

Geochemical and diatom records of recent changes in depositional environment of a tropical wetland, central west coast of India

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Abstract Two mudflat sediment cores collected from a sub-channel (S-61) and the main channel (S-60) of a tropical wetland, along central west coast of India, were investigated for recent changes in depositional environment using geochemical (sediment grain size, total organic carbon, total nitrogen, carbon/nitrogen ratio (TOC/TN), selected metals and pH) and diatom records. The sub-channel (S-61) represents river environment which opens into main channel (S-60) which represents marine environment being close to the sea. We report a transition from river-dominated to marine-dominated depositional environment over the years. The relatively higher sand percentage together with elevated carbon/nitrogen ratio and predominance of freshwater diatoms suggested greater river runoff in the past while marine influence is supported by decrease in TOC/TN ratio and increased dominance of marine diatoms in recent years. In the main channel (S-60), distribution of metals is regulated by organic matter (total nitrogen and total organic carbon) while in the sub-channel (S-61), Fe–Mn oxyhydroxides play a significant role in trace metal distribution. The highest numbers of diatoms were recorded in the sub-channel (S-61) which is also characterized by higher total nitrogen concentration.

Geochemical and diatom signatures thus have helped to infer spatial and temporal variations in depositional environment.

Keywords Depositional environment · Geochemical · Diatoms · Wetlands · Central west coast of India

Introduction

Creeks and estuaries are an integral part of the coastal wetlands which have been identified as high-risk zones from the point of global climate change (IPCC 2007). These coastal bodies are important sites of biogeochemical transformations including biological production, sediment retention and nutrient transformation (Bianchi 2007). They receive inputs of organic matter and nutrients from land and also exchange large amounts of matter and energy with the open ocean (Gattuso et al. 1998). Environment changes and human activities have an important bearing on the delivery of terrestrially derived catchment material to the adjacent coastal environment and offshore region (Milliman and Syvitski 1992).

Mudflats are sub-environments developed along intertidal part of wetlands representing large unvegetated areas that are exposed during low tide and submerged during high tide (Reineek 1972). Due to high percentage of fine particles and organic matter concentration, mudflat sediments exhibit cohesive properties. Organic matter deposition in mudflat sediment is known to be affected by changes in river discharge, catchment area disturbance and fluctuations in relative sea level (Volvoikar et al. 2014). The sediments deposited within mudflats therefore represent the complete sequence of past environmental changes (Volvoikar and Nayak 2013b; Singh et al. 2013).

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Proxies including metal concentration, organic matter (total organic carbon and total nitrogen), carbon/nitrogen (TOC/TN) ratio and sediment grain size have been largely used to characterize sediment source, depositional environment and prevailing hydrodynamic conditions (Ribeiro et al. 2010; Xia et al. 2011; Singh et al. 2013; Volvoikar et al. 2014). The TOC/TN ratio acts as an indicator to identify the source of organic matter (Wilson et al. 2005; Ruiz-Fernández et al. 2011). In marine organic matter, TOC/TN ratio range from 4 to 10, while in terrestrial organic matter, TOC/TN ratio is greater than 20 (Meyers and Teranes 2001) with characteristic ranges being 175–400 for wood, 20–50 for tree leaves, and 25–80 for grass and herbaceous plants (Hedges et al. 1986). Diatoms belonging to class Bacillariophyceae are also the important bio-indicators of environmental changes. They respond directly to changes in salinity, nutrients, pH, light and temperature (Stevenson and Pan 1999). Diatom assemblages have earlier been widely used to interpret changes in the degree of marine (Zong 1997) and fresh water influence (Almeida and Gil 2001). Similarly physical, chemical and biological interactions between riverine and marine systems have profound influences on the transport and fate of trace metals as well (Venkatramanan et al. 2014).

In the water column, metals exist in different forms where they interact with suspended sediment matter, slowly settle down and get deposited in the bottom sediments (Kennish 2002). However, several physical, chemical and biological processes which take place at sediment–water interface may result in mobilization of metals. The accumulation of metal contaminants in sediments can therefore pose serious environmental problems to the surrounding areas as accumulated metals in the food chains cannot be eliminated chemically or biologically (Chapman and Wang 2001). In sediments however distribution and accumulation of metals are mainly regulated by sediment grain size, organic matter, pH, Fe–Mn oxyhydroxides, aluminosilicates and associated processes (Chatterjee et al. 2007). Thus, the present study is carried out with the following objectives: (1) to reconstruct the recent environmental changes using geochemical and diatom records and (2) to understand the sources and factors controlling the distribution of metals in two different creek channels within the same catchment.

Materials and methods

Study area

Rajapuri creek lies along the central west coast of India in Raigad district of Maharashtra (Fig. 1). The catchment area is a moderately dissected plateau of Deccan trap. Basaltic

rocks are flat-topped and descend to the plain in terraces (Subramanya 1987). The predominant soils in the region are of lateritic nature. The soil colour varies from bright red to brownish red owing to the preponderance of hydrated iron oxides (Das and Mukherjee 2002). The creek is fed by Mandad River which originates in the Western Ghats, follows a meandering course and opens in Rajapuri creek. The total length of the river is 24.99 km. The basin perimeter of Mandad River is 92.69 km and basin area is 166.92 km² (Shindikar 2006). Tides in this region are semi-diurnal in nature. The region receives an average annual rainfall of 3,750 mm of which nearly 95 % occurs during the monsoon period (June–September). The catchment area of Rajapuri creek is covered by forest land and agricultural area. Mandad River receives effluents from domestic, urban and other diffuse sources as the river passes through the township and cities. Several industries located in the coastal areas of the Arabian Sea also discharge untreated or semi-treated effluents into the creek.

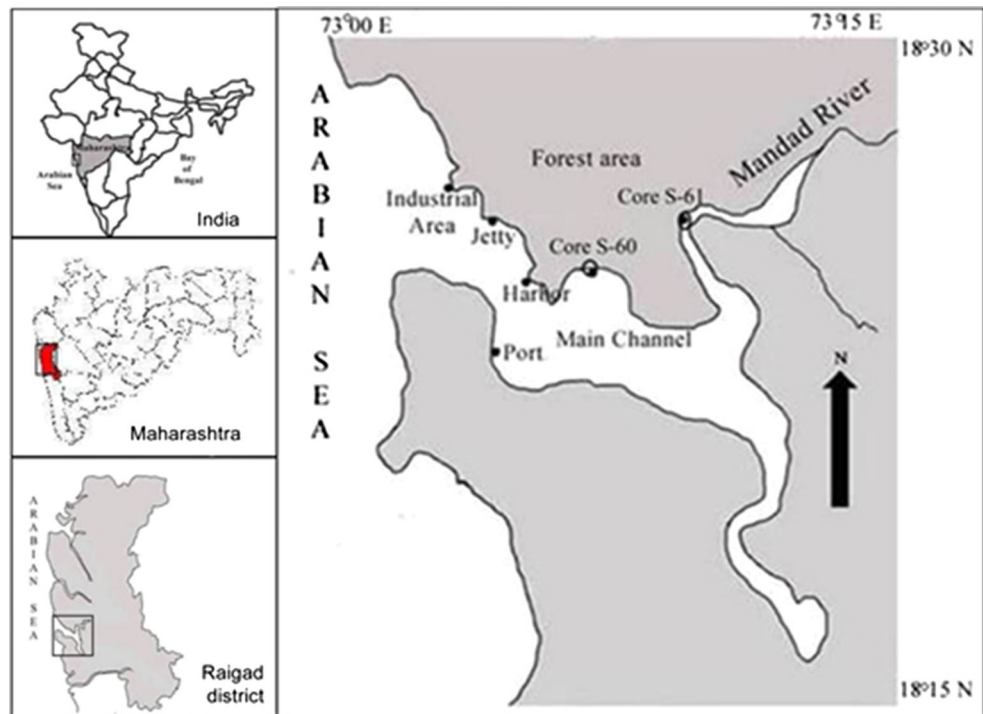
Sampling

Two mudflat sediment cores, one representing lower channel of Mandad River (S-61) and other from the main channel of Rajapuri creek (S-60), were collected using hand-driven PVC coring tube of 63 mm inner diameter (Fig. 1). The locations show distinct geomorphology and sedimentological settings. The core length varied from 74 cm in core S-61 to 98 cm in core S-60. Colour changes were noted for both the cores. The sub-sampling was done at 2 cm interval. Each sub-sample was analyzed for sediment grain size, total organic carbon, metals (Fe, Mn, Al, Ni, Cr, Co, Zn and Pb) and pH while selected alternate sub-samples were studied for diatoms and total nitrogen.

Laboratory analysis

In the laboratory, pH was determined using pH meter (Thermo Orion 420 A+ model). The sediment was dried in the oven at 60 °C for further analysis. Sediment grain size analysis was carried out by Pipette method detailed by Folk (1968). Part of the dried sediment was finely powdered using agate-mortar and kept in pre-cleaned vials for the analysis of total organic carbon, total nitrogen and selected metals (Fe, Mn, Al, Ni, Cr, Co, Zn and Pb). Total organic carbon was estimated using the method detailed by Gaudette et al. (1974) in which exothermic heating and oxidation with K₂Cr₂O₇ and concentrated H₂SO₄ are followed by titration of excess dichromate with 0.5 N Fe(NH₄)₂(-SO₄)₂·6H₂O. Total nitrogen was determined using a nitrogen–carbon soil elemental analyzer (Thermo FLASH 2000 model). Sediment samples for major (Al, Fe and Mn) and trace elements (Ni, Cr, Co, Zn and Pb) were digested

Fig. 1 Study area map with core location



using hydrofluoric–perchloric–nitric acid mixtures in Teflon beakers. Complete digestion was ensured by repeating the digestion steps until clear solutions were obtained (Jarvis and Jarvis 1985). The concentrations of major and trace elements were determined using Varian AA 240 FS flame atomic absorption spectrometry (AAS) with an air/acetylene flame for all of the above elements except for Al for which nitrous oxide/acetylene flame was employed at specific wavelengths. The instrument was calibrated by running blank and standard solutions prior to each element analysis. Recalibration check was performed at regular intervals. All chemicals used in the study were of analytical grade. Together with the samples, certified reference standard from the Canadian national bureau of standards (BCSS-1) was digested and run, to test the analytical and instrument accuracy of the method. The recoveries were between 86 and 91 % for Fe, Ni and Al; 87–92 % for Mn and Co; 80–85 % for Pb and Zn; 90–95 % for Cr, with a precision of 6 %.

Diatom analysis was done following the method detailed by Battarbee (1986). Briefly, ~0.5–1.0 g of un-ground sediment was heated with 30 % H₂O₂ and 10 % HCl to remove organic matter and carbonates, respectively. Two to five drops of digested sample were pipetted on to cover slips which were subsequently mounted onto the glass slide using Canada balsam as a mounting medium. Identification and counting of diatoms were performed using an Olympus light microscope Normanski optics, under 1,000×

magnification in oil immersion lens. A minimum of 200–300 complete diatom valves were counted for each sample, except in 11 samples mainly representing depth interval from 46 cm up to bottom in both cores in which total diatom dominance was very low (<50 valves counted on three slides). However, these samples were included in the results, providing information with regard to diatom species distribution (Sylvestre et al. 2004). The identification of diatoms was done after Desikachary (1986), Gonzalves and Gandhi (1952, 1953, 1954) and Mishra (1956). Diatoms were classified into freshwater and marine habitat following Gopinathan (1975, 1984) and Gandhi (1956).

To evaluate the level of pollution in sediments, we used the index of geo-accumulation (*I*_{geo}) using the formula of Muller (1979), given below.

$$I_{geo} = \log_2 C_n / 1.5 \times B_n$$

where *I*_{geo} is index of geo-accumulation, *C*_{*n*} is measured concentration of element “*n*”, *B*_{*n*} is element content in “average shale” (Turekian and Wedepohl 1961) and the factor 1.5 is used because of possible variation of the background data due to lithogenic effects. Muller (1979) classified the level of pollution into seven classes based upon index of geo-accumulation (*I*_{geo}) values viz “very strongly polluted”—*I*_{geo} class 6 (*I*_{geo} > 5); “Strong to very strong polluted”—*I*_{geo} class 5 (*I*_{geo} 4–5); “Strongly polluted”—*I*_{geo} class 4 (*I*_{geo} 3–4); “Moderately to strongly polluted”—*I*_{geo} class 3 (*I*_{geo} 2–3); “Moderately

polluted”— I_{geo} class 2 (I_{geo} 1–2); “Unpolluted to moderately polluted”— I_{geo} class 1 (I_{geo} 0–1) and “Unpolluted”— I_{geo} class 0 ($I_{\text{geo}} < 0$).

Statistical analysis

The principal component analysis (PCA) and factor analysis were applied to the dataset using the software C2 and SPSS 16.0. Paired sample *t* test analysis was used to assess the statistical differences between the two cores (S-61 and S-60). The difference is regarded as statistically significant if *p* value is lower than 0.05 and insignificant if *p* value is higher than 0.05.

Results

Colour

Colour variations from brown to light grey and dark grey to black were seen visually in both the cores from surface to bottom. Sediment colour was brown to light grey from 0 to 30 cm in core S-61 and from 0 to 39 cm in core S-60. The remaining part of the cores (S-61 and S-60) was dark grey to black.

Sediment grain size

Each core has been divided into two zones depending upon the distribution pattern of sediment grain size namely, zone 1 and zone 2 (Fig. 2a, b). In core S-61 (Fig. 2a), zone 1 is characterized by large variations in sand, silt and clay percentages. Sand percentage is relatively higher in this zone (average ~8 %). In zone 2, from 28 to 10 cm, clay percentage shows an overall increasing trend while silt and sand percentages show an overall decreasing trend. From 10 cm to surface, clay percentage shows an overall decreasing trend while sand and silt percentages show an overall increasing trend. In core S-60 (Fig. 2b), zone 1 is characterized by the dominance of mud (silt + clay), sand percentage being very low (average <1 %). Silt and clay percentages show large variations in this zone. In zone 2, sand percentage shows a rapid increase from 38 to 24 cm, with highest positive peak at 32 cm (average ~20 %). From 16 cm to surface, sand, silt and clay percentages show almost uniform profiles.

To understand the hydrodynamic condition of depositional environment, ternary diagram proposed by Pejrup (1988) is plotted (Fig. 3). Plot (Fig. 3) reveals that the core collected from the sub-channel (S-61) falls largely within section II indicating that sediments were deposited under a less-violent prevailing condition while the core S-60 which was collected from main channel falls largely within

sections IV–II indicating violent to less-violent hydrodynamic conditions (Fig. 3).

Total organic carbon, total nitrogen and pH

In zone 1 of core S-61 (Fig. 2a), a major portion of total organic carbon falls above the average line while in zone 2 values fall below their respective average line. The pH in zone 1 and 2 is basic (Fig. 2a). In core S-60 (Fig. 2b), zones 1 and 2 show a nearly constant trend for total organic carbon except from 98 to 82 cm, where values fall above the average lines and from 46 to 32 cm and 10 cm to surface, where the values fall below the average lines. The pH is mostly basic in zone 1 in this core (Fig. 2b). In zone 1 of both the cores (S-61 and S-60), total nitrogen generally falls below average line, while in zone 2 total nitrogen concentration shows overall increase.

TOC/TN ratio

In core S-61 and S-60, TOC/TN ratio is generally more than 20 in zone 1; however, in zone 2 TOC/TN ratio shows overall decreasing trend (Fig. 4a, b). The enhanced values of carbon–nitrogen ratio in all the samples in core S-60 (Fig. 4b) may be due to deposition of terrestrially transported organic matter which contains vascular plant debris with lower nitrogen content since the site location of core S-60 is surrounded by reserved forest area. Meyers (1997) also made a similar observation.

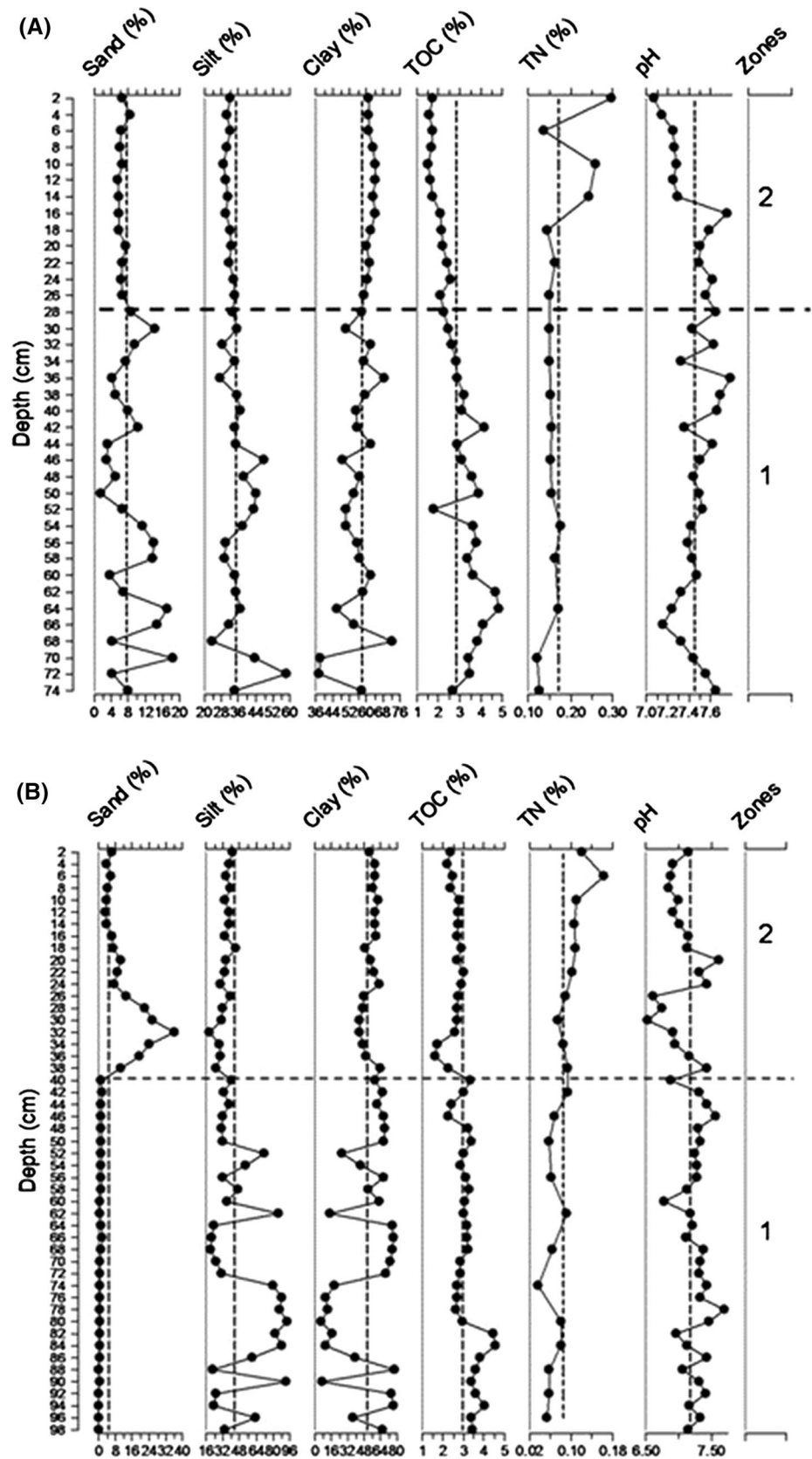
Major elements (Fe, Mn and Al)

In zone 1 of core S-61 (Fig. 5a), significant variations in Mn and Al profiles are noted. Fe fluctuates around its average line. In zone 2, from 28 to 10 cm, Fe, Mn and Al show an overall decreasing trend while from 10 cm to surface they show an overall increasing trend. In zone 1 of core S-60 (Fig. 5b), Fe, Mn and Al are nearly constant with values falling below their respective average lines. In zone 2, Fe and Al show an increasing trend while Mn shows a decreasing trend with values falling above their respective average lines. The diagenetic enhancement in Fe and Mn concentration near zone 2 in both the cores (S-61 and S-60) (Fig. 5a, b) is also confirmed by variation in sediment colour with brown to light grey in zone 2 which indicated more oxic environment and dark grey to black sediments in zone 1 which indicated reducing environment (Spencer 2002).

Trace elements (Ni, Cr, Co, Zn and Pb)

In zone 1 of core S-61 (Fig. 5a), trace metal profiles show wide variability with an overall increasing trend except Ni

Fig. 2 Zone-wise distribution of sediment grain size, total organic carbon (TOC), total nitrogen (TN) and pH with vertical lines of average value for (a) sub-channel (S-61) and main channel (S-60) (b)



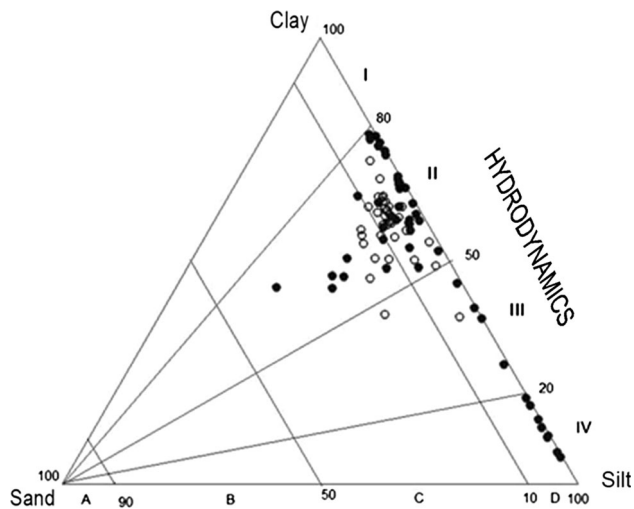


Fig. 3 Ternary diagram for the classification of hydrodynamic conditions after Pejrup (1988) for sub-channel (S-61—empty circles) and main channel (S-60—filled circles)

which seems to follow the trend of Fe. In zone 2, from 28 to 10 cm, trace metals show an overall decreasing trend while from 10 cm to surface they show an overall increasing trend. In core S-60 (Fig. 5b), zone 1 shows nearly constant profiles of trace metals with values below their respective average lines, while in zone 2 trace metals (except Pb) show an overall increasing trend with values above their respective average lines. The higher value of Pb from 98 to 84 cm and Ni from 98 to 90 cm roughly coincides with intervals of high total organic carbon content (Figs. 5b, 2b).

Diatoms

A total of 18 diatom genera were identified. Diatoms were mainly represented by genera *Cyclotella*, *Nitzschia*, *Pleurosigma*, *Coscinodiscus*, *Chaetoceros*, *Thalassionema*, *Surirella*, *Navicula*, *Diploneis*, *Grammatophora*, *Hyalodiscus*, *Campylodiscus*, *Triceratium*, *Pinnularia*, *Biddulphia*, *Cerataulina*, *Thalassiosira* and *Syndra*. Most genera identified in the present study have earlier been reported in the water column of Rajapuri creek (Gajbhiye et al. 1995) and other estuaries along west coast of India (Patil and Anil 2008; D'Costa and Anil 2010). Diatom genera with <1 % representation were not used for interpretation.

In core S-61 (Fig. 6a), *Cyclotella meneghiniana* and *Nitzschia cocconeiformis* are the dominant diatoms present in every sediment sample. Freshwater diatoms ranged from 56 to 94 % while marine diatoms ranged from 6 to 44 %. Zone 1 is characterized by predominance of freshwater forms like *Cyclotella meneghiniana* (range 33–67 %) and *Nitzschia cocconeiformis* (range 12–30 %) while in zone 2

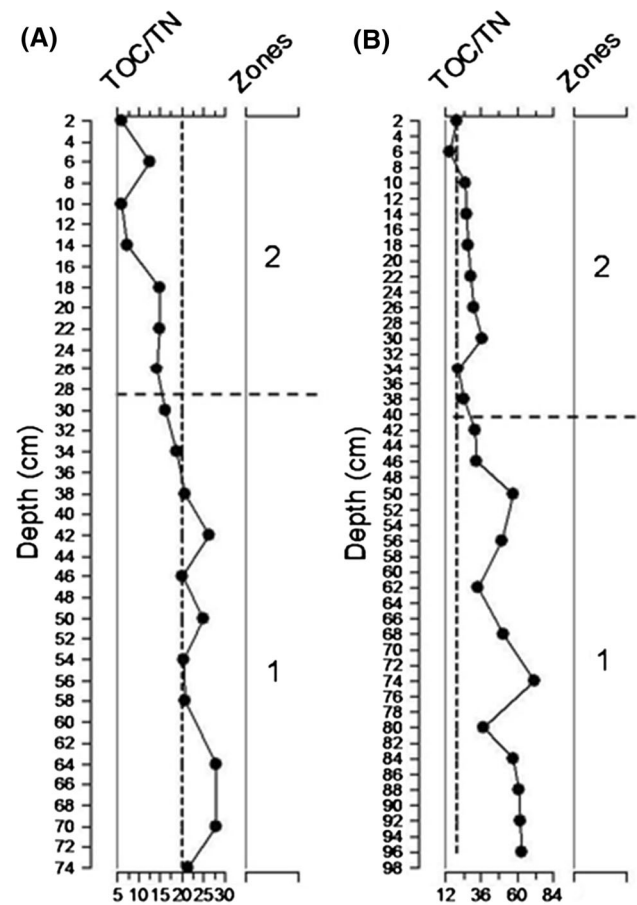


Fig. 4 Zone-wise distribution of carbon/nitrogen (TOC/TN) ratio with vertical dashed line representing TOC/TN value of 20 as threshold between aquatic and terrestrial sources for (a) sub-channel (S-61) and (b) main channel (S-60)

marine forms like *Chaetoceros* sp., *Hyalodiscus subtilis*, *Grammatophora oceanica* and *Diploneis* sp. show relatively high dominance. In core S-60 (Fig. 6b), *Cyclotella meneghiniana* was the most common diatom occurring in every sample, in some cases with relative dominance >50 %. The freshwater diatoms ranged from 20 to 77 % while marine diatoms ranged from 23 to 80 %. *Cyclotella meneghiniana* was most dominant throughout in zone 1 (range 80–90 %) and in zone 2, *Hyalodiscus subtilis* and *Chaetoceros* sp. were predominant.

Principal component analysis (PCA)

A PCA allows an easy visualization of the relationships existing among the variables in large data sets (Passos et al. 2010). It represents correlation between the variables, directions and intensities of the variation (arrow length) (Virkanen 1998). The multivariate ordination by PCA revealed two main directions of variations (Fig. 7). The first axis ($\lambda_1 = 0.3279$) is mainly defined by gradients of

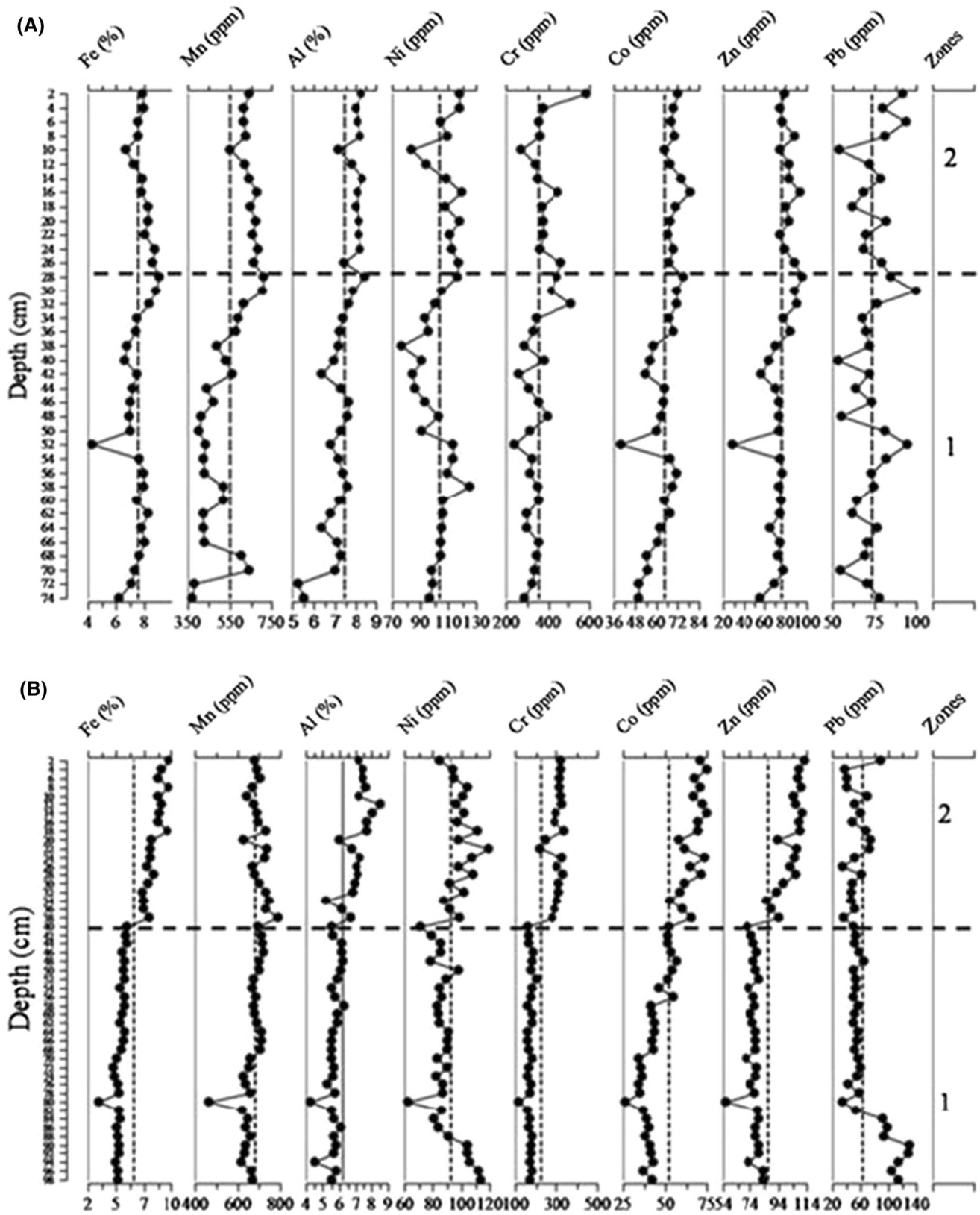


Fig. 5 Zone-wise distribution of major (Fe, Mn and Al) and trace elements (Ni, Cr, Co, Zn and Pb) and pH with vertical dashed lines of average value for (a) sub-channel (core S-61) and (b) main channel (core S-60)

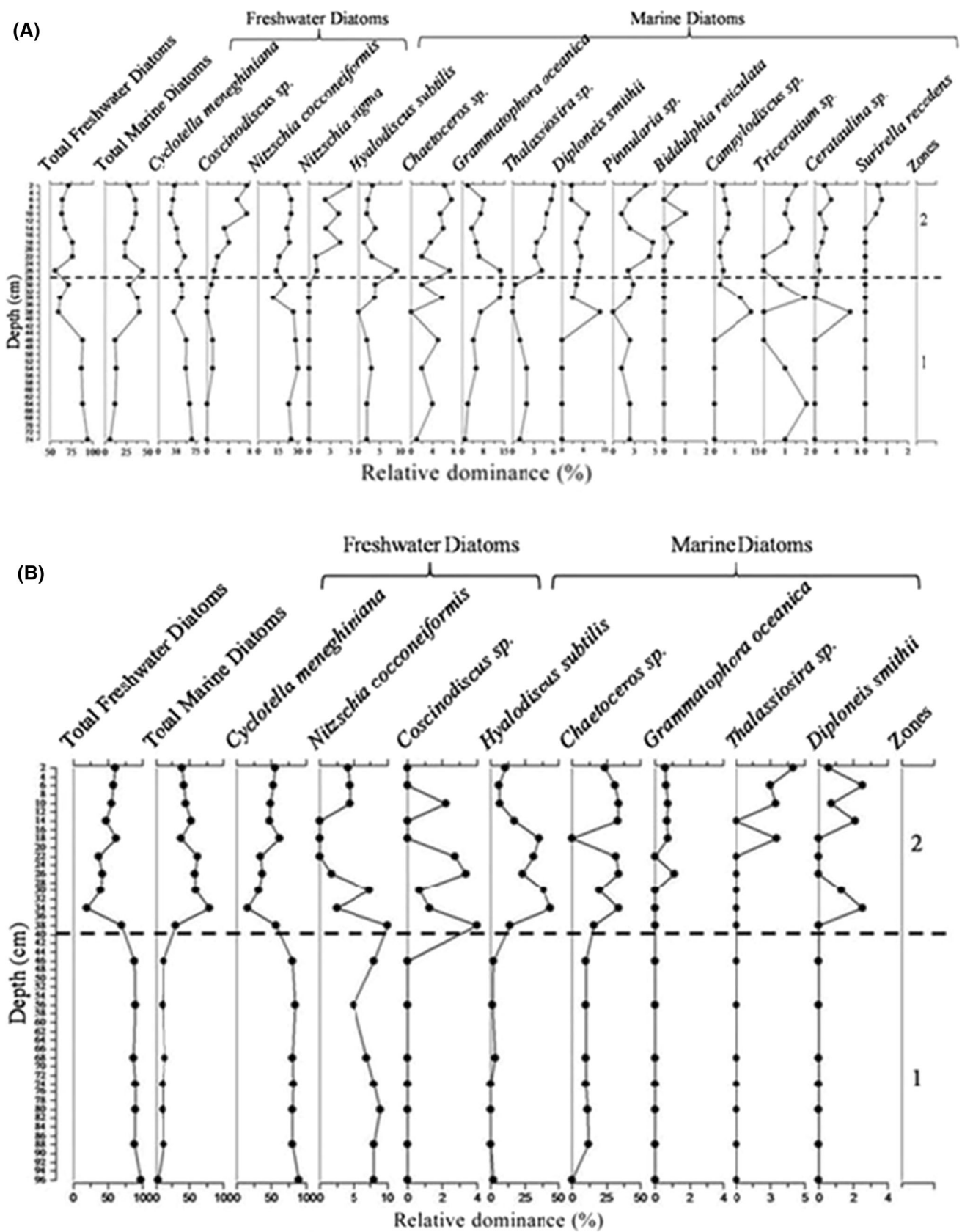


Fig. 6 Zone-wise distribution of diatoms for (a) sub-channel (core S-61) and (b) main channel (core S-60)

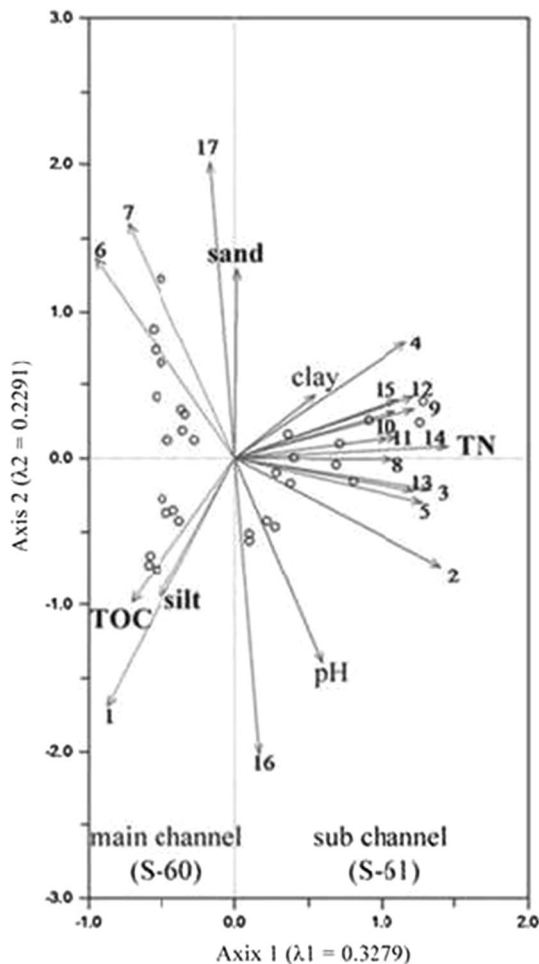


Fig. 7 Statistical relationship between diatoms and environmental variables in using multivariate principal component analysis (PCA). 1 *Cyclotella meneghiniana*, 2 *Nitzschia cocconeiformis*, 3 *Nitzschia sigma*, 4 *Coscinodiscus* sp., 5 *Pinnularia* sp., 6 *Chaetoceros* sp., 7 *Hyalodiscus* sp., 8 *Grammatophora* sp., 9 *Thalassiosira* sp., 10 *Biddulphia* sp., 11 *Campylodiscus* sp., 12 *Diploneis* sp., 13 *Triceratium* sp., 14 *Cerataulina* sp., 15 *Surirella* sp., 16 Total fresh-water diatoms, 17 Total marine diatoms. TN total nitrogen, TOC total organic carbon, O samples

total nitrogen, *Grammatophora oceanica*, *Nitzschia cocconeiformis*, *Diploneis* sp., *Thalassiosira* sp. and *Triceratium* sp. while sand, total marine diatoms and *Hyalodiscus subtilis* accounted for variations along the second axis ($\lambda_2 = 0.2291$).

Factor analysis

Factor analysis was employed to identify the important variables that control trace metal distribution. The three factors (*F1*, *F2* and *F3*) correspond to 69.34 and 78.33 %, respectively, in core S-61 and S-60. In core S-61, *F1*, *F2* and *F3* accounted for 34.90, 21.96 and 16.02 %, respectively. *F1* showed significant positive loadings on Fe

(0.91), Mn (0.66), Al (0.72), Ni (0.79), Cr (0.78), Co (0.82), Zn (0.78) and Pb (0.56). *F2* showed significant positive loadings on sand (0.72), silt (0.60) and TOC (0.83). Fe showed significant positive loadings on TN (0.90) and good positive loadings on sand (0.41). In core S-60, *F1*, *F2* and *F3* accounted for 40.35, 21.96 and 16.02 %, respectively. *F1* showed significant positive loadings on Fe (0.92), Al (0.90), Ni (0.50), Cr (0.90), Co (0.82), Zn (0.94) and TN (0.76) and good positive loadings on sand (0.42). *F2* showed significant positive loadings on clay (0.93), Mn (0.73) and Ni (0.52). *F3* showed significant positive loadings on Pb (0.85) and TOC (0.77).

Index of geo-accumulation (I_{geo})

In zones 1 and 2 of core S-61, the average I_{geo} value for Mn and Zn falls in class 0 which suggests background value for these elements (Table 1); Fe falls in class 1 which indicates that sediments are unpolluted to moderately polluted; Cr, Co and Pb fall in class 2 indicating moderate pollution (Table 1). Ni falls in class 0 in zone 1 and class 1 in zone 2 reflecting an increase in contamination in the recent years. In zones 1 and 2 of core S-60, the average I_{geo} (Table 1) for Mn, Ni and Zn falls in class 0 suggesting their background concentration. The average I_{geo} value for Fe falls in class 0 in zone 1 and class 1 in zone 2; Cr and Co fall in class 1 in zone 1 and class 2 in zone 2 reflecting an increase in Fe, Cr and Co contamination in the recent years. Pb, on the other hand, falls in class 2 in zone 1 and class 1 in zone 2 indicating a decrease in Pb contamination over the years (Table 1).

Discussion

Sub-channel (core S-61)

Sediment sources

A sub-channel largely consists of river-brought terrigenous sediments. The transportation and deposition of sediment are controlled by processes such as river runoff, tides and waves within creeks and estuaries. At the time of high river runoff, sediments are transported downstream near the channel outlet whereby coarse-grained sediments selectively settle down as the flow velocity declines while the fine sediments move to a greater distance. The dominance of sand (range 4–18 %) noted between 74 and 52 cm probably reflects high river runoff conditions (Fig. 2a). The alternating high proportion of sand (74–52 cm), silt (52–40 cm) and clay (40–32 cm) may reflect tide- and wave-induced variations in flow strength (Dalrymple and

Table 1 Range and average of index of geo-accumulation (I_{geo}) in zone 1 and 2 for (A) sub-channel (core S-61) and (B) main channel (core S-60)

(A) Sub-channel (core S-61)					(B) Main channel (core S-60)			
Metals	Range	Average	I_{geo} class	Pollution intensity	Range	Average	I_{geo} class	Pollution intensity
Zone 1 (74–28 cm)					Zone 1 (98–40 cm)			
Fe	−0.83 to 0.45	0.10	1	UP to MP	−1.07 to −0.30	−0.47	0	UP
Mn	−1.77 to −0.84	−1.36	0	UP	−1.47 to −0.82	−0.95	0	UP
Ni	−0.42 to 0.30	−0.03	0	UP	−0.71 to 0.15	−0.22	0	UP
Cr	0.04 to 1.93	1.27	2	MP	−0.24 to 0.57	0.32	1	UP to MP
Co	0.48 to 1.40	1.10	2	MP	−0.13 to 1.00	0.57	1	UP to MP
Zn	−2.31 to −0.57	−1.01	0	UP	−1.36 to −0.78	−0.91	0	UP
Pb	0.83 to 1.74	1.26	2	MP	0.19 to 2.12	1.10	2	MP
Zone 2 (28–0 cm)					Zone 2 (40–0 cm)			
Fe	−0.05 to 0.45	0.24	1	UP to MP	−0.31 to 0.40	0.16	1	UP to MP
Mn	−1.21 to −0.84	−0.98	0	UP	−1.03 to −0.69	−0.87	0	UP
Ni	−0.29 to 0.23	0.10	1	UP to MP	−0.53 to 0.23	−0.07	0	UP
Cr	0.99 to 2.11	1.50	2	MP	0.21 to 1.32	1.12	2	MP
Co	1.17 to 1.47	1.30	2	MP	0.88 to 1.40	1.20	2	MP
Zn	−0.93 to −0.57	−0.79	0	UP	−1.01 to −0.34	−0.50	0	UP
Pb	0.84 to 1.64	1.33	2	MP	0.18 to 1.55	0.80	1	UP to MP

UP unpolluted, MP moderately polluted

Choi 2007) (Fig. 2a). The large variations in Mn (range 373–711 ppm, standard deviation ± 101.13) and Al (range 5.3–8.5 %, standard deviation ± 0.69) profiles in zone 1 (Fig. 5a) strongly support the changes in sediment origin (e.g. terrigenous sediments) (Zwolsman et al. 1993). The organic matter input into the river channel also increases during the periods of high river discharge (Simenstad 1983). Peak total organic carbon values (range 1.79–4.82 %), elevated TOC/TN ratio (range 16–28) and predominance of freshwater diatoms (range 60–94 %) throughout in zone 1 (Figs. 2a, 4a, 6a) probably suggest large contribution from fluvial land-derived terrestrial organic matter and small input from marine sources (Meyers and Ishiwatari 1993). Similar deposition of organic matter of terrestrial origin in the past is also reported earlier in intertidal sediments of Vaitarna (Volvoikar et al. 2014) and Amba estuary (Pande 2013) located along west coast of India.

Zone 2 (Fig. 2a) has almost homogenous grain size distribution suggesting uniform sediment transport and depositional processes. This is attributed to conditions when the river runoff is less and there is regular resuspension, transport and deposition in response to tidal inflow and waves. The decreasing trend of TOC/TN ratio (range 15–6) from 26 cm to surface in zone 2 provides evidence of greater marine input (Fig. 4a). This coincides with relatively high proportion of total marine diatoms (range 44–23 %) (Fig. 6a). Here, marine genera namely *Grammatophora oceanica*, *Chaetoceros* sp., *Hyalodiscus*

subtilis, *Diploneis* sp. and *Campylodiscus* sp. showed their peak dominance (Fig. 6a). The higher proportion of finer sediments (range 58–65 %) in zone 2 also suggests decrease in rainfall in recent years, thus favouring the deposition of finer particles. A similar process in recent years has been reported from nearby Dudh creek (Volvoikar and Nayak 2013a), Vaitarna estuary (Volvoikar et al. 2014), Amba estuary (Pande 2013) and Manakudy estuary (Kumar and Edward 2009) along west coast of India. The sedimentation rates (210 Pb dating) reported from mudflats located close to the study area are 2.72 cm/year (Fernandes 2011) and 1.21 cm/year in lower estuary (Singh et al. 2013) and 1.46 cm/year in middle estuary (Fernandes 2011). The sedimentation rate reported from near shore and estuarine areas are 1.94 cm/year (Sharma et al. 1994) and 0.62 cm/year (Borole 1988) respectively. The sedimentation rate in the intertidal region is mainly controlled by tidal inundation, wind–wave activities, sediment grain size, organic carbon and vegetation cover (Temmerman et al. 2003). Considering the average rate of sedimentation from lower estuary and near shore and estuarine areas as 1.97–1.28 cm/year, it can be said that the sediment core we studied may represent around last 100 years.

Sediment geochemistry

The increasing and varying distribution pattern of trace metals in zone 1 (Fig. 5a) may be due to non-uniform grain

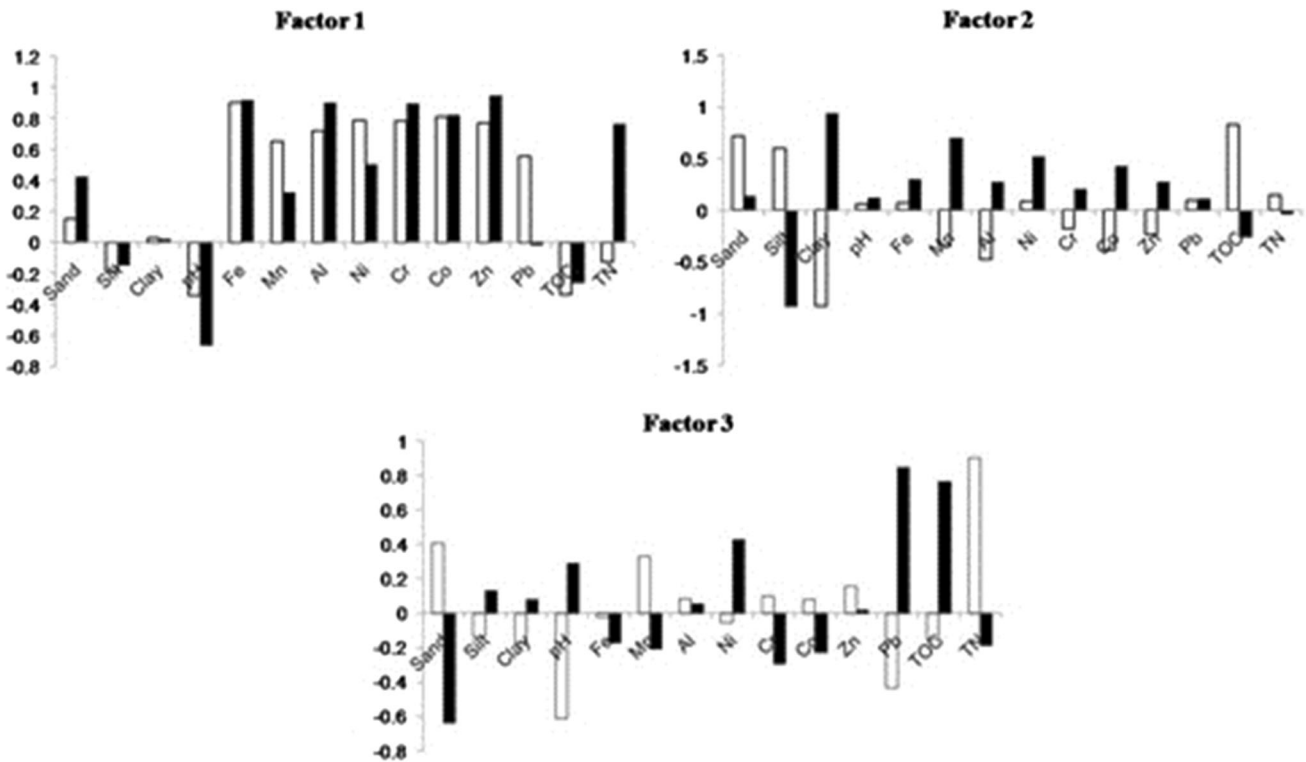


Fig. 8 R-mode factor analysis for sub-channel (S-61—empty bar) and main channel (S-60—filled bar), TOC total organic carbon, TN total nitrogen

size and varying amount of anthropogenic contribution. It is important to mention here that the rock type in the catchment area is mainly basalts. Higher Fe concentration (range 6.24–8.76 %) compared to lower Al concentration (range 5.25–7.56 %) in zone 1 is attributed to rock composition from which sediments are derived. In zone 2, the enrichment of Fe (range 7.9–8.3 %) and Mn (range 615–643 ppm) from 8 cm to surface reflects early diagenetic process. A sharp decrease in Fe (8.3–6.9 %) and Mn (644–552 ppm) at 14–10 cm is suggestive of oxic/suboxic interface (Ayyamperumal et al. 2006). This probably explains the dissolution of Fe and Mn in partly reduced sediment layers producing Fe^{+2} and Mn^{+2} species, which migrate upward in the sediment column and get precipitated near the oxic–suboxic interface (Santschi et al. 1990). The similar distribution of trace metals with Fe and Mn at 14–0 cm may indicate readsorption by Fe and Mn oxyhydroxides (Zwolsman et al. 1993). Fe and Al are major constituents of clay minerals, feldspars and amorphous aluminosilicate gels. The significant positive association between Fe and Al (Fig. 8) and similar distribution profiles at 40–28 and 14–0 cm may indicate that Fe is mainly associated with the clay mineral fraction and that the sediments come from the same detrital source (Ruiz-Fernández et al. 2011). Further, significant positive

association of trace metals (Ni, Cr, Co, Zn and Pb) with Fe, Mn and Al as indicated by factor analysis (Fig. 8) probably suggested their natural or terrestrial sources (Zhou et al. 2004). However, average I_{geo} value showed moderate enrichment for Co and Cr (Table 1). The average I_{geo} value also showed moderate enrichment for Pb and increase in Ni contamination in the recent years (in zone 2) (Table 1).

Main channel (core S-60)

Sediment sources

The possible sediment source for the main channel comes from the adjacent watersheds and their drainage systems, the sea and the sub-channels. The enhanced deposition of mud (range 95.7–99.9 %) and paucity of sand noted in zone 1 (Fig. 2b) probably reflects high river runoff when the river carries a large amount of suspended sediments and continuous winnowing transports fine sediments near sheltered areas (Semeniuk 1981). The variations in fine-grained sediments (silt standard deviation ± 26.18 , clay standard deviation ± 25.93) (Fig. 2b) may be due to regular resuspension by changing fresh water interaction with tidal currents which are more likely to affect fine- (<63 μm) rather than coarse-grained particles (>63 μm) depending

on cohesiveness in a protected sheltered environment (Stephens et al. 1992). The similar distribution of major (Fe, Mn and Al) and trace metal (Ni, Cr, Co and Zn) (Fig. 5b) indicates that sediments are derived from the same source or have undergone similar post-depositional processes. The predominance of silt between 98 and 74 cm roughly coincides with intervals of high total organic carbon content (Fig. 2b). The decline in total organic carbon from 46 to 42 cm coincides with decrease in pH (Fig. 2b). The organic matter content depends on both the retention capacity of the sediment and the rate of microbial degradation (Clarke and Wharton 2001). The organic matter in zone 1 is enriched in total organic carbon (range 2.25–4.59 %) but depleted in total nitrogen content (range 0.03–0.09 %) (Fig. 2b). The microbial decomposition of organic matter would result in more loss of nitrogen as nitrogen is more easily degraded than carbon (Soto and Martinez 2012). The large changes in TOC/TN ratio (range 32–72, standard deviation ± 14) can occur during decomposition of organic matter (Fig. 4b) (Yu et al. 2010). The elevated TOC/TN ratio suggests that the decomposed organic matter has lost more nitrogen in comparison to carbon and/or changes in land- and marine-derived organic matter content.

The sand is transported as bedload mainly from the seaward direction when strong tidal currents capable of transporting the coarse particles deposit them as the tidal current velocity weakens. The high percentage of sand (range 7–36 %) noted from 38 to 22 cm must have been transported from the seaward direction (Fig. 2b). This is supported by significant decrease in TOC/TN ratio which also indicated increase in marine influence (Fig. 4b). Also, the relative dominance of marine diatom assemblages from 38 to 22 cm varies between 30 and 80 %, with a large number of samples representing >50 %, indicating a constant marine supply to the main channel (Fig. 6b). *Hyalodiscus subtilis*, a marine benthic species, (Federico and Marcela 2009) shows its peak dominance (range 44–39 %) from 34 to 30 cm (Fig. 6b). The significant positive correlation of marine diatom *Hyalodiscus subtilis* with sand further supports a strong marine influx from seaward direction (Fig. 7). *Chaetoceros* sp., another marine planktonic diatom (Suto 2006), appeared more frequently (range 34–20 %) from 34 to 22 cm (Fig. 6b). Diatom genera *Thalassiosira*, *Grammatophora*, *Diploneis*, *Coscinodiscus* and *Nitzschia cocconiformis* were either totally absent or less frequent at this depth interval (Fig. 6b). This may be attributed to substrate disturbance by sudden change in depositional conditions (Ribeiro et al. 2010). The low total organic carbon (range 3.33–1.64 %) and total nitrogen concentration (range 0.09–0.07 %) from 40 to 30 cm are because of dilution by large supply of coarser sediments and oxidation of organic matter due to constant decrease in

pH (range 7.43–6.53) (Fig. 2b) (Zourarah et al. 2009). The significant increase in total nitrogen concentration from 18 cm to surface also coincides with increase in fine sediments probably due to better preservation of nitrogen by absorption onto fine-grained sediment (Figs. 2b, 4b) (Mada et al. 2002). The low total organic carbon value at surface (8 cm to surface) probably reflects mixing processes.

Sediment geochemistry

The similarity in Fe and Mn profiles particularly in zone 1 (Fig. 5b) indicates strong association to geochemical matrix between the two elements (Chatterjee et al. 2007). The uniform distribution profiles of trace metals, major elements together with sand and total organic carbon in zone 1 are likely to reflect the background concentration or homogenization by sediment mixing (Figs. 5b, 2b). The average I_{geo} value also showed background concentration for Mn, Ni, Zn and Fe in zone 1 (Table 1). In zone 2 however all metals except Pb showed higher concentration. Fe showed minor enrichment while Cr and Co showed moderate enrichment (Table 1). The peak of Ni, Cr, Co and Zn at 38 cm coincides with Fe–Mn peak (Fig. 5b). This probably reflects reprecipitation of trace metal on Fe–Mn oxide and hydroxide coatings (Millward and Moore 1982). The decreasing trend of Mn in zone 2 (Fig. 5b) is attributed to preferential migration of Mn near sediment–water interface, since Mn sulphides are less stable (Chatterjee et al. 2007). The association of trace metals with major elements (Fe and Al) and organic matter (TN and TOC) as indicated by factor analysis (Fig. 8) suggests lithological input, i.e. the elements come from the terrigenous detrital matter, transported and absorbed by organic matter then deposit as discussed above.

Sub-channel (S-61) vs main channel (S-60)

The two channels differ from each other with respect to catchment area, hydrodynamics and industrial activities. Statistical paired *t* test analysis ($p < 0.05$) indicates significant difference in the distribution of metals. The observed major differences between the two channels are as follows: first, in the sub-channel (S-61), metals are associated with Fe and Mn while in the main channel (S-60) metals show significant association with Fe only (Fig. 8). The association of metals with Fe and/or Mn depends upon the metals and the nature of its source, ability of environment to buffer or disperse input of metals through tidal energy (Turner 2000). The significant association of metals with Fe and no significant correlation with Mn could indicate faster co-precipitation in a protected sheltered environment of relatively low tidal energy.

Second, in the main channel (S-60), the distribution of metals is regulated by organic matter (total nitrogen and total organic carbon) (Fig. 8). This indicates that organic matter is the main geochemical carrier of metals in the main channel. While in sub-channel (S-61) lack of association of metals with organic matter suggests different depositional processes (Fig. 8). Third, sand showed good positive correlation with metals and marine diatoms in the main channel (S-60) while in the sub-channel (S-61) sand does not control their distribution (Fig. 8). This can be explained by considering marine influx from the seaward side which carries metals along with sand as sands show good positive association with metals and marine diatoms. Aloupi and Angelidis (2002) found significant correlation of metals with sand fraction in areas affected by pollution from harbour and industries located in coastal areas. Main channel is surrounded by old, rusty and stranded barges around Agardanda harbour, Dighi Port and Rajapuri jetty (Fig. 1). Fourth, relatively higher diatom dominance in the river channel (S-61) as compared to the main channel (S-60) is attributed to higher nitrogen concentration in the river channel resulting in increase in primary productivity and phytoplankton abundances (Weikert 1987).

Conclusion

The distribution of sediments in creek channel is controlled mainly by river runoff, tides and waves. During the periods of higher rainfall, mixed coarse and fine sediments are deposited in the sub-channel while in the main channel fine sediments are deposited. In the sub-channel, in lower section of the core (zone 1), organic matter showed enrichment in total organic carbon. The major and trace metal profiles showed variations in distribution. On the other hand, in the main channel, in zone 1, organic matter is depleted in total nitrogen concentration. The major and trace metal showed nearly constant profiles. During the periods of lower rainfall, tidal influence provides quiet depositional site in the sub-channel while in the main channel tide-dominated coarser sediments are deposited. The increasing proportion of marine diatoms and decreasing trend of carbon nitrogen ratio in upper section of the core (zone 2) suggest stronger tidal influence in the main channel as well as in the sub-channel. The I_{geo} value of Pb, Cr and Co suggests that sub-channel is moderately polluted while main channel is unpolluted to moderately polluted with respected to these trace metals.

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