Pradhan et al., 2014).

Most of the Indian estuaries are dominated by river-borne  $\text{OM}_{\text{terr}}$  supply during the southwest monsoon, which decreases substantially during the non-monsoon season and is dominated by in situ autochthonous OM (Pradhan et al., 2014).  $\text{OM}_{\text{terr}}$ , which is composed primarily of lignin-rich compound, is more refractory and undergoes less mineralization. It

exhibits a 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 as the net source of  $\text{CO}_2$  released into the atmosphere due to extensive heterotrophic bacterial decomposition of transported  $\text{OM}_{\text{terr}}$ . Thus, quantifying the source of SOM in sediments can provide greater insight into the 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, evaluating the histories of climate change, and assessing the impact of human activities on local ecosystems (Zillén et al., 2008; Chakraborty and Babu, 2015d; Chakraborty et al., 2011). However, the impact of human activity on SOM from tropical estuarine system has not been studied in detail. This is the first attempt to understand and characterize the distribution of SOM across a tropical estuary, so as to better understand human-induced changes in local and regional environmental systems.

The 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 (Saratadevi et al., 1992; Verma et al., 2002; Reddy, 2003; Priju and Narayana, 2010; Selvam et al., 2012; Gireeshkumar et al., 2013; Shivaprasad et al., 2013). Only two reports have described the SOM distribution in the southern part of the Vembanad Lake (Veerayya and Murty, 1974; Verma and Subramanian, 2002). However, the source and distribution of SOM across the lake has not been studied.

In 1974, a bund was built near Thannirmukkam to prevent the intrusion of saline water into the southern part of the lake. The construction of this bund has been reported to alter the hydrodynamics of the area.

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These changes have been assessed over the last four decades (Kumar et al., 2014). In addition to the shrinkage in terms of both geographic size and volume by siltation, the sluggish activity 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 based on their sources in the estuary. These data were further compared with the published literature to understand the impact 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 situated between 09° 30' to 10° 13' N and 76° 10' to 76° 30' E, spanning a length of 90 km and covering an area of nearly 260 km<sup>2</sup> (Verma and Subramanian, 2002). The width of the lake varies from 500 m to 4 km, with a depth ranging between 1.5 and 6 m (Murty and Veerayya, 1973). It is permanently well connected to the Arabian Sea through two openings (at Kochi and Azhikode). Due to its connection to the Arabian Sea, this lake is regularly influenced by mixed semidiurnal tides (Nath et al., 2000; Revichandran et al., 2011). However, a 1.5-km-long bund was built at Thannirmukam in 1974–1975 to prevent saltwater intrusion, which divided the whole lake into two parts: north and south. The bund remains closed during the summer (December to March). Thus, the northern part is brackish and the southern part is predominantly freshwater (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, Pullot, Chalakudi, Muvattupuzha, Ittupuzha, and Kari) discharge in the northern part of the lake.

The surface salinity close to the bar mouth opening into the sea ranges from freshwater conditions (during S–W monsoon, June to September) to 34‰ (during inter-monsoon, October to May) (Verma and Subramanian, 2002). The average salinity of the southern part of the lake reduced from 23‰ to 2.8‰ due to the construction of the Thannirmukkam bund. The average dissolved oxygen (DO) at the surface during the pre-monsoon period remained high at ~5 mg/l, with pH varying from 5.86 to 8.91 (Nasir, 2010). Sediments undergo periodic anoxia ( $E_h \approx -242$  to  $-160$  mV) below an oxygenated water column (Gireeshkumar, 2013). Very high concentrations of chlorophyll-a were found at the Cochin estuary due to additional input of nutrients from anthropogenic activities. The freshwater discharge via the rivers is maximum during the monsoon season ( $1346 \text{ m}^3 \text{ s}^{-1}$ ), totaling to  $22.41 \times 10^3 \text{ mm}^3 \text{ year}^{-1}$  (Revichandran et al., 2011). A very high sedimentation rate ( $\sim 0.5 \text{ cm} \cdot \text{year}^{-1}$ ) was reported for this lake (Nasir, 2010) due to the deposition of large amounts of sediment brought by rivers ( $3,29,106 \text{ t} \cdot \text{year}^{-1}$ , Thomson, 2002). The southern part of the lake has been reclaimed for agricultural practice and intensely cultivated, whereas the northern part of the lake is mostly urbanized. Twenty-five stations covering the majority of the lake (Fig. 1) were selected for this study. Sediment sampling was conducted using a Van Veen grab during the months of March–April of 2012 (the bund was closed during the sampling time). The 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 with a mesh of 63- $\mu\text{m}$  size. The sediment retained on the 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 using a laser diffraction

particle size analyzer. This method has been described in detail elsewhere (Ramasmwamy and Rao, 2006).

Sediments were separated into four size fractions – 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 associated with each size fraction. The sediments were wet-sieved through a 63- $\mu\text{m}$  sieve to separate sand (+63  $\mu\text{m}$ ) and the silt + clay fraction (<63  $\mu\text{m}$ ). The clay-sized sediment (<2  $\mu\text{m}$ ) was separated from the <63- $\mu\text{m}$  fraction following standard pipette analytical techniques (Folk, 1980) by repeated collections. The remaining suspension with particles of 2–63- $\mu\text{m}$  size was again sieved through 25- $\mu\text{m}$  sieves in order to separate particles of sizes 2–25 and 25–63  $\mu\text{m}$ . All the samples were dried in a hot air oven at 35 °C, ground in an 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. The TC and TN contents in sediments were determined using a Flash 2000 CHN elemental analyzer (Thermo Fisher Scientific Incorporation). The precision of the analysis was within  $\pm 5\%$ . The soil NC content (0.37% N and 3.5% C) was used as the certified reference material. TIC was determined by coulometry (UIC Coulometrics). Calcium carbonate (12% C) was used as a standard material. The relative standard deviation of the analysis was within  $\pm 2\%$ . The total organic carbon (OC) content was derived by deducting TIC from TC.

### 2.4. Stable isotopes of C and N in OM

To determine the  $\delta^{13}\text{C}_{\text{org}}$ , subsamples of sediments were acidified with HCl (10%) to remove carbonates (Schubert and Nielsen, 2000). The dried and grounded samples were then used for carbon isotope analysis. The untreated samples were used for N isotope analysis. Analysis was conducted using a Thermo Finnigan Flash 1112 elemental analyzer, linked with a Thermo Finnigan Delta V plus IRMS at CSIR-National Institute of Oceanography (NIO). Calibration was performed using sucrose ( $\delta^{13}\text{C} = -10.449\%$ ) and ammonium sulfate ( $\delta^{15}\text{N} = 20.3\%$ ) of IAEA-grade standard for stable isotope analyses of carbon and nitrogen, respectively. The stable isotopic ratios of OC and TN were represented using delta notation relative to the standard as follows:

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

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  $\text{N}_2$  was used as the standard for  $\delta^{15}\text{N}$ . The overall analytical precision for replicate samples was within  $\pm 0.2\%$  for  $\delta^{13}\text{C}_{\text{org}}$  and  $\pm 0.1\%$  for  $\delta^{15}\text{N}$ .

### 2.5. Determination of major elements

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

### 2.6. Mixing calculations using end-member values: quantifying OM contribution from different sources

The relative contribution to OM of freshwater phytoplankton ( $\text{OM}_{\text{freshwater phytoplankton}}$ ), terrestrial C3 plants ( $\text{OM}_{\text{C3}}$ ), marine OM ( $\text{OM}_{\text{marine}}$ ), and soil OM ( $\text{OM}_{\text{soil}}$ ) was calculated using a four-end-

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