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Baseline

Distribution and sources of sedimentary organic matter in a tropical estuary, south west coast of India (Cochin estuary): A baseline study

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A B S T R A C T

Surface sediments samples were collected from 9 stations of the Cochin estuary during the monsoon, post-monsoon and pre-monsoon seasons and were analyzed for grain size, total organic carbon (OC), total nitrogen (TN) and stable isotopic ratios of carbon ($\delta^{13}C$) and nitrogen ($\delta^{15}N$) to identify major sources of organic matter in surface sediments. Sediment grain size is found to be the key factor influencing the organic matter accumulation in surface sediments. The $\delta^{13}C$ values ranges from −27.5‰ to −21.7‰ in surface sediments with a gradual increase from inner part of the estuary to the seaward side that suggest an increasing contribution of marine autogenous organic matter towards the seaward side. The $\delta^{15}N$ value varies between 3.1‰ and 6.7‰ and it exhibits complex spatial and seasonal distributions in the study area. It is found that the dynamic cycling of nitrogen through various biogeochemical and organic matter degradation processes modifies the OC/TN ratios and $\delta^{15}N$ to a considerable degree. The fraction of terrestrial organic matter in the total organic matter pool ranges from 13% to 74% in the surface sediments as estimated by $\delta^{13}C$ based two end member mixing model.

Organic matter in estuarine systems can be derived from a range of sources which include autochthonous inputs of planktonic and benthic primary productivity, along with allochthonous inputs such as terrigenous, river run off and anthropogenic sources (Graham et al., 2001). A significant portion of organic matter sinks through the water column and are ultimately preserved in sediments (Hu et al., 2006) by the interaction of series of physical, chemical and biological processes (Liu et al., 2006). The terrestrial organic matter represent a substantial fraction of organic matter in estuarine sediments (Prahl et al., 1994) and varies with production patterns, transport pathway and environmental conditions (Dai and Sun, 2007). Better knowledge of sources of organic matter in estuarine sediments and the factors controlling their distribution is important to the understanding of global biogeochemical cycles (Hu et al., 2006).

A series of bulk parameters such as OC/N, $\delta^{13}C$ and $\delta^{15}N$ have been employed in organic geochemical studies to assess the source, fate and seasonal variations of sedimentary organic matter (Zhang et al., 1997; Andrews et al., 1998; Goni and Thomas, 2000; Goni et al., 2003; Wu et al., 2003; Liu et al., 2006; Rumolo et al., 2011; Gao et al., 2012). The efficacy of OC/N, $\delta^{13}C$ and $\delta^{15}N$ relies on the fact that there exist characteristic source specific bulk elemental and isotopic signatures for terrigenous, anthropogenic, marine and in situ organic matter. The bulk elemental and isotopic ratio methods approach is based on the following two assumptions: (i) the bulk elemental and isotopic ratios of sedimentary organic matter are conservative and (ii) existence of a linear response to physical mixing among the end members (Liu et al., 2006; Rumolo et al., 2011).

Like most of the major estuarine systems of the world, the Cochin estuary has also been increasingly affected by anthropogenic activities such as intertidal land reclamation, effluent discharges, expansion for harbor development and dredging activities and urbanization (Gopalan et al., 1983; Menon et al., 2000). Cochin estuary has also received a high influx of anthropogenic nutrients, heavy metals and organic matter from increased agricultural activities, domestic sewage inputs, industrial effluents and marine fish farming, during the last two decades (Qasim, 2003; Balachandran et al., 2005; Thomson, 2002; Martin et al., 2008, 2010). However, the geochemical characteristics of carbon and nitrogen stable isotopes in surface sediments of Cochin estuary have not been previously reported. The present study aims (i) to investigate the spatial and seasonal variations of carbon and nitrogen stable isotopes in sedimentary organic matter of the Cochin estuary, (ii) to elucidate the sources of organic matter accumulated in surface sediments and (iii) to estimate the fraction of terrestrial derived organic matter in surface sediments of Cochin estuary. The study provides a baseline data which could be valuable for further isotopic studies in this region.

The Cochin estuary is a tropical micro-tidal estuarine system with two permanent openings to the Arabian Sea and sustains high biological production (Qasim, 2003). It is the second largest estuarine system in India, six rivers discharging about

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291,010 m^3 $year^{-1}$ of fresh water (Srinivas et al., 2003) and 329,106 tons $year^{-1}$ of sediment flux from its catchments (Thomson, 2002). The estuary is topographically divided into two arms; a southern arm extends from Cochin barmouth to Thanneermukkam bund and a northern arm extends from Cochin barmouth to Azhikode. The estuary is generally wide (0.8–1.5 km) and deep (4–13 m) towards the south, but narrow (0.05–0.5 km) and shallow (0.5–2.5 m) towards the north (Balachandran et al., 2008).

The annual rain fall in the estuary is about 3.2 m, varying considerably from year to year. There are three seasons prevailing in the estuary; monsoon (June–September), post-monsoon (October–January) and pre-monsoon (February–May). More than 70% of annual rain fall occurs during the monsoon period resulting in heavy fresh water discharge to the estuary. During monsoon, the estuary is virtually converted into a freshwater basin even in the areas around bar mouth and frequently develops stratification resulting in less dense river water at surface and high dense seawater at the bottom layers. In post-monsoon season, the discharge from river gradually diminishes and tidal influence gains momentum, thereby changing the estuarine conditions to partially mixed type. In pre-monsoon season, the river discharge is in minimum and the sea water influence is in maximum upstream, leaving the estuary well mixed, and homogeneity exists in the water column (Menon et al., 2000).

Surface sediment samples were collected from nine sites in the southern arm of Cochin estuary (Fig. 1) in year 2007 during the monsoon (July), post-monsoon (November) and pre-monsoon (February) seasons. Sediment samples were collected using a van Veen grab (0.042 m^2). Although box corers and multiple corers are suitable to obtain undisturbed sediment samples, van Veen grabs can also be successfully used, with caution, for the present kind of studies. Several deployments per stations were done to obtain well preserved sediment samples, to avoid any unfairness that could happen due to the wash out of supernatant water resulting in the disturbance of surface sediment during the grab operation. Samples were transported to the laboratory, immediately frozen at −20 °C and were stored until analysis.

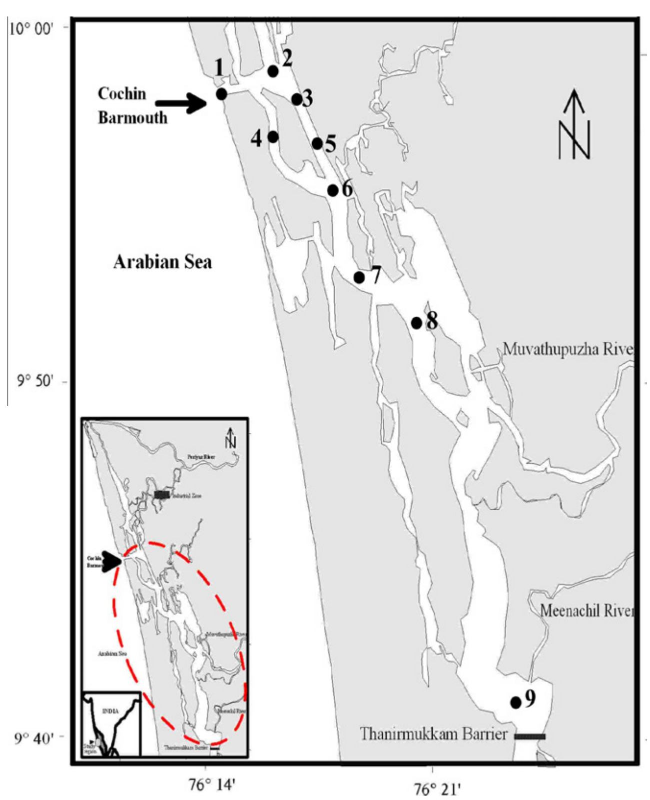

Fig. 1. Study area showing location of sampling sites.

Grain sizes of sediments were determined by pipette analysis using wet sediment samples (Folk, 1980). The sediment samples for OC, TN, $\delta^{13}C$ and $\delta^{15}N$ analyses were freeze dried homogenized and powdered using mortar and pestle. The analyses were preceded by treatment of samples with 1M HCl to remove carbonates. The process was repeated two/three times in order to ensure the complete exclusion of carbonates and samples were washed with Milli-Q water to remove salts and finally freeze dried. Organic carbon (OC) and total nitrogen (TN) were determined using Vario EL III CHNS Analyzer. Samples were run with blank cups in order to correct the carbon and nitrogen associated with tin/silver cups. Acetanilide standards were used to calibrate the elemental analyzer. The detection limits for OC and TN are 0.07% and 0.01% respectively. $\delta^{13}C$ and $\delta^{15}N$ analyses were carried out using Flash EA 1112 interfaced with IRMS (DELTA V PLUS, Thermo Electron Corporation). Samples were run with blank cups and urea standards. All analyses were carried out in triplicates and mean of the three measurements were obtained.

Stable isotopic ratio values are reported in ‰ notation.

$$\delta(‰) = (R_{\text{sample}} - R_{\text{reference}})/R_{\text{reference}} \times 1000 \quad (1)$$

δ‰ stands for $\delta^{13}C$ or $\delta^{15}N$, and R_{sample} and $R_{\text{reference}}$ are the isotopic ratios of the sample and reference, respectively. For carbon the reference is Peedee belemnite (PDB) and for N the reference is air. The precision of analysis is ±0.2‰ and ±0.3‰ for $\delta^{13}C$ and $\delta^{15}N$ respectively.

About 0.5 g of freeze dried homogenized sediments were sonicated with 10 ml of acetone: methanol: water (45:45:10) solvent mixture and the pigments were extracted for 24 h at 0 °C. Chlorophyll a (Chl a) concentrations were determined spectrophotometrically using standard equations (Joye et al., 1996).

The grain size distribution of surface sediments from Cochin estuary is depicted in Fig. 2. Grain size distribution presented large spatial variation in the study region. Silt and clay particles predominated in stations 2, 3, 4 and 6, while sand predominated towards the inner part of the estuary (stations 5, 7, 8 and 9). A seasonal fluctuation in grain size distribution was observed at station 1 (bar mouth). This can be attributed to the dredging activities undertaken in that area as station 1 is located in the main navigation channel of Cochin Port. There were no pronounced seasonal variations observed in grain size distribution.

Chl a (Fig. 3) concentrations in the surface sediments ranged from 0.48 to 4.76 μg g^{-1} (2.17 ± 1.46) and 5.79 to 18.62 μg g^{-1} (10.54 ± 5.07) and 0.05 to 10.78 μg g^{-1} (7.13 ± 3.42) in monsoon, post-monsoon and pre-monsoon respectively. It was found that there was a pronounced seasonal difference in the sedimentary Chl a content (ANOVA, $p < 0.05$) with relatively greater concentrations in the post-monsoon season and lower concentrations in the monsoon season.

Fig. 4a and b show the spatial and seasonal variability of OC and TN in surface sediments of Cochin estuary. The OC concentrations ranged from 0.30% to 3.26% (2.10 ± 0.90) and the spatial distribution of OC indicated that the presence of OC content is comparatively higher in stations 1, 2, 3, 4 and 6 than in the other stations. However it was observed that there was no significant seasonal difference in OC content of surface sediments. Concentrations of TN were relatively lower in the surface sediments of Cochin estuary which varied from 0.03% to 0.32% (0.19 ± 0.09). TN varied significantly among the sampling sites but it did not show any seasonal differences.

The spatio-temporal variation in $\delta^{13}C$ and $\delta^{15}N$ values of surface sediments is presented in Fig. 5a and b respectively. The $\delta^{13}C$ from the surface sediment of Cochin estuary ranged from −27.5‰ to