

# Reconstruction of depositional environment of a tropical estuary and response of $\delta^{13}\text{C}_{\text{org}}$ and TOC/TN signatures to changing environmental conditions

Samida P. Volvoikar<sup>a</sup>, G.N. Nayak<sup>a,\*</sup>, Aninda Mazumdar<sup>b</sup>, Aditya Peketi<sup>b</sup>

<sup>a</sup> Department of Marine Sciences, Goa University, Taleigao Plateau, Goa 403206, India

<sup>b</sup> Geological Oceanography, National Institute of Oceanography, Dona Paula, Goa 403004, India

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## ABSTRACT

The distribution of sediment components, organic carbon, aluminium normalized metals, bulk sedimentary organic stable carbon isotope ratios i.e.  $\delta^{13}\text{C}_{\text{org}}$  and elemental TOC/TN ratios were studied within the sediment of Vaitarna estuary. Deposition of coarser sediment was favored under higher energy conditions prevailing in the past. Prevalence of relatively calm environment in recent years favored deposition of finer particles. Changes in depositional environment of Vaitarna estuary were very well reflected in distribution pattern of metals,  $\delta^{13}\text{C}_{\text{org}}$  and TOC/TN ratios. The narrow range ( $-22.9\text{‰}$  to  $-22.0\text{‰}$ ) and absence of distinct trend for  $\delta^{13}\text{C}_{\text{org}}$  in core collected towards the mouth (core S4) was attributed to prevalence of higher hydrodynamic energy conditions at this location. While protected environment of core S9 indicated a gradual change in the proportion of organic matter input to the estuary over a period of time.  $\delta^{13}\text{C}_{\text{org}}$  values in this core increased from  $-28.4\text{‰}$  at the bottom to  $-20.7\text{‰}$  at the surface and showed a corresponding decrease in TOC/TN ratio. All these changes will significantly alter the biogeochemical processes within the Vaitarna estuary and adjoining coastal waters.

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## 1. Introduction

The occurrence of estuarine mudflats and mangroves at the fluvio–marine interface allows deposition of material originating from diverse sources (Cook et al., 2004a,b; Volvoikar and Nayak, 2013). At tropical latitude, mangroves grow at the upper tidal flats and are the least inundated parts of estuarine mudflats (Pande and Nayak, 2013). Because of their sheltered nature, mudflats and mangroves accumulate large quantities of organic matter (Jickells and Rae, 1997; Cook et al., 2004a; Sanders et al., 2010b). They are highly productive ecosystems and have high impact on the carbon budget of the tropical and global coastal zone (Bouillon et al., 2008). Clastic particulates are derived from the weathering of source rocks, while, organic matter includes autochthonous marine planktons, fresh water planktons and terrestrial plant material including mangrove litter. Material from anthropogenic discharges such as sewage and industrial effluents are also deposited in the sediment.

Organic matter deposition in estuarine mudflat and mangrove sediment is affected by changes in river discharge, catchment area disturbance and fluctuations in relative sea level (Lamb et al., 2007). Heavy rainfall leads to increased addition of terrestrial organic matter along with greater freshwater discharge to estuarine environment (Zong et al., 2006). While, construction of dams leads to changes in natural flow of fresh water as well as morphology of estuaries resulting in changes in the sedimentation patterns and increase in salinity (Schoer, 1990; Rodriguez et al., 2001). Such modifications have been found to change the chemical and biological characteristics of estuaries and adjacent coastal regions (Nichols et al., 1986; Alber, 2002; Kimmerer, 2002; Montagna et al., 2002; Surge et al., 2003). Thus major changes affecting biogeochemical processes operating within estuarine environments worldwide are reduction in freshwater due to diversion or dam building (Rodriguez et al., 2001), local sea level fluctuations (Sanders et al., 2010a) in addition to that of metal pollution.

Vaitarna estuary is one of the major estuaries located along the west coast of India (Fig. 1). Similar to other estuaries, Vaitarna estuary is also under tremendous natural and anthropogenic pressures. Large numbers of dams have been built on Vaitarna and joining rivers (Pinjal, Surya, Tansa, etc.) over the last few decades. Freshwater is also being diverted for drinking and agricultural

\* Corresponding author.

E-mail addresses: [Samida2010@gmail.com](mailto:Samida2010@gmail.com) (S.P. Volvoikar), [nayak1006@rediffmail.com](mailto:nayak1006@rediffmail.com), [gnnayak@unigoa.ac.in](mailto:gnnayak@unigoa.ac.in) (G.N. Nayak), [maninda@nio.org](mailto:maninda@nio.org) (A. Mazumdar), [adipeketi@gmail.com](mailto:adipeketi@gmail.com) (A. Peketi).

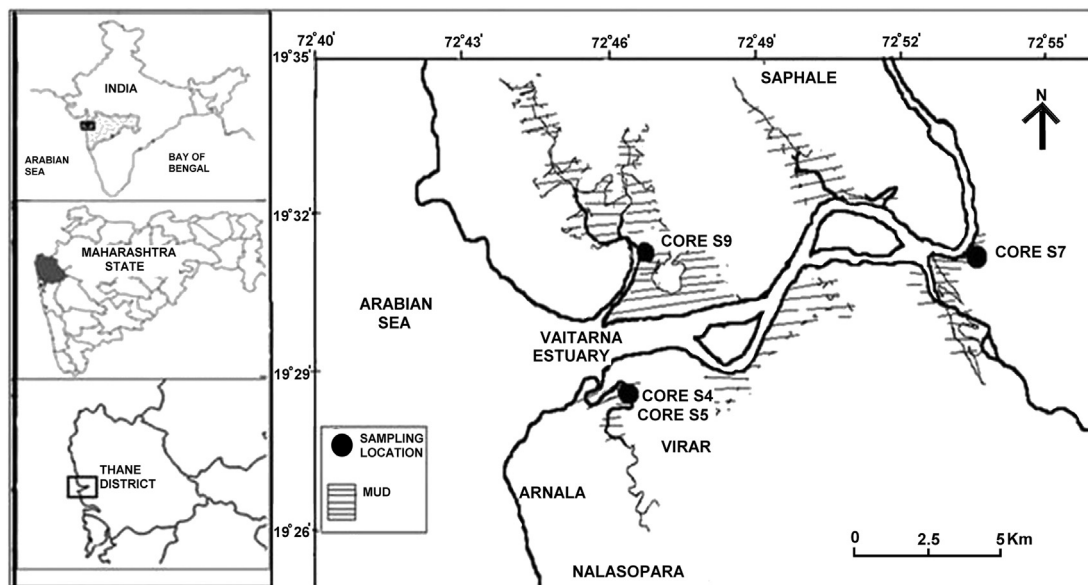


Fig. 1. Location of cores collected in the Vaitarna estuary, Maharashtra, India.

purposes. The region has also experienced a change in precipitation pattern over the past few years. Estimates of mean sea level rise made from past tide gauge data at selected stations along the coast of India has indicated a rise of slightly less than 1 mm/year (Unnikrishnan et al., 2006). All these processes must have therefore, resulted in, change in deposition pattern of sediment particles, organic matter and metal input within sediment of Vaitarna estuary over a period of time.

Bulk sedimentary organic stable carbon isotope ( $\delta^{13}\text{C}_{\text{org}}$ ) and TOC/TN ratios, together, have been widely, successfully used as markers to estimate the changes in relative proportions of terrigenous and marine organic matter in coastal sediment (Chmura and Aharon, 1995; Müller and Voss, 1999; Dehairs et al., 2000; Gonnesa et al., 2004; Kennedy et al., 2004; Ogrinc et al., 2005; Wilson et al., 2005; Usui et al., 2006; Lamb et al., 2007; Zhang et al., 2007; Ramaswamy et al., 2008; Böttcher et al., 2010). Marine organic matters are typically enriched in  $^{13}\text{C}$  than the terrestrial plant material (Schubert and Calvert, 2001) owing to differences in photosynthetic mechanism and carbon sources (Meyers, 1997; Zhang et al., 2009). Terrestrial C3 vascular plants and C4 plants employ different photosynthetic pathways and produce different  $\delta^{13}\text{C}$  values. The  $\delta^{13}\text{C}$  of C3 plants ( $-26\text{‰}$  to  $-28\text{‰}$ ) and C4 plants ( $-12\text{‰}$ – $-14\text{‰}$ ) and C/N ratio of  $>12$  indicates terrestrial end member (Ku et al., 2007); while, the  $\delta^{13}\text{C}$  of  $-19\text{‰}$  to  $-22\text{‰}$  (Hu et al., 2006) and C/N ratio of  $<8$  suggests aquatic end member.

Tropical estuarine mudflat and mangrove sedimentary sequences preserve an undisturbed record of various environmental changes (Singh and Nayak, 2009). Thus, in the present study, an attempt has been made to reconstruct changes in the depositional environment of tropical Vaitarna estuary using geochemical proxies namely  $\delta^{13}\text{C}_{\text{org}}$ , TOC/TN ratios and trace metals.

### 1.1. Study area

Vaitarna River is approximately 154 km long. The drainage area of 3647 sq km covers the entire northern sections of the Thane district. It falls under macro-tidal estuary with the tidal influence observed up to 50 km from the mouth (Gazetteer, 1982). Both tide and wind dominate the regime; leading to well-mixed conditions almost throughout the year (Swamy, 1994). Geologically, Thane

district forms the part of the Deccan volcanic province (DVP) or Deccan Trap (Shankar and Mohan, 2006). Climate of Thane district is humid almost throughout the year. Mangrove species reported from this region are *Avicennia alba*, *Avicennia marina*, *Sonneratia apetala*, *Avicennia officinalis*, *Rhizophora mucronata* and *Rhizophora apiculata*.

### 2. Materials and methods

Four intertidal sediment cores were collected from Vaitarna estuary with the help of hand operated PVC corer. Core S4 having length of 88 cm ( $19^{\circ}28'56.3''\text{N}$ ;  $72^{\circ}46'58.7''\text{E}$ ) and core S5 of length 102 cm were collected towards the mouth. The distance between core S5 and core S4 was approximately 100 m. Core S9 with a length of 52 cm was collected from the lower middle estuary ( $19^{\circ}31'23.9''\text{N}$ ;  $72^{\circ}47'11.3''\text{E}$ ), while core S7 having length of 66 cm was collected from the upper middle estuary ( $19^{\circ}31'35.0''\text{N}$ ;  $72^{\circ}53'37.5''\text{E}$ ). Amongst these, cores S4, S9 and S7 represented mudflat sediment while core S5 represented mangrove sediment. Sampling stations were located with the help of hand held GPS. Sediment cores were sectioned at 2 cm interval with a plastic knife immediately after the extraction. The sub-samples were then packed in clean plastic bags, labeled and stored in ice box. Sediment sub samples were then oven dried at  $60^{\circ}\text{C}$  in the laboratory. The dried sub samples were used for further analyses. Percentage of sediment components (sand: silt: clay) in all the sub samples was determined using Pipette method (Folk, 1968). Portion of the dried samples was finely powdered and homogenized using an agate mortar and pestle. Estimation of organic carbon (OC) was carried out following Walkley–Black method (Gaudette et al., 1974). A known quantity of sediment was digested completely with the help of  $\text{HF}:\text{HNO}_3:\text{HClO}_4$  (7:3:1) acid mixture. Digested samples were analyzed for metals by aspirating the sample solutions into the flame Atomic Absorption Spectrophotometer (Varian AA240FS). Reproducibility of the instrument was checked by carrying out duplicate analyses for the studied metals after every ten samples. All the reagents used in the present study were of analytical grade. Contamination during the time of sampling, storage and analyses was minimized by taking due care. The accuracy of the analytical procedure was assessed using certified reference standard from the

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