

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

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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 ‰ to -22.0 ‰) 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‰ at the bottom to -20.7‰ 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.

Keywords: Anthropogenic; Carbon isotope ratio; Environments; Estuaries; Fresh water; Metals

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., 2004; 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 & 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 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 1mm/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; Gonnee et al., 2004; Kennedy et al., 2004; Ogrinc et al., 2005; Wilson et al., 2005a, b; 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}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‰ - -28‰) and C4 plants (-12‰ - 14‰) and C/N ratio of >12 indicates terrestrial end member (Ku et al., 2007); while, the $\delta^{13}\text{C}$ of -19 ‰ to -22‰ (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*, *A. officinalis*, *Rhizophora mucronata* and *R. 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°28'56.3"N; 72°46'58.7"E) and core S5 of length 102 cm were collected towards the mouth. The distance between core S5 and core S4 was approximately 100m. Core S9 with a length of 52 cm was collected from the lower middle estuary (19°31'23.9"N; 72°47'11.3"E), while core S7 having length of 66 cm was collected from the upper middle estuary (19°31'35.0"N; 72°53'37.5"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°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 Walkey-Black method (Gaudette et al., 1974). A known quantity of sediment was digested completely with the help of HF: HNO₃: HClO₄ (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 Canadian National Bureau of Standards (BCSS-1). Accuracy was 95% for Mn, Co, 94% for Fe, Cu, Ni and Al, 91% for Zn and Pb. Ternary diagram proposed by Pejrup (1988) was used to understand the hydrodynamic energy conditions under which sediment (sand:silt:clay) was deposited within the Vaitarna estuary. Sections I to IV reflect increasingly violent hydrodynamic energy conditions. Depending upon the sand content, each section is further divided into four classes (A to D). Wherein, the energy decreases from sandy end member (A) to muddy end member (D). Altogether ternary diagram therefore exhibits sixteen groups each having unique characteristics.

For $\delta^{13}\text{C}_{\text{org}}$ analysis, powdered oven dried sediment sub-samples were treated with 2N HCl to remove inorganic carbon while un-acidified samples were run separately for total nitrogen analysis. For the acidification, 2N HCl was added to one gram powdered sediment sample, and allowed to mix for five hours on a roto-spin. The sample was then centrifuged for 10-15 minutes at 8000 rpm. Supernatant was thrown out, while residue was washed three to four times with milli Q water for pH to come to 7. The sample was then kept in an oven for drying. The dried sample was again finely powdered with agate mortar and pestle and used for the analysis. Stable carbon isotope ratios of total organic carbon ($\delta^{13}\text{C}_{\text{org}}$) and total organic carbon to total nitrogen (TOC/TN) analyses were carried out on an elemental analyzer coupled with a continuous flow stable isotope ratio mass spectrometer (IRMS) at National Institute of Oceanography (NIO), Goa, India. The carbon stable isotope ratios are reported in per mil deviations from international standard VPDB.

3. Results

3. 1. Vertical distribution of grain size and Organic carbon (OC)

Based on the distribution pattern of sand % and mud % (silt % +clay %), the cores are divided into three sections (Fig.2A-D). In mudflat core S4, sand content shows a decrease from section I to section III with high SD % values (Table 1a). Highest clay content is noted in uppermost section III while OC % is noted to be high in section II. In mangrove core S5 (Table. 1b), very high average sand percentage is noted in section I. Sand exhibits a decreasing trend while clay shows an increasing trend from section I to section III. OC shows an increase in section II. While in mudflat core S9 (Table. 1c), all the sedimentological parameters namely sand, silt and clay together with OC show high SD % values in section I indicating large variation in their input. Sand shows a decreasing trend while clay shows an increasing trend from section I to section III. Organic carbon is noted to be high in section I. In mudflat core S7 (Table 1d), large increase in sand percentage in section II is compensated by large decrease in clay percentage. Silt is also noted to be high in this section. Average OC values show a decrease from section I to section III.

Further, sediment grain size when plotted on ternary diagram indicates, data points in the three sections of core S4 (Fig. 2a) to be widely scattered and falling under classes II and III which represents less violent and relatively violent hydrodynamic energy conditions respectively. In cores S5 (Fig. 2b), S9 (Fig. 2c) and S7 (Fig. 2d) most of the data points in the three sections fall under hydrodynamic class II; except few points of section I of cores S5 and S9 and of section II of core S7 which fall mainly under class III.

3. 2. Vertical distribution of aluminium normalized metal contents.

Cu/Al, Zn/Al, Co/Al and Ni/Al ratios show similarity with Fe/Al and Mn/Al in the three sections of mudflat core S4 (Fig. 3a). Relatively higher values of Fe/Al, Mn/Al, Cu/Al, Zn/Al and Ni/Al are noted in section III as compared to sections I and II. V/Al shows gradual decreasing trend in section I and II. In section III, a large gradual increasing trend above 22 cm depth is observed. However, in section I of mangrove core S5 (Fig. 3b), Fe/Al, Mn/Al, Co/Al and Ni/Al ratios exhibit higher enrichment. In section II, Fe/Al and Mn/Al decreases while Co/Al, Ni/Al, Pb/Al and V/Al ratios show large fluctuating trend. Cu/Al and Zn/Al show an increasing trend in sections I and II. In section III, all the studied metals except V/Al exhibit gradual increasing trend towards the surface with a prominent peak at 6 cm depth. V/Al shows large increase between 50 cm to 34 cm depths and at 18 cm depth, followed by gradual decrease towards the surface. Thus in section I and II, Fe/Al, Mn/Al, Co/Al and Ni/Al ratios show higher values with decreasing trend similar to that of sand. While in section III almost all the metals are observed to show increase towards the surface. In section I of mudflat core S9 (Fig. 4a), all the studied metals show a large fluctuating trend. In section II, metals show gradual decrease except for Cu/Al, Zn/Al and V/Al ratios. A peak value at 22 cm depth is notable for almost all the metals. While in section III, all the metals exhibit almost a constant trend with slight increase above 8 cm depth. Thus, all the studied trace metals show almost same variation pattern as that of Fe/Al and Mn/Al except V/Al. V/Al shows an increasing trend from bottom to top of the core. While in mudflat core S7 (Fig. 4b), relatively higher values are observed for Fe/Al between 58 - 52 cm and between 40 - 30 cm depths. Sudden large increase above 18 cm depth is also notable. Mn/Al shows gradual increasing trend in sections I and II. Sudden large increase above 18 cm depth is noted similar to that of Fe/Al. In general, all the normalized trace metals show very high values above 18 cm depth and show similarity with the distribution patterns of Fe/Al and Mn/Al. However, Pb/Al indicates a fluctuating trend and V/Al shows large increase in section II.

3. 3. Vertical distribution of $\delta^{13}\text{C}_{\text{org}}$ and TOC/TN ratio

The range and average values of $\delta^{13}\text{C}_{\text{org}}$ and TOC/TN ratio for the studied cores are given in table 2. In mudflat core S4 (Fig. 5a), $\delta^{13}\text{C}_{\text{org}}$ values fluctuate between a narrow range of -22.9 ‰ and -22.0 ‰ from bottom i.e. section I to 34 cm depth of section II, with the exception of highest value of -21.6 ‰ at 84 cm and the lowest value of -23.4 ‰ at 70 cm depth. In section III, enrichment of $\delta^{13}\text{C}_{\text{org}}$ is observed reaching value of -21.9 ‰ at the surface. TOC/TN ratio (Fig. 6a) shows highest value of 14.6 at the bottom of the core. It shows opposite variation pattern to that of $\delta^{13}\text{C}_{\text{org}}$ below 30 cm i.e. in sections I and II and range from 11.5 to 14.6. In section III, TOC/TN ratio shows a gradual decreasing trend up to the surface with TOC/TN value of 12.9 at 30

cm and 8.87 at the surface. In mangrove core S5 (5b and 6b), isotopically lighter values (avg. -22.8 ‰) and higher TOC/TN ratios (avg. 16.1) are noted below 50 cm i.e. in sections I and II. Whereas, $\delta^{13}\text{C}_{\text{org}}$ is relatively heavier (avg. -20.5 ‰) and TOC/TN ratio relatively lower (avg. 11) in section III. Lowest value of -23.8 ‰ is noted at the bottom; while sudden shift in $\delta^{13}\text{C}$ to heavier value of -19.7 ‰ is evident at 40 cm depth. The variation pattern of $\delta^{13}\text{C}_{\text{org}}$ and TOC/TN is almost the same all along the length of the core. In mudflat core S9 (Fig. 5c), gradual increase in $\delta^{13}\text{C}$ isotopic signatures is noted from section I to section III i.e. from bottom to surface of the core. In section I, the lowest $\delta^{13}\text{C}$ value of -28.4‰ is observed at the bottom which gradually increases to -22.5‰ at 30 cm depth. Enrichment of $\delta^{13}\text{C}_{\text{org}}$ continues further in section II and section III reaching heavier value of -20.2‰ at 8 cm depth. Above 8 cm, less significant but gradual negative shift is observed with $\delta^{13}\text{C}_{\text{org}}$ value of -20.7‰ at the surface. Similarly, TOC/TN ratio (Fig. 6c) shows a smooth gradual decreasing trend from 46 cm to surface of the core i.e. from section I to section III (data for TOC/TN ratio below 46 cm is not available). However, very high value at 42 cm depth, a peak value at 32 cm depth and a small increase at 14 cm depth is noted. In mudflat core S7 (Fig. 5d), the bottommost sample is close to the average value of -23.0‰. Large negative shift is noted in section II, i.e. between 50 and 42 cm depths, with an average $\delta^{13}\text{C}_{\text{org}}$ value of -24.1‰. In section III, $\delta^{13}\text{C}_{\text{org}}$ values then remain almost constant, close to the average value above 36 cm depth. Slight enrichment of $\delta^{13}\text{C}_{\text{org}}$ to -22.8 ‰ is however noted within the upper 4 cm of the core. Increase in TOC/TN ratio is noted in section II between 50 cm and 42 cm depths with highest value of 11.1 at 48 cm (Fig. 6d). In section III, a peak value at 36 cm depth is noted; further TOC/TN ratio shows gradual increasing trend from 24 cm to surface of the core; wherein TOC/TN ratio increases from 8.01 to 9.05. Thus relatively higher TOC/TN values are noted below 34 cm depth in this core.

4. Discussion

4. 1. Temporal variation of sediment grain size and organic carbon

High SD % values of sand in all the three sections of mudflat core S4 indicate varying depositional energy conditions. This is well supported by distribution of points in ternary diagram. Lower sand percentage and corresponding increase in clay percentage in section III, however point towards rise in deposition of finer clay particles in recent years. A gradual up-core increase in finer particles (mud %) in mangrove core S5 indicates a gradual change in the depositional environment at this location. While, in core S9, the variation pattern of mud and results of ternary diagram, indicate three different stages of sediment deposition. Sediment seems to be deposited under relatively high and variable hydrodynamic energy conditions in past. This slowly changed to a uniform and more stable environment further changing to very calm low energy environment favoring greater deposition of clay particles in the recent years. Sudden decrease in mud percentage and an increase in sand percentage in section II of core S7 indicate a period of relatively higher energy conditions prevailing in the past at this location. This is further supported by ternary diagram wherein the data points in section II of this core are widely spaced, thus indicating large variation in energy conditions in the past. The grain size distribution of tidal wetlands may also be affected by other factors such as changes in sediment source and biological factors in addition to hydrodynamics (Yang et al., 2008).

Larger fluctuations in OC % in sections I and II as compared to section III of cores S4 and S5 indicate larger variation in deposition of organic matter in the past under varying energy conditions. Similarly very high and variable OC % noted in section I of core S9 point towards deposition of recalcitrant organic matter of terrestrial origin at greater depths (Álvarez-Iglesias et al., 2006) under varying energy conditions prevailing in the past. While large increase in OC concentration in section II of core S5 reflects change in the characteristics and magnitude of inputs into the river (Ouyang et al., 2006) in past in this section.

4. 2. Sources and processes governing metal distribution with time

Higher metal/Al values towards the surface of the cores S4, S5 and S7 indicate anthropogenic addition of metals in the form of sewage, wastes, etc. to sediment in recent years. Similar observation was made earlier by Lin et al. (2002) and Yang et al. (2004). Similarity in distribution pattern of aluminium normalized trace metals with that of normalized Fe and Mn indicate co-precipitation of trace metals with Fe-Mn oxyhydroxides. It also points towards common source and processes of deposition for all the metals (Acquavita et al., 2010). Enrichment of normalized Fe, Mn, Ni, Co and Pb below 60 cm depth of core S5, and section I of core S9 point towards precipitation/deposition of trace metals along with Fe and Mn at greater depths. These metals were probably associated with coarser sand particles (Aloupi and Angelidis, 2002) in the past. Fe oxide coatings on surfaces of coarser particles are known to play an important role in adsorption of metals (Achyuthan et al., 2002). While elevated concentration of metals towards the surface of cores except core S9 indicates their diagenetic enrichment in addition to anthropogenic input. Organic matter decay and/or reductive dissolution of Fe and Mn oxyhydroxides in sub-surface sediment result in release of reduced metal species to pore water. These metal species tend to migrate towards the oxic surface sediment, where they are re-adsorbed by the Fe and Mn oxyhydroxides (Ruiz-Fernandez et al., 2007; Ruiz-Fernandez et al., 2011). Unlike other cores, core S9 did not show enrichment towards the surface, thus anthropogenic deposition and diagenetic enrichment of metals towards surface is not observed at this location. The similarity of normalized V with that of Fe and Mn especially towards the bottom of core S7 may be the result of association of V in the form of vanadates with Fe and Mn-hydroxides (Swarzenski et al., 2008) in coarser sedimentary deposits at greater depths.

4. 3. Factors controlling distribution of $\delta^{13}\text{C}_{\text{org}}$ and TOC/TN ratio signatures in Vaitarna estuary

The variation in $\delta^{13}\text{C}_{\text{org}}$ and C/N ratio along the length of the core is used to reconstruct mixing scenarios of terrigenous v/s marine plant material (Rosenbauer et al., 2009) in estuarine sediments. The relatively depleted values of $\delta^{13}\text{C}_{\text{org}}$ towards bottom (i.e. between 50 to 42 cm depth, below 32 cm and below 60 cm depth in cores S7, S9 and S5 respectively), and enriched values towards the surface of the cores, indicate increase in addition of organic matter of marine origin in recent years as compared to the past (Hubeny et al., 2009). While, corresponding decrease in TOC/TN ratios from bottom to surface, suggest, decrease in deposition of organic matter of terrestrial origin in recent years. Up-core variation in $\delta^{13}\text{C}_{\text{org}}$ and TOC/TN values, therefore, point towards estuary-wide change in the proportion of marine and terrestrial organic matter deposited within

the sediment, over a period of time. The observed high temporal variability in organic matter distribution may therefore have a major impact on the overall carbon dynamics in intertidal ecosystems (Bouillon et al., 2003).

Rate of sedimentation for the area available is 0.7 – 1.9 cm/yr (Sharma et al., 1994) and 0.24 – 2.72 cm/yr (Fernandes, 2012). Average sedimentation considered for the area based on the data available is 1.4 cm/yr. Cores collected in the present study therefore represent less than seventy-five years of sediment accumulation. Rainfall data of last hundred years, obtained from the Indian Meteorological Department (IMD), Pune from various stations located in Thane district, indicated heavy rainfall between 1954 and 1961 (Fig.7), which further decreased in successive years. Heavy monsoons therefore must be responsible for the addition of higher proportion of terrestrial organic matter as runoff in the past. The absence of distinct trend of $\delta^{13}\text{C}_{\text{org}}$ signature in core S4 has been linked to large variation in hydrodynamic energy conditions at this location. The large fluctuating trend of $\delta^{13}\text{C}_{\text{org}}$ and TOC/TN ratio below 30 cm, 40 cm and 30 cm depth of cores S4, S5 and S9 respectively, further, indicate addition of variable amounts of organic matter probably resulting from variation in fresh water influx in the past.

Decrease in rainfall following the year 1958, construction of dams, diversion of freshwater, as well as local relative sea level rise, together, seem to have resulted in reduction in terrestrial organic matter input in recent years, and is probably reflected as heavier $\delta^{13}\text{C}_{\text{org}}$ and lower TOC/TN ratio signatures towards the surface. According to Lamb, et al. (2006) the direction of change in $\delta^{13}\text{C}_{\text{org}}$ and C/N ratio is the most important factor in interpreting environmental changes (e.g. relative sea level) rather than the absolute values.

4.4. Spatial variation in $\delta^{13}\text{C}_{\text{org}}$ and TOC/TN ratio signatures

Larger fluctuations in $\delta^{13}\text{C}_{\text{org}}$ and TOC/TN values in the lower portion of the cores reflects variation in organic matter input under varying hydrodynamic energy conditions prevailing in the past. While gradual change towards surface, point towards deposition of organic matter under relatively less dynamic energy conditions in recent years. Sediment components and metals had also shown fluctuating trend in section I and a gradual change towards surface similar to that of $\delta^{13}\text{C}_{\text{org}}$ and TOC/TN. The amplitude of change in $\delta^{13}\text{C}_{\text{org}}$ signature is very high in core S9 as compared to the other three cores. Core S9 is collected from a protected area and according to Andrews et al. (1998) in the least well-flushed parts of an estuary, down-core variation in $\delta^{13}\text{C}_{\text{org}}$ and TOC/TN profiles should be quite smooth or progressive. The protected area of core S9 therefore seem to have favored deposition of sediment along with associated organic matter and metals under relatively less dynamic environment, thus systematically recording changes.

Lighter $\delta^{13}\text{C}_{\text{org}}$ between 50 cm and 42 cm depth of core S7 together with corresponding rise in TOC/TN and sand percentage probably indicate, higher deposition of land derived organic matter along with coarser particles in the past. The slight enrichment of $\delta^{13}\text{C}_{\text{org}}$ values above 22 cm depth further indicates increasing marine influence in recent years. However, TOC/TN ratio gave contrasting results; in this portion, it increases and tends to point towards decreasing marine influence. The other three cores collected closer to the mouth i.e. cores S4, S5 and S9, indicated increased marine influence in deposition of organic matter in recent years.

Similarly, core S7 must be indicating increase in marine influence in recent years as evident from the readings of $\delta^{13}\text{C}_{\text{org}}$. Core S7 is collected from upper middle portion of the estuary which is directly connected to major rivers on its upper reaches. Increasing TOC/TN values towards the top must therefore be pointing towards increased sewage contribution (Yang et al., 2011) to upper middle estuarine region in recent years. All the studied metals had also shown large increase towards surface of the core, thus pointing towards anthropogenic input in addition to that of diagenetic enrichment.

TOC v/s TN plots indicates significant positive correlation in core S4 and S7, (Fig. 8a,b). This indicates common source or similar depositional processes for TOC and TN in cores S4 and S7. In core S4, relatively heavier $\delta^{13}\text{C}_{\text{org}}$ values are noted all along the length, except slightly depleted values at 70 cm and 30 cm depths. While in core S7, all the $\delta^{13}\text{C}_{\text{org}}$ values are relatively depleted. This difference in $\delta^{13}\text{C}_{\text{org}}$ values is attributed to the location of the two cores. Core S4 is located further seaward than core S7 and therefore seem to deposit relatively higher proportion of marine organic matter. While in cores S9 and S5, TOC and TN did not show significant association (Fig. 8c,d) and are therefore assumed to have different origin or dissimilar processes of deposition. The similarity in distribution and association of organic matter in cores S5 and S9 may be attributed to relatively protected environments from which they are collected, i.e. mangroves and a more protected narrow sub channel respectively. Comparing these two cores, core S5 collected towards the mouth of the estuary, is found to accumulate organic matter with heavier $\delta^{13}\text{C}_{\text{org}}$ values and lower TOC/TN ratio relative to core S9 collected from the lower middle estuary (Table 2). Thus, suggesting decrease in marine contribution with increasing distance from the mouth to the upstream of the estuary. It also indicates dilution of fluvially derived terrestrial organic matter towards the mouth of the estuary.

Further, cores S4 and S5 are compared to understand the spatial variation between adjacent mudflat and mangrove sediment collected towards the mouth of the estuary. The results indicate high range and average values of TOC/TN in mangrove core S5 as compared to mudflat core S4 (Table 2). Thus, pointing towards greater deposition of mangrove litter in mangrove sediment as compared to adjacent mudflat. In mangrove ecosystems, mangrove plant litter fall is the main supplier of terrestrial organic matter fraction to the sedimentary organic matter pool (Prasad and Ramanathan, 2009).

4.5. Inter-relationship between geochemical proxies ($\delta^{13}\text{C}_{\text{org}}$, TOC/TN and metals)

It is known that humic substances have high metal binding capacity (Sondi et al., 2008) and if they are of marine origin then these humic substances form more stable complexes (Übner et al., 2004) than freshwater/terrestrial source. Higher and variable concentration of metals towards the bottom of core S9 and higher concentration of Fe, Mn and some of the trace metals below 60 cm depth of core S5 coincided with relatively lighter $\delta^{13}\text{C}_{\text{org}}$ values and higher TOC/TN ratios. Thus, metals, Fe-Mn oxyhydroxides and coarser sedimentary particles seem to have been associated and deposited under greater terrestrial influence in the past. While, heavier $\delta^{13}\text{C}_{\text{org}}$, lower TOC/TN ratio values and high metal concentration towards the surface of cores S4 and core S5, point towards association of metals with organic matter deposited under greater marine

influence in recent years. The higher deposition of metals and finer particles towards surface of the cores may therefore be attributed to reduction in freshwater input and resulting increase in salinity.

5. Conclusion

Vaitarna estuary indicates prevalence of relatively higher and variable hydrodynamic energy conditions in the past as compared to the present. Sediment was also found to preserve variable amount of recalcitrant organic matter of terrestrial origin towards the bottom of the cores. Metals were found to be associated with Fe-Mn oxyhydroxides in all the studied cores and showed enrichment in recent years. $\delta^{13}\text{C}_{\text{org}}$ and TOC/TN ratios indicated decrease in terrestrial influence and simultaneous increase in marine influence in deposition of organic matter within sediment of Vaitarna estuary from past to present. Variation in amount and type of organic matter deposited within sediment is attributed to, decrease in freshwater input resulting from reduction in precipitation, construction of dams, and diversion of fresh water, in addition to that of relative sea level rise. Thus, all these changes strongly suggest, possibility of alteration in natural biogeochemical processes occurring within the Vaitarna estuary and adjacent coastal environments over a period of time.

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References:

- Achyuthan, H., Richardmohan, D., Srinivasalu, S., Selvaraj, K., 2002. Trace metals concentrations in the sediment cores of estuary and tidal zones between Chennai and Pondicherry, along the east coast of India. *Indian Journal of Marine Sciences* 31 (2), 141-149.
- Acquavita, A., Predonzani, S., Mattassi, G., Rossin, P., Tamberlich, F., Falomo, J., Valic, I., 2010. Heavy metal contents and distribution in coastal sediments of the Gulf of Trieste (Northern Adriatic Sea, Italy). *Water Air Soil Pollution* 211, 95-111. doi. 10.1007/s11270-009-0284-5.
- Alber, M., 2002. A conceptual model of estuarine freshwater inflow management. *Estuaries*, 25 (6B), 1246-1261.
- Aloupi, M., Angelidis, M. O., 2002. The significance of coarse sediments in metal pollution studies in the coastal zone. *Water Air Soil Pollution* 133, 121-131.
- Álvarez-Iglesias, P., Rubio, B., Pérez-Arlucea, M., 2006. Reliability of subtidal sediments as “geochemical recorders” of pollution input: San Simón Bay (Ría de Vigo, NW Spain). *Estuarine, Coastal and Shelf Science* 70, 507-521.
- Andrews, J. E., Greenaway, A. M., Dennis, P. F., 1998. Combined Carbon Isotope and C/N Ratios as Indicators of Source and Fate of Organic Matter in a Poorly Flushed, Tropical Estuary: Hunts Bay, Kingston Harbour, Jamaica. *Estuarine, Coastal and Shelf Science* 46, 743-756.
- Böttcher, M. E., Voss, M., Schulz-Bull, D., Schneider, R., Leipe, T., Knöller, K., 2010. Environmental changes in the Pearl River Estuary (China) as reflected by light stable isotopes and organic contaminants. *Journal of Marine Systems* 82, S43-S53.

- Bouillon, S., Connolly, R. M., Lee, S. Y., 2008. Organic matter exchange and cycling in mangrove ecosystems: Recent insights from stable isotope studies. *Journal of Sea Research* 59, 44-58.
- Bouillon, S., Dahdouh-Guebas, F., Rao, A. V. V. S., Koedam, N., Dehairs, F., 2003. Sources of organic carbon in mangrove sediments: variability and possible ecological implications. *Hydrobiologia* 495, 33-39.
- Chmura, G. L., Aharon, P., 1995. Stable carbon isotope signatures of sedimentary carbon in coastal wetlands as indicators of salinity regime. *Journal of Coastal Research* 11 (1), 124-135.
- Cook, P. L. M., Revill, A. T., Butler, E. C. V., Eyre, B. D., 2004. Carbon and nitrogen cycling on intertidal mudflats of a temperate Australian estuary. II. Nitrogen cycling. *Marine Ecology Progress Series* 280, 39-54.
- Cook, P. L. M., Revill, A. T., Clementson, L. A., Volkman, J. K., 2004. Carbon and nitrogen cycling on intertidal mudflats of a temperate Australian estuary. III. Sources of organic matter. *Marine Ecology Progress Series* 280, 55-72.
- Dehairs, F., Rao, R. G., Mohan, P. C., Raman, A. V., Marguillier, S., Hellings, L., 2000. Tracing mangrove carbon in suspended matter and aquatic fauna of the Gautami-Godavari Delta, Bay of Bengal (India). *Hydrobiologia* 431, 225-241.
- Fernandes, L. L., 2012. Reconstructing pollution history from intertidal regions of estuaries along Mumbai coast, India. Ph.D. Thesis, University of Goa, India.
- Folk, R. L., 1968. *Petrology of Sedimentary rocks*. Austin, Texas: Hemphills pp.177.
- Gaudette, H. E., Flight, W. R., Toner, L., Folger, D. W., 1974. An inexpensive titration method for the determination of organic carbon in recent sediments. *Journal of Sedimentary Petrology* 44, 249-253.
- Gazetteer of India, Maharashtra State Gazetteers, Thane District (Revised Edition), 1982. Bombay, Gazetteers Department, Government of Maharashtra.
- Gonneea, M. E., Paytan, A., Herrera-Silveira, J. A., 2004. Tracing organic matter sources and carbon burial in mangrove sediments over the past 160 years. *Estuarine, Coastal and Shelf Science* 61, 211-227.
- Hu, J., Peng, P., Jia, G., Mai, B., Zhang, G., 2006. Distribution and sources of organic carbon, nitrogen and their isotopes in sediments of the subtropical Pearl River estuary and adjacent shelf, Southern China. *Marine Chemistry* 98, 274-285.
- Hubeny, J. B., King, J. W., Cantwell, M., 2009. Anthropogenic influences on estuarine sedimentation and ecology: examples from the varved sediments of the Pettaquamscutt River Estuary, Rhode Island. *Journal of Paleolimnology* 41, 297-314. doi: 10.1007/s10933-008-9226-2.
- Jickells, T. D., Rae, J. E., (eds) 1997. *Biogeochemistry of intertidal sediments*, Vol 9. Cambridge University Press, Cambridge.
- Kennedy, H., Gacia, E., Kennedy, D. P., Papadimitriou, S., Duarte, C.M., 2004. Organic carbon sources to SE Asian coastal sediments. *Estuarine, Coastal and Shelf Science* 60, 59-68.
- Kimmerer, W. J., 2002. Effects of freshwater flow on abundance of estuarine organisms: physical effects or trophic linkages?. *Marine Ecology Progress Series* 243, 39-55.
- Ku, H-W., Chen, Y-G., Chan, P-S., Liu, H-C., Lin, C-C., 2007. Paleo-environmental evolution as revealed by analysis of organic carbon and nitrogen: A case of coastal Taipei Basin in Northern Taiwan. *Geochemical Journal* 41, 111-120.

- Lamb, A. L., Vane, C. H., Wilson, G. P., Rees, J. G., Moss-Hayes, V. L., 2007. Assessing $\delta^{13}\text{C}$ and C/N ratios from organic material in archived cores as Holocene sea level and palaeoenvironmental indicators in the Humber estuary, UK. *Marine Geology* 244, 109-128.
- Lamb, A. L., Wilson, G. P., Leng, M. J., 2006. A review of coastal palaeoclimate and relative sea-level reconstructions using $\delta^{13}\text{C}$ and C/N ratios in organic material. *Earth-Science Reviews* 75, 29-57.
- Lin, S., Hsieh, I-J., Huang, K-M., Wang, C-H., 2002. Influence of the Yangtze River and grain size on the spatial variations of heavy metals and organic carbon in the East China Sea continental shelf sediments. *Chemical Geology* 182, 377-394.
- Meyers, P. A., 1997. Organic geochemical proxies of paleoceanographic, paleolimnologic, and paleoclimatic processes. *Organic Geochemistry* 27, 213-250.
- Montagna, P. A., Kalke, R. D., Ritter, C., 2002. Effect of restored freshwater inflow on macrofauna and meiofauna in upper Rincon Bayou, Texas, USA. *Estuaries* 25 (6B), 1436-1447.
- Müller, A., Voss, M., 1999. The palaeoenvironments of coastal lagoons in the southern Baltic Sea, II. $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ ratios of organic matter – sources and sediments. *Palaeogeography, Palaeoclimatology, Palaeoecology* 145, 17-32.
- Nichols, F. H., Cloern, J. E., Luoma, S. N., Peterson, D. H., 1986. The modification of an estuary. *Science* 231, 567-573. doi:10.1126/science.231.4738.567.
- Ogrinc, N., Fontolan, G., Faganeli, J., Covelli, S., 2005. Carbon and nitrogen isotope compositions of organic matter in coastal marine sediments (the Gulf of Trieste, N Adriatic Sea): indicators of sources and preservation. *Marine Chemistry* 95, 163-181.
- Ouyang, Y., Zhang, J. E., Ou, L.-T., 2006. Temporal and spatial distributions of sediment total organic carbon in an Estuary river. *Journal of Environmental Quality* 35, 93-100. doi:10.2134/jeq2005.0221.
- Pande, A., Nayak, G. N., 2013. Understanding distribution and abundance of metals with space and time in estuarine mudflat sedimentary environment. *Environmental Earth Science* 70, 2561-2575. doi: 10.1007/s12665-013-2298-y.
- Pejrup, M., 1988. The triangular diagram for classification of estuarine sediments: A new approach. In: de Boer, P. L., Van Gelder, A., and Nios, S. D., (eds), *Tide Influenced Sedimentary Environments and Facies*, pp. 289-300.
- Prasad, M. B. K., Ramanathan, A. L., 2009. Organic matter characterization in a tropical estuarine-mangrove ecosystem of India: Preliminary assessment by using stable isotopes and lignin phenols. *Estuarine, Coastal and Shelf Science* 84, 617-624.
- Ramaswamy, V., Gaye, B., Shirodkar, P. V., Rao, P. S., Chivas, A. R., Wheeler, D., Thwin, S., 2008. Distribution and sources of organic carbon, nitrogen and their isotopic signatures in sediments from the Ayeyarwady (Irrawaddy) continental shelf, northern Andaman Sea. *Marine Chemistry* 111, 137-150.
- Rodriguez, C. A., Flessa, K. W., Dettman, D. L., 2001. Effects of upstream diversion of Colorado River water on the Estuarine bivalve mollusc *Mulinia coloradoensis*. *Conservation Biology* 15 (1), 249-258.
- Rosenbauer, R. J., Swarzenski, P. W., Kendall, C., Orem, W. H., Hostettler, F. D., Rollog, M. E., 2009. A carbon, nitrogen, and sulfur elemental and isotopic study in dated sediment cores from the Louisiana Shelf. *Geo-Marine Letters* 29 (6), 415-429.

- Ruiz-Fernández, A. C., Hillaire-Marcel, C., Páez-Osuna, F., Ghaleb, B., Caballero, M., 2007. ^{210}Pb chronology and trace metal geochemistry at Los Tuxtlas, Mexico, as evidenced by a sedimentary record from the Lago Verde crater lake. *Quaternary Research* 67, 181-192.
- Ruiz-Fernández, A. C., Marrugo-Negrete, J. L., Paternina-Urbe, R., Pérez-Bernal, L. H., 2011. ^{210}Pb -derived sedimentation rates and Corg fluxes in Soledad Lagoon (Cispatá Lagoon System, NW Caribbean Coast of Colombia). *Estuaries and Coasts* 34, 1117-1128. doi: 10.1007/s12237-011-9394-6.
- Sanders, C. J., Smoak, J. M., Naidu, A. S., Araripe, D. R., Sanders, L. M., Patchineelam, S. R., 2010a. Mangrove forest sedimentation and its reference to sea level rise, Cananea, Brazil. *Environmental Earth Science* 60, 1291-1301. doi: 10.1007/s12665-009-0269-0.
- Sanders, C. J., Smoak, J. M., Naidu, A. S., Araripe, D. R., Sanders, L. M., Patchineelam, S. R., 2010b. Organic carbon burial in a mangrove forest, margin and intertidal mud flat. *Estuarine, Coastal and Shelf Science* 90, 168-172.
- Schoer, J. H., 1990. Determination of the origin of suspended matter and sediments in the Elbe Estuary using natural tracers. *Estuaries* 13 (2), 161-172.
- Schubert, C. J., Calvert, S. E., 2001. Nitrogen and carbon isotopic composition of marine and terrestrial organic matter in Arctic Ocean sediments: implications for nutrient utilization and organic matter composition. *Deep-Sea Research I* 48, 789-810.
- Shankar, M. N. R., Mohan, G., 2006. Assessment of the groundwater potential and quality in Bhatsa and Kalu river basins of Thane district, western Deccan volcanic province of India. *Environmental Geology* 49: 990-998. doi: 10.1007/s00254-005-0137-5.
- Sharma, P., Borole, D. V., Zingde, M. D., 1994. ^{210}Pb geochronology and trace element composition of the sediments in the vicinity of Bombay, west coast of India. *Marine Chemistry* 47: 227-241.
- Singh, K. T., Nayak, G. N., 2009. Sedimentary and geochemical signatures of depositional environment of sediments in mudflats from a microtidal Kalinadi estuary, central west coast of India. *Journal of Coastal Research* 25 (3): 641-650.
- Sondi, I., Lojen, S., Juračić, M., Prohić, E., 2008. Mechanisms of land-sea interactions- the distribution of metals and sedimentary organic matter in sediments of a river-dominated Mediterranean karstic estuary. *Estuarine, Coastal and Shelf Science* 80, 12-20.
- Surge, D. M., Lohmann, K. C., Goodfriend, G. A., 2003. Reconstructing estuarine conditions: oyster shells as recorders of environmental change, Southwest Florida. *Estuarine, Coastal and Shelf Science* 57, 737-756.
- Swamy, G. N., 1994. Training programme in Modeling and Monitoring of Coastal Marine Pollution (MAMCOMP), November 21 - Dec 16, Lecture notes comp. by: Sinha P C. 591-593 pp.
- Swarzenski, P. W., Campbell, P. L., Osterman, L. E., Poore, R. Z., 2008. A 1000-year sediment record of recurring hypoxia off the Mississippi River: The potential role of terrestrially-derived organic matter inputs. *Marine Chemistry* 109, 130-142.
- Übner, M., Treuman, M., Viitak, A., Loop, M., 2004. Properties of humic substances from the Baltic Sea and Lake Ermistu mud. *Journal of Soil Sediments* 4, 24-29.
- Unnikrishnan, A. S., Kumar, K. R., Fernandes, S. E., Michael, G. S., Patwardhan, S. K., 2006. Sea level changes along the Indian coast: Observations and projections. *Current Science* 90 (3), 362-368.

- Usui, T., Nagao, S., Yamamoto, M., Suzuki, K., Kudo, I., Montani, S., Noda, A., Minagawa, M., 2006. Distribution and sources of organic matter in surficial sediments on the shelf and slope off Tokachi, western North Pacific, inferred from C and N stable isotopes and C/N ratios. *Marine Chemistry* 98, 241-259.
- Volvoikar, S. P., Nayak, G. N., 2013. Depositional environment and geochemical response of mangrove sediments from creeks of northern Maharashtra coast, India. *Marine Pollution Bulletin* 69, 223-227.
- Wilson, G. P., Lamb, A. L., Leng, M. J., Gonzalez, S., Huddart, D., 2005 a. $\delta^{13}\text{C}$ and C/N as potential coastal palaeoenvironmental indicators in the Mersey Estuary, U. K. *Quaternary Science Reviews* 24, 2015-2029.
- Yang, M., Kostaschuk, R., Chen, Z., 2004. Historical changes in heavy metals in the Yangtze estuary, China. *Environmental Geology* 46, 857-864. doi: 10.1007/s00254-004-1072-6.
- Yang, S., Tang, M., Yim, W. W.-S., Zong, Y., Huang, G., Switzer, A. D., Saito, Y., 2011. Burial of organic carbon in Holocene sediments of the Zhujiang (Pearl River) and Changjiang (Yangtze River) estuaries. *Marine Chemistry* 123, 1-10.
- Yang, S. L., Li, H., Ysebaert, T., Bouma, T. J., Zhang, W. X., Wang, Y. Y., Li, P., Li, M., Ding, P. X., 2008. Spatial and temporal variations in sediment grain size in tidal wetlands, Yangtze Delta: On the role of physical and biotic controls. *Estuarine, Coastal and Shelf Science* 77, 657-671.
- Zhang, J., Wu, Y., Jennerjahn, T. C., Ittekkot, V., He, Q., 2007. Distribution of organic matter in the Changjiang (Yangtze River) estuary and their stable carbon and nitrogen isotopic ratios: Implications for source discrimination and sedimentary dynamics. *Marine Chemistry* 106, 111-126.
- Zhang, L., Yin, K., Wang, L., Chen, F., Zhang, D., Yang, Y., 2009. The sources and accumulation rate of sedimentary organic matter in the Pearl River Estuary and adjacent coastal area, Southern China. *Estuarine, Coastal and Shelf Science* 85, 190-196.
- Zong, Y., Lloyd, J. D., Leng, M. J., Yim, W. W. -S., Huang, G. Q., 2006. Reconstruction of the Holocene monsoon history from the Pearl River Estuary, southern China, using diatoms and organic carbon isotope ratios. *Holocene* 16, 251-263.

Table 1: Average \pm standard deviation values of sediment components and OC in the three sections

	Sand (%)	Silt (%)	Clay (%)	OC (%)
a. Core S4				
Section III(surface to 28 cm)	35.2 \pm 10.3	27.6 \pm 8.1	37.2 \pm 9.4	1.1 \pm 0.1
Section II (30 cm to 58 cm)	39.4 \pm 9.4	29.0 \pm 6.4	31.7 \pm 6.3	1.6 \pm 0.4
Section I (60 cm to 88 cm)	43.1 \pm 10.3	23.4 \pm 5.7	33.5 \pm 9.8	1.4 \pm 0.3
b. Core S5				
Section III (surface to 48cm)	6.5 \pm 3.2	24.3 \pm 3.9	69.2 \pm 5.4	0.7 \pm 0.1
Section II (50 cm to 78 cm)	17.0 \pm 9.3	30.2 \pm 6.3	52.7 \pm 9.0	1.5 \pm 0.3
Section I (80 cm to 102 cm)	53.3 \pm 12.0	22.5 \pm 3.3	24.3 \pm 10.8	0.7 \pm 0.3
c. Core S9				
Section III (surface to 14cm)	5.8 \pm 1.5	37.0 \pm 2.3	57.2 \pm 3.7	1.0 \pm 0.06
Section II (16 cm to 28 cm)	11.8 \pm 1.6	36.8 \pm 1.6	51.3 \pm 2.4	1.0 \pm 0.09
Section I (30 cm to 52 cm)	14.8 \pm 5.6	38.5 \pm 14.2	46.8 \pm 16.1	2.5 \pm 1.6
d. Core S7				
Section III (surface to 40cm)	8.2 \pm 3.1	40.0 \pm 4.0	51.7 \pm 6.0	1.2 \pm 0.3
Section II (42 cm to 56 cm)	23.2 \pm 12.7	43.0 \pm 6.8	33.8 \pm 12.3	1.3 \pm 0.3
Section I (58 cm to 66 cm)	4.8 \pm 2.9	31.8 \pm 8.0	63.4 \pm 9.5	1.5 \pm 0.2

Table 2: Range and average values of C %, N %, $\delta^{13}\text{C}_{\text{org}}$ ‰ and TOC/TN

	C %	N %	$\delta^{13}\text{C}_{\text{org}}$ ‰	TOC/TN
Core S4	0.61 to 1.09 (0.80)	0.04 to 0.08 (0.07)	-23.4 to -21.6 (-22.5)	8.87 to 14.6 (12.2)
Core S5	0.23 to 1.06 (0.61)	0.02 to 0.08 (0.05)	-23.8 to -19.7 (-21.7)	7.00 to 30.8 (13.7)
Core S9	0.77 to 3.63 (1.28)	0.04 to 0.10 (0.08)	-28.4 to -20.2 (-22.6)	10.5 to 59.5 (17.5)
Core S7	0.60 to 1.30 (0.89)	0.07 to 0.13 (0.10)	-24.2 to -21.7 (-23.0)	7.90 to 11.1 (8.87)

Figure captions:

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

Fig. 2: Ternary diagram showing deposition of sand, silt and clay under varying hydrodynamic energy conditions after Pejrup (1988): **a)** mudflat core collected towards the mouth (core S4); **b)** mangrove core collected towards the mouth (core S5); **c)** mudflat core collected from the lower middle estuary (core S9); **d)** mudflat core collected from the upper middle estuary (core S7). Circles represent section I, triangles indicate section II and diamonds represent section III.

Fig. 3: Distribution of aluminium normalized metals with depth: **a)** mudflat core collected towards the mouth (core S4); **b)** mangrove core collected towards the mouth (core S5).

Fig. 4: Distribution of aluminium normalized metals with depth: **a)** mudflat core collected from the lower middle estuary (core S9); **b)** mudflat core collected from the upper middle estuary (core S7).

Fig. 5: Distribution of $\delta^{13}\text{C}_{\text{org}}$ with depth: **a)** mudflat core collected towards the mouth (core S4); **b)** mangrove core collected towards the mouth (core S5); **c)** mudflat core collected from the lower middle estuary (core S9); **d)** mudflat core collected from the upper middle estuary (core S7).

Fig. 6: Distribution of TOC/TN with depth: **a)** mudflat core collected towards the mouth (core S4); **b)** mangrove core collected towards the mouth (core S5); **c)** mudflat core collected from the lower middle estuary (core S9); **d)** mudflat core collected from the upper middle estuary (core S7).

Fig. 7: Rainfall data of last 100 years for three different stations in Thane district.

Fig. 8: Scatter plots illustrating coefficient of determination (R^2) between C% and N%: **a)** mudflat core collected towards the mouth (core S4); **b)** mangrove core collected towards the mouth (core S5); **c)** mudflat core collected from the lower middle estuary (core S9); **d)** mudflat core collected from the upper middle estuary (core S7)

Fig. 1

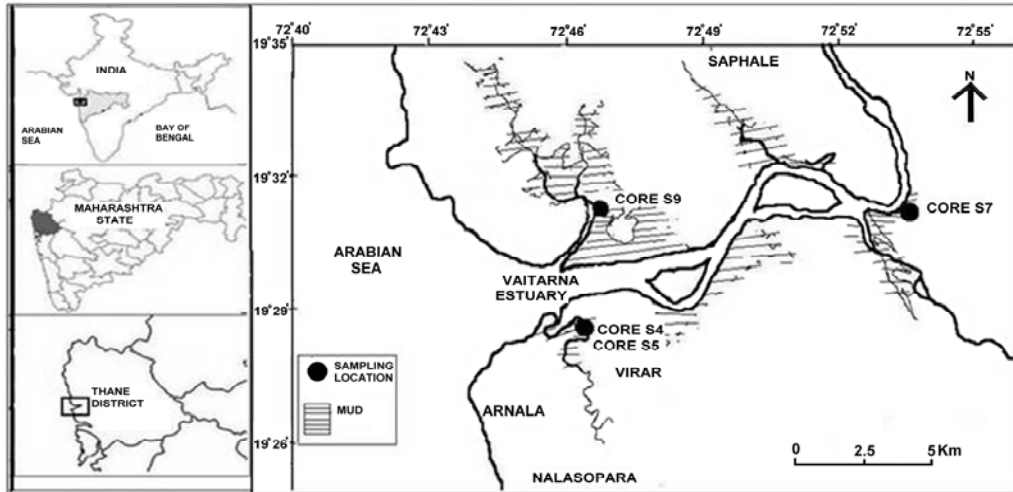


Fig. 2

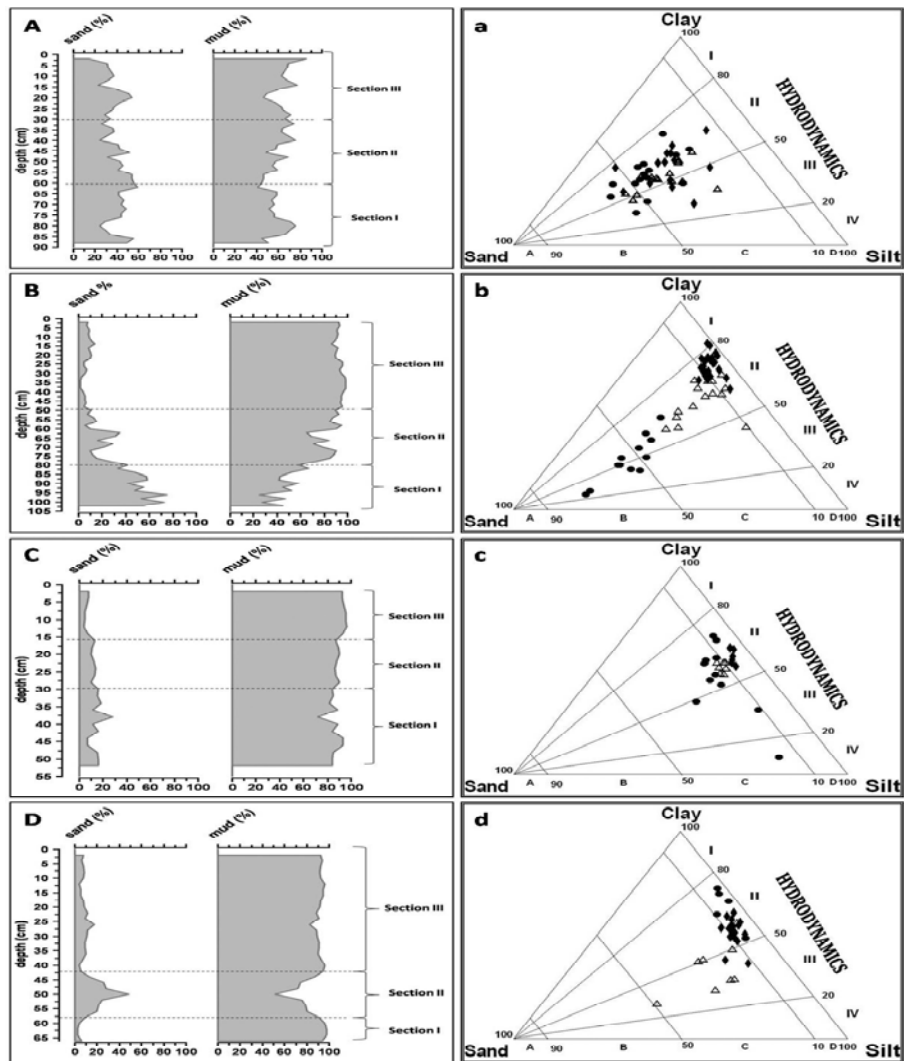


Fig. 3

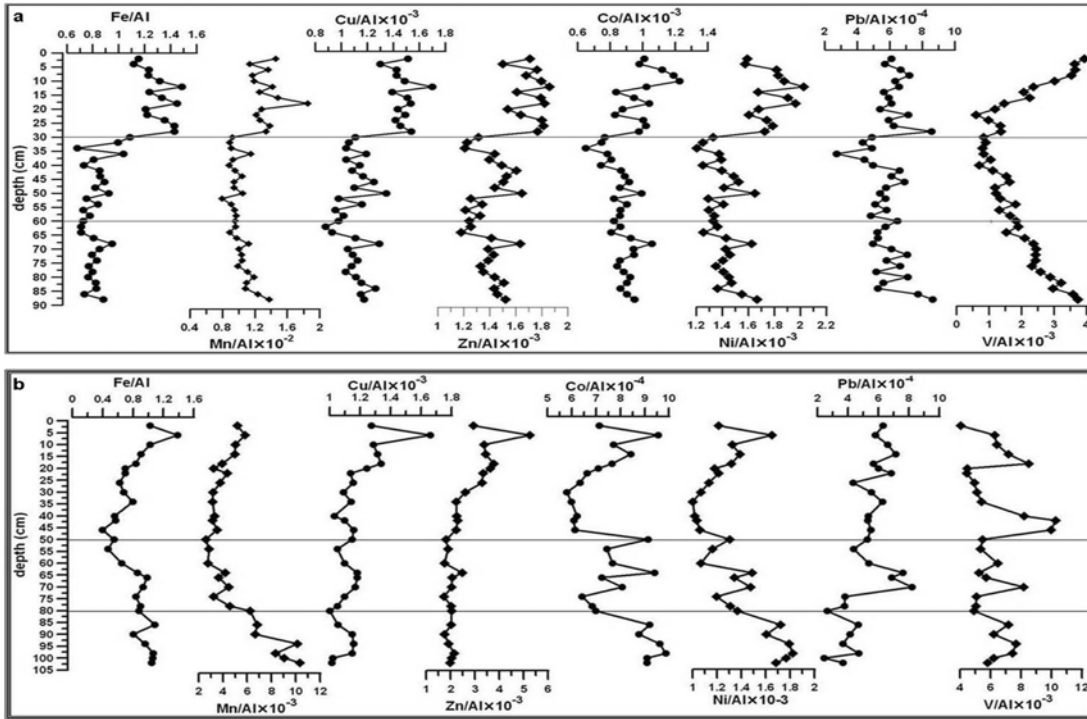


Fig. 4

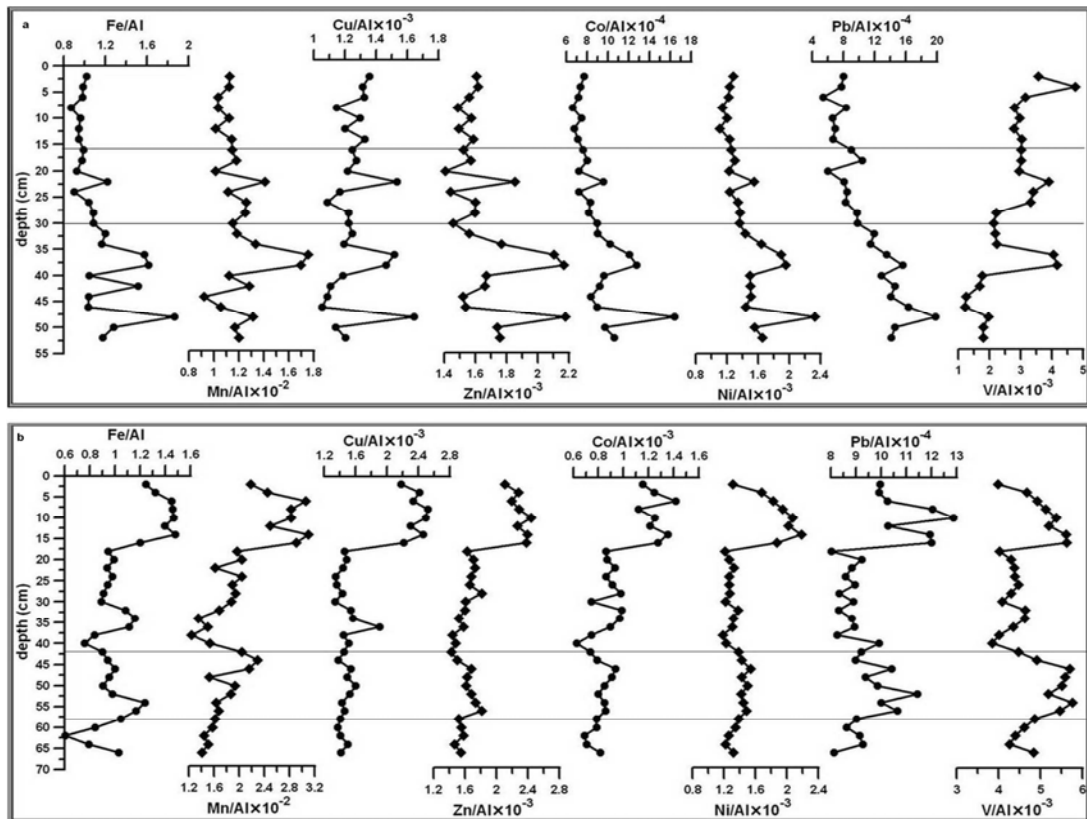


Fig. 5

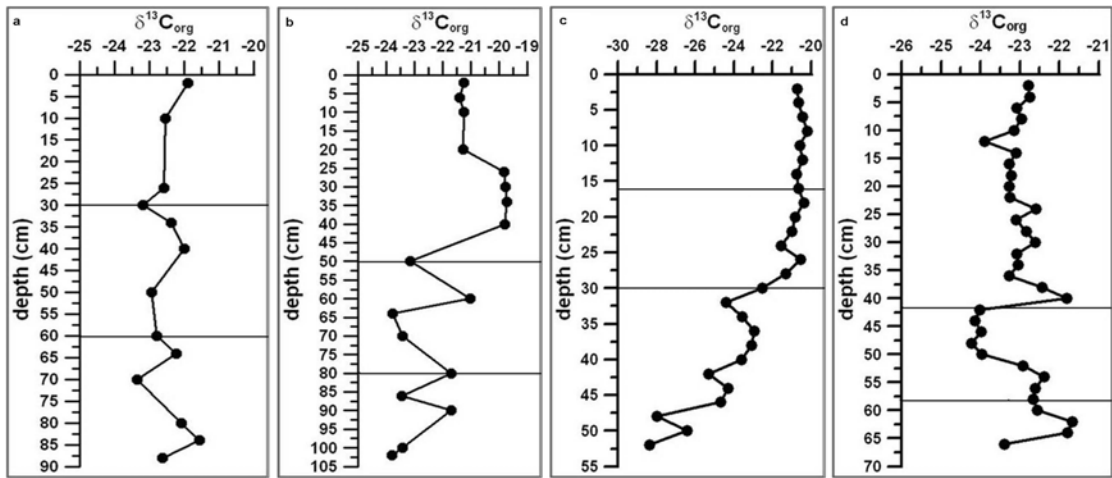


Fig. 6

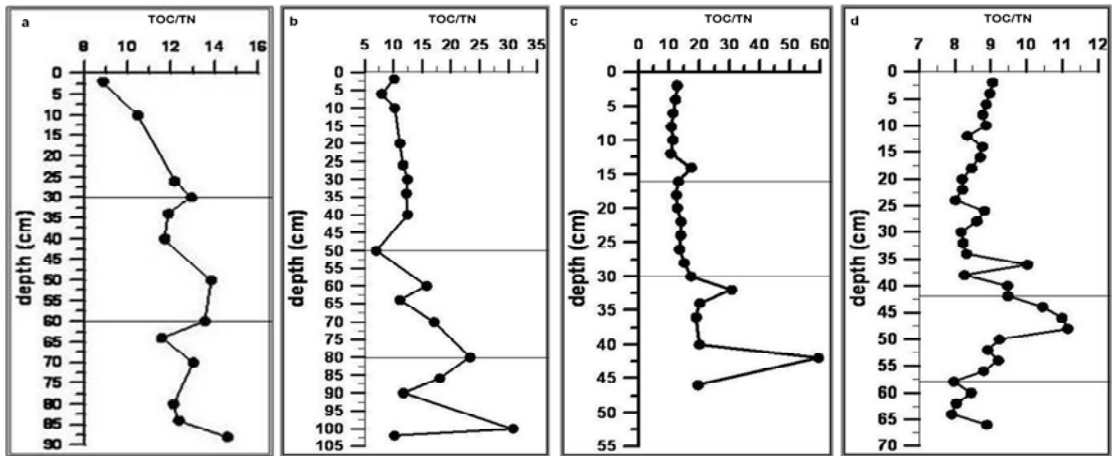


Fig. 7

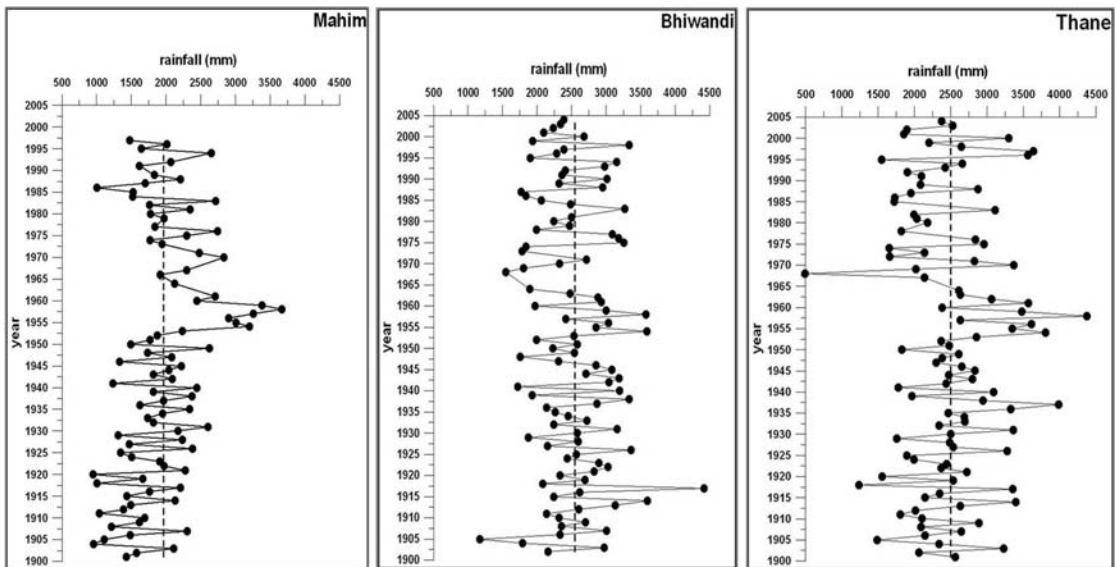


Fig. 8

