

Geochemistry of the suspended sediment in the estuaries of the Mandovi and Zuari Rivers, Central west coast of India

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Abstract Geochemistry of the suspended particulate matter (SPM) collected during the monsoon was determined to identify the sources of SPM and to understand the physico-chemical processes in the Mandovi and Zuari River estuaries. The concentrations of SPM decrease seaward in both estuaries, but are relatively high at bay stations. Kaolinite is the most dominant clay mineral in the upstream of both rivers. Smectite increases seaward in both estuaries and is abundant in the bay. Upstream stations of Mandovi, where ore deposits are stored on the shore, exhibit high Fe, Mn, Σ REE and, middle REE- and heavy REE-enriched REE patterns. Channel stations of both estuaries exhibit middle REE- and light REE-enriched patterns, which gradually changed seaward to middle REE- and heavy REE enriched patterns. Canal stations exhibit highest concentrations of major and trace metals. High metal/Al ratios occur at stations in the upstream of Zuari and at the confluence of canal in the Mandovi estuary. Enrichment factors of metals indicate that Mn is significantly polluted while other metals are moderately polluted. The $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ of organic matter indicate that the terrigenous organic matter at the upstream is diluted seaward by marine organic matter. Organic matter at bay stations is largely marine and altered-type. The compositions of SPM are controlled by the particulates from ore dust, geology of the drainage basins and physico-chemical processes in the estuaries. Particulates resuspended from the bay are dominated by ore dust, which are advected into the channels of both estuaries during the lull periods of monsoon.

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Introduction

Studies on the composition and transport of suspended particulate matter (SPM) in estuaries have received considerable attention in recent years. This is due to the fact that SPM is an important carrier of various trace, nutrient and pollutant elements and most of these elements are trapped within the estuaries (Chester and Stones 1975; Olsen et al. 1982; Figueres et al. 1985; Turner et al. 1991 and 1994; Turner and Millward 1994; Zwolsman 1994; Negrel 1997; Zwolsman and van Eck 1999). The physico-chemical changes at the mixing zone of river water and seawater lead to a variety of reactions, particle/solute interactions: flocculation, coagulation and sedimentation (Sholkovitz 1976; Van der Weijden et al. 1977; Mayer 1982; Hoyle et al. 1984; Elderfield et al. 1990; Tanizaki et al. 1992; Zhou et al. 2003) and part of the organic / inorganic material being transported by the river is modified before reaching the coastal seas (Yaun- Hui et al. 1984; Morris et al. 1987; Bowers and Yeats 1989). Resuspension of bed sediments and diffusion of metals from sediments to the overlying water column will also effect the composition of SPM (Liu 1996; Liu et al. 1998). The composition of SPM therefore can be explained by mixing of different source inputs and complex biogeochemical processes occurring in the mixing zone. On the other hand, suspended matter transport is determined by the strength of two opposing flows, i.e., river flow and, tidal and wind-induced currents. It has been recognized that the fine-grained particles (<63 μm) are readily transported even in very slow flows and therefore the material being transported is controlled by its source (Knighton 1984; Dyer 1988). Although some studies have dealt with variations of SPM in large tropical and temperate rivers (Thomas and Martin 1982; Turner et al. 1991; Zhang and Liu 2002), very little work has been done on the distribution or comparison of SPM in minor tropical rivers. It is challenging to understand (1) whether any two estuaries are alike in terms of SPM composition when rivers are adjacent to each other and draining similar rock formations and (2) the processes that influence the transport and distribution of SPM. In order to address these questions the estuaries of the two adjacent rivers, the Mandovi and Zuari, were studied for their SPM. The purpose of this paper is to report variability in the composition of SPM collected on the same day during the monsoon along transects of these estuaries to better understand the factors that influence its composition and transport. Previous studies on SPM of these estuaries are few (Kessarkar et al. 2009, 2010; Rao et al. 2011; Shynu et al. 2012).

Study area

The Mandovi and Zuari (Ma-Zu) Rivers are two major rivers of Goa in the central west coast of India (Fig. 1), adjacent to each other and share some common features. Both originate in the Western Ghats

(mountain regions) and drain through a narrow coastal plain with nearly identical lengths (~50 km each). Both rivers drain through rocks of Goa Group belonging to the Dharwar Super Group of Archaean-Proterozoic age (Gokul et al. 1995). The Bicholim Formations, green schists and Sanvordem Formations covered by ferruginized laterites occur in the drainage basins of both rivers. The Bicholim Formations, however, occupy large area in the upstream of Mandovi River, whereas Sanvordem Formations occupy large area in the downstream of Zuari River basin (Mascarenhas and Kalavampara 2009). The Bicholim Formations consist of schists, phyllites, limestones, banded-iron formations and manganeseiferous cherts, while the Sanvordem Formations include metagreywacke, conglomerate and argillites (Gokul et al. 1995). The estuaries of both rivers are classified as 'monsoonal estuaries' (Shetye et al. 2007; Vijith et al. 2009), which receive abundant river discharge only during the monsoon (June-September) and negligible discharge in the remaining period. The river runoff of Mandovi measured at the head during June–October is $\sim 258 \text{ m}^3\text{s}^{-1}$ and $\sim 6 \text{ m}^3\text{s}^{-1}$ during November-May (Vijith et al. 2010). The Zuari River was dammed at the upper estuary and the runoff measured at Sanguem and Kushavati tributaries (see Fig. 1 for locations) during the monsoon (June–September), post-monsoon (October–January) and pre-monsoon (February-May) are $\sim 147 \text{ m}^3\text{s}^{-1}$, $7.3 \text{ m}^3\text{s}^{-1}$ and $0.8 \text{ m}^3\text{s}^{-1}$, respectively. These estuaries are mesotidal and the tidal ranges are $\sim 2.3 \text{ m}$ and 1.5 m during the spring and neap tides, respectively (Manoj and Unnikrishnan 2009). The currents in the estuaries are tide-dominated. The tidal oscillations have been observed and saline waters penetrate $\sim 45 \text{ km}$ upstream from the river mouth into the main channels of both rivers during dry season, i.e., October to May (Shetye et al. 2007). A narrow canal, called the Cumbarjua canal, connects the two estuaries in the downstream. The rivers are connected to the sea through bays and, the Aguda Bay off Mandovi is semi-circular and is at least four times smaller than that of the funnel-shaped, Mormugao Bay off Zuari. Rao et al. (2011) reported an extended zone of turbidity maximum in the Zuari estuary compared to that in Mandovi during the monsoon and suggested that the effect of tidal and wind-induced currents is much stronger in the former than in latter.

The Ma-Zu Rivers play an important role in the economy of mining industry in Goa by providing a cheap and efficient means of ore transport. Several big open cast iron and manganese ore mines operate in the drainage basins of the rivers. Fe, Mn ores brought from mines are stored on the shore of the estuary (Fig. 2A), loaded on to barges (Fig. 2B) at loading points and transported through the estuary to the port or mid-stream point, from where the ore is exported in giant ships. Mandovi has 37 loading points with 1500 trips of barges per year while Zuari has 20 loading points with 1800 trips per year. Ore transport through rivers increases annually from 14 million tonnes (mt) in 1980 to 30.7 mt in 2004. Of this, 19.1 mt of ore was transported through the Mandovi and 11.6 mt was through Zuari. Part

of the ore (11 mt) carried through the Mandovi is diverted to the port through Cumbarjua Canal during the monsoon (Rangaraj and Raghuram, 2005). During heavy monsoon rains abundant ore material is being flushed into the estuaries. Since ore handling i.e., loading in barges, transporting and reloading at the port or mid-stream in gaint ships, is done in an open system and one would expect abundant spilled-over ore material into the estuaries. Industries such as Fe-pellet making factory and ship-building are located on the shores of the Zuari estuary. Here we investigate the geochemistry of the suspended particulate matter (SPM) in these river estuaries during the monsoon and report the sources and controls on SPM distribution.

Materials and methods

Twenty five liters of surface water were collected at each station during neap tide along transects of the Mandovi and Zuari estuaries (Fig. 1), using two mechanized boats on 30th July 2009. Sampling started at upstream stations and continued downstream in both estuaries. Tide gauge station is located at Verem (between stations M1 and M2; see Fig. 1) and automatic weather station (AWS) for measuring wind speed, temperature, humidity and atmospheric pressure is installed on the terrace of the Institute's (NIO) building (see Fig. 1). Sampling time at each station and, tidal height and wind speed measured at the tide gauge and weather stations, respectively, were given in Table 1. Rainfall measured at four rain gauge stations were shown in Fig. 1. The water collected was filtered through 0.4- μm Millipore filter paper and the suspended particulate matter (SPM) retained on the filter papers was dried and weighted. Fig. 3 shows the distribution of SPM at each station. The dried sample was carefully removed from the filter paper. Part of the sample was used for X-ray diffraction studies for mineralogy (Fig. 4), following the procedure given in Kessarkar et al. (2010). The remaining sample was powdered and 25 mg of the powder was weighed from each sample, transferred to clean Teflon beakers and digested on a hot plate by open acid digestion, using HNO_3 -HF- HClO_4 solution for 8 hours at 190-200°C. The samples were transferred into Teflon bombs using 1 ml HNO_3 and 1 ml HF and digested in an oven at 180°C. Subsequently, the sample solution was transferred into the Teflon beaker using 3 ml HNO_3 and dried to near total dryness. The sample was brought into solution using 1 ml water and 1 ml HNO_3 and then made to 50 ml. Major and trace element concentrations were determined using Thermo Finnigan ELEMENT2 HR-ICP-MS at the State Key Laboratory of Estuarine and Coastal Research (SKLEC), East China Normal University (ECNU), Shanghai, China. Accuracy and reproducibility of the analytical results were checked by repeated measurements of standards BCR667, GSD9, GBW01314 and samples. The difference in elemental concentrations obtained in this study and the certified values is $\leq 10\%$. Reproducibility of the measurements for all elements was better than $\pm 9\%$.

Concentrations of Al, Fe, Mn, Mg and Σ REE and, metal/Al ratios at each station were shown in Figs. 5 and 6, respectively. Post-Archaean average Australian Shale (PAAS)-normalized REE patterns of SPM at each station were shown in Fig. 7. The enrichment factor (EF) of metals (Taylor and McLennan 1995) with reference to the World River average suspended particulate matter (WRSPM-Viers et al., 2009) was used to understand the behavior of metals and is defined as:

$$EF = [(X)/(Al)]_{\text{sample}} / [(X)/(Al)]_{\text{WRSPM}}$$

where (X) represents the concentrations of the reference metal X, and (Al) the Al concentration. The mean enrichment factor of metals for each domain of the estuary was plotted against the metal and shown in Fig. 8. The defined categories for the degree of pollution based on the EF of metals suggested by Sutherland (2000) were also shown in Fig. 8.

Total nitrogen content and nitrogen isotopes were determined from the powdered samples, whereas particulate organic carbon and stable organic carbon isotopes were determined from the carbonate free sample (treated with 0.1 M HCl and dried) powders, using GC-C-IRMS system that employed an Agilent 6890N GC interfaced with a Finnigan GC Combustion III unit followed by GV Isoprime isotope mass spectrometry (Model: Delta plus *XP*) at the SKLEC, ECNU, Shanghai, China. The $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ are expressed in parts per thousand (per mil; ‰) relative to their ratios in the Pee Dee Belemnite (PDB) and air standards, respectively. The analytical standard deviation based on replicates of laboratory standards was $\pm 0.3\text{‰}$ for $\delta^{13}\text{C}$ and $\pm 0.2\text{‰}$ for $\delta^{15}\text{N}$. Distribution of total organic carbon and total nitrogen and their isotopes were shown Fig. 9 and Table 3.

Results

Sampling stations in the Mandovi estuary are from the main channel, whereas those from the Zuari estuary include both the main channel and bay (Fig. 1). For convenience of description of results, the sampling stations M8 to M6 of the Mandovi are here referred to as 'ore stations', because pulverized Fe-Mn ore deposits are stored on the shore of the estuary and loaded onto barges at these stations (Fig. 2). Stations M5 to M1 and Z7 to Z4 are referred to here as 'channel stations' of the Mandovi and Zuari, respectively. Stations Z3 to Z0 are referred to as 'bay stations'. Stations C0 to C3 are from the Cumberjua canal and are referred to as 'canal stations'.

Salinity variations and SPM concentrations

The salinity of the surface waters and SPM concentrations at each station are shown in Fig. 3 and Table 1. Salinity was low and varied between 0.03 and 0.18 in the Mandovi estuary. SPM concentrations were, however, higher at ore stations than at channel stations and decreased seaward of the estuary (Fig. 3). Salinity ranged from 0.03 to 0.2 and from 0.4 to 10.4 in the channel and bay stations of Zuari, respectively. SPM concentrations decreased seaward in the channel stations of Zuari, but were higher at stations in the bay (Fig. 3). In the Cumbarjua canal salinity variations (0.04 to 0.18) were within the range of channel stations of the Ma-Zu estuaries. The SPM concentrations were high at stations (C0 and C3) on either side close to the Mandovi and Zuari estuaries and low at centre stations, C1 and C2 (Fig. 3).

Mineralogy of the suspended matter

Abundant kaolinite (K), followed by minor goethite, gibbsite and illite were characteristic at ore stations of the Mandovi and, upstream stations of the channel in Zuari (Fig. 4). Smectite (S), which occurred in traces in the upstream increased seaward in both estuaries, marginally in Mandovi (with K/S of 3.3) and more distinctly in Zuari (K/S=0.63; Fig. 4). In bay stations smectite was the most dominant mineral (av. K/S=0.3), followed by kaolinite, gibbsite, goethite and illite. The kaolinite and smectite-rich phases (K/S=1.1) at station C3 of Cumbarjua canal were identical to that at Z4 (nearby station) in Zuari. Kaolinite-dominated SPM was characteristic at C0, C1 and C2 stations of the canal and M5 and M6 stations in the Mandovi (see Fig. 4). Smectite (K/S= 3.0) was a minor component at centre stations, C1 and C2.

Geochemistry of the suspended matter

The concentrations of major and trace elements vary from one estuary to the other and within different domains of same estuary. Most notable among them were Al, Fe and trace metals. The average concentrations of Al, Fe, Cr, Ni and Cu were highest in the Cumbarjua canal followed by the Mandovi and Zuari estuaries (Table 2). The average Pb and Zn concentrations were, however, highest in the Zuari estuary, followed by the Cumbarjua canal and Mandovi estuary. The concentrations of major elements (Al, Mg, Fe and Mn), trace metals (Cr, Cu, Ni, Zn, Pb and Co) and total rare-earth elements (Σ REE) were high at ore stations, decreased sharply at stations M4 and M5 of the channel and again increased seaward in the Mandovi estuary (Fig. 5; Table 2). The M/Al ratios of major and trace metals were high at stations M4 and M5 and decreased gradually towards both the sea-end as well as the

river-end stations of the estuary (Fig. 6). PAAS-normalized REE patterns showed middle rare earth elements (MREE)- and heavy rare earth elements (HREE)-enrichment with positive Ce and Eu anomalies at ore stations (Fig. 7). Here the average ratios of normalized light rare earth elements (LREE) to MREE ($(L/M)_n$) and LREE to HREE ($(L/H)_n$) were 0.52 and 0.9, respectively (Table 2). Stations M4 and M5, however, showed MREE- and LREE-enrichment. The values of $(MREE)_n$ and $(HREE)_n$ increased gradually from 3.95 to 5.72 and from 2.01 to 3.35, respectively as one proceeds seaward from station M5 to M1 (Table 2) and, MREE- and HREE-enriched pattern was characteristic at M1 (Fig. 7).

In Zuari estuary, the average concentrations of Al, Mg and Σ REE were lower and Mn was higher at stations in the channel than in the bay (Fig. 5; Table 2). Fe values remained similar in both domains. Trace metal concentrations and metal to Al (M/Al) ratios were much higher at Z7 when compared with those of World River SPM (Fig. 6; Table 2) and decreased seaward of the channel. A sharp decrease in M/Al ratios occurred at bay stations (Fig. 6). As in the Mandovi channel (M4 and M5), MREE- and LREE-enriched REE patterns with positive Ce and Eu anomalies were characteristic at Z7 to Z5 of the Zuari channel (Table 2). $(HREE)_n$ exhibited least variations between Z7 and Z5, but at station Z4 (sea-end of the channel) MREE-enriched pattern with near equal $(LREE)_n$ and $(HREE)_n$ was typical (Table 2). Among 4 stations of the bay, MREE- and HREE-enriched REE patterns (av. $(L/M)_n=0.55$; $(L/H)_n = 0.93$) with positive Eu anomaly were typical at three stations (Z0, Z2 and Z3 - see Fig. 7) and MREE- and LREE-enriched patterns with positive Ce and Eu anomalies at one station (Z1; Fig. 7).

The concentrations of Al, Mg, Fe, Mn, trace metals and Σ REE in Cumbarjua canal were high at station C3 and decreased gradually towards C0 (Fig. 5). The M/Al ratios of these metals (Fig. 6) were, however, high at C0 (Mandovi side) and decreased towards C3 (Zuari side). A gradual decrease in M/Al ratios was seen in the order M5, M4, C0, C1, C2, C3 and Z4. The MREE- and LREE-enriched patterns (Fig. 7) with $(L/M)_n$ of 0.61 and $(L/H)_n$ of 1.16 at station C0 resembled those at M4 and M5 of Mandovi with average $(L/M)_n$ of 0.6 and $(L/H)_n$ of 1.19. The MREE- and HREE-enrichment at C3, C2 and C1 was slightly lower than that of ore stations but higher than those at Z4 of Zuari (Table 2). Positive Ce and Eu anomalies were present at all stations (Table 2). Ce anomaly was, however, least at station C3 and increased towards station C0.

Enrichment factor (EF) of the metals indicates that the Mn concentrations in the entire Mandovi estuary, Zuari channel and Cumbarjua canal and, Co and Ni from the Mandovi channel fall in the range

of significant pollution (Fig. 8). Metals such as Fe, Co, Cr, Cu, Ni and Zn from different domains of both estuaries and canal and, Pb from the Zuari channel were in the range of moderate pollution. Pb from other domains, Zn from the Mandovi ore stations and Cumbarjua canal and Cd from all stations of estuaries and canal were in the range of minimal pollution.

Organic matter

The total organic carbon (OC) and total nitrogen (TN) contents of SPM were higher in Zuari (8 to 3.7%; 1.38 to 0.58%) than in the Mandovi (6 to 3.98%; 0.7 to 0.38%) estuary. Their ranges in Cumbarjua canal were from 7.17 to 2.83% and from 0.89 to 0.43%, respectively (Fig. 9A-D; Table 3). The ratio of total organic carbon to total nitrogen (OC/TN) steeply decreased seaward in the Mandovi estuary. While in Zuari it decreased seaward in channel stations and maintained nearly similar values in bay stations (Table 3; Fig. 9E-F)). The stable isotope ratios of organic carbon ($\delta^{13}\text{C}$) ranged from -26.6‰ to -24.6‰ and from -25.7‰ to -24.0‰ in the Mandovi and Zuari estuaries, respectively and become heavier seaward in both estuaries. The isotopic ratio of nitrogen ($\delta^{15}\text{N}$) also increased seaward and ranged from 1.5‰ to 2.8‰ and from 4.12‰ to 5.91‰ in the Mandovi and Zuari estuaries, respectively. In the Cumbarjua canal the isotopes of carbon (-25.8‰ to -24.8‰) and nitrogen (1.6‰ to 2.8‰) were within the range of values reported for Mandovi estuary (Table 3).

Discussion

Mineralogy of SPM and its relation to source rocks

Kaolinite, gibbsite and goethite are dominant in the upstream stations of both estuaries (Fig. 4). Tropical environments favour intense chemical weathering on source rocks. The Ma-Zu Rivers originate in mountain regions and receive heavy rainfall (av. 2500 mm/yr) only during the southwest monsoon. High rainfall on elevated regions leads to active drainage permitting strong to very strong hydrolytic processes on parent rocks. As a consequence, intense leaching takes place and more mobile ions like Na, K, Ca, Mg and Sr released from parent rocks are exported away leaving less mobile ions (Al, Ti, Si and Fe) in the weathering zone. This favours the formation of clay minerals that are depleted in cations. Chamley (1989) reported the formation of kaolinite under strong hydrolysis and gibbsite under very strong hydrolysis. Ferruginized laterites produce goethite in association with kaolinite. Abundant kaolinite along with gibbsite and goethite in the upstream stations of both estuaries thus reflect the intense chemical weathering products in response to rainfall, drainage and topography.

Smectite increases seaward, marginally in Mandovi and more distinctly in the downstream and bay stations of Zuari (Fig. 4). The variations in salinity (0.03 to 0.2) are identical in channel stations of both estuaries (Fig. 3). Therefore, differential flocculation and size segregation of clay minerals in response to salinity change (Gibbs 1977) are not factors for smectite variations. As smectite occurs in traces in the upper estuary of both rivers (Fig. 4) it may not have been transported from the upstream. The plausible explanations for smectite should include contribution from lithological formations in the drainage basins in downstream of rivers and/or transport of smectites from offshore into the estuarine region. The Bicholim Formations in the upstream laterally change to Sanvordem Formations in the coastal plain, downstream areas and the latter are predominantly widespread in the drainage basin of Zuari River. It is likely that in low plains and in less permeable argillite-covered (Sanvordem Formations) regions the leaching solutions with more and more dissolved elements released from hydrolysis are not entirely evacuated by running water, but tend to be stored and concentrated in soil profiles. During dry conditions these elements combine and form new minerals such as smectite. In regions where ground water levels are high, the smectites thus formed may migrate upwards and replace formerly well-drained kaolinite soils through a progressive ionic saturation of weathering profiles (Chamley 1989). Thus the soils in the coastal plain, downstream areas are enriched by smectite and kaolinite and are transported into the estuary. More stations showing distinct smectite in the lower estuary of Zuari than in Mandovi may be due to the larger drainage basin in coastal, low plains for the Zuari River.

The other source for high smectite at bay stations could be the transport of smectite from offshore. We propose this explanation because smectite is an abundant component in the inner shelf sediments (Nair et al. 1982; Rao and Rao 1995) and is derived from the Deccan Trap Basalts that cover the hinterland north of the study area. Since the coastal current during SW monsoon is directed southwards, smectite-dominated sediments transported by this current are probably advected into the bays by the prevailing tidal and wind-induced currents. Sr-Nd isotopes of the suspended matter would help in determining the sources of smectite more precisely.

Geochemistry of the SPM

Sources of SPM at ore stations (M8-M6)

Ore stations are characterized by high SPM concentrations, highest Fe and Mn, high Σ REE and, MREE- and HREE-enriched REE patterns (Figs. 3, 5 and 7). Since Σ REE shows strong correlation with Al ($r=0.98$) and Fe ($r=0.73$) aluminosilicates and colloidal Fe-oxyhydroxides may be important carriers

for REEs (Taylor and McLennan 1995). Elderfield et al. (1990), Andersson et al. (2005) and Marmolejo-Rodriguez et al. (2007) demonstrated large scale removal of REEs by co-precipitation and adsorption onto Fe-O-OH surfaces. The Mandovi River drains through Bicholim formations consisting of banded-iron formations and Mn deposits. Fe and Mn ore deposits are also stored on the shore and then loaded into barges at these stations (Fig. 2). Several workers reported MREE- and HREE-enriched REE patterns with positive Ce and Eu anomalies in banded-iron formations, Fe-Mn bearing arenites, Tonalite-Trondhjemite Gneisses and mafic-ultramafic complexes of the Precambrian formations, including those in Goa region (Dhondial et al. 1987; Manikyamba and Naqvi 1997; Naqvi 2005; Desai et al. 2009). Moreover, the REE patterns of Fe-Mn ores also show MREE- and HREE-enriched patterns with positive Ce and Eu anomalies and closely resemble that of suspended matter at ore stations (see Fig. 7). Heavy rainfall during the monsoon would have flushed Fe-Mn deposits stored on the shore and Fe-Mn minerals along with their leachates transported to the estuary. We therefore suggest that the SPM at stations M8-M6 is largely contributed by ore deposits.

Sources of SPM at channel stations (M5 to M1; Z7 to Z4)

Stations M5 and Z7 exhibit low SPM, low Fe and Al and, MREE- and LREE-enriched REE patterns. The seaward decrease in SPM concentrations from M5 to M1 (Fig. 3) is accompanied by an increase in Al, Mg, Fe and Mn concentrations (Fig. 5; Table 2). Since smectite increase from M5 to M1 is marginal (Fig. 4), smectite (Fe, Mg aluminosilicate) alone cannot account for the increased elemental concentrations. Metal concentrations are usually higher in finer particles. Since finer particles are transported farther the SPM at sea end stations may contain more finer-sized particles and contributed increased concentrations of Fe, Mg and Al seaward. On the other hand, the MREE- and LREE-enriched REE patterns at M5 and M4 stations are distinct from that of ore stations (M8-M6 - Fig. 7). As Cumbarjua canal joins the Mandovi estuary at stations between M4 and M5 (see Fig. 1), the suspended material at these stations could be a mixture received from lithological formations in the low plain, downstream and, ore dust from upstream. The former may have dominated the latter and thus resulted in MREE- and LREE-enriched REE patterns. Furthermore, ΣREE and $(\text{HREE})_n$ also increased seaward from M4 to M1 (Fig. 5). The MREE- and LREE-enriched patterns at M4 gradually changed to MREE- and HREE-enriched patterns at M1 (Fig. 7). In other words, the gradual increase in Fe, Mn, Al, Mg, ΣREE and $(\text{HREE})_n$ and, change in REE patterns from M5 to M1 indicate that the SPM at sea-end stations is characteristic of ore dust and of clays to some extent. The source for the ore dust may be the spilled-over material during transport of Fe, Mn ores through the estuary and/or ore handling at the port or mid-stream. As the port/mid-stream loading points are located in the vicinity of the bays, this

dust most probably transported to the bay and then to the channel by monsoon currents. Alternately, the previously deposited ore dust and clay in the bay may have been resuspended and transported into the estuary channel by monsoon currents. Magnetic susceptibility values of the sediments suggest that the bay sediments are Fe-rich compared to that in the adjacent channels (V. P. Rao, unpublished data).

The M/Al ratios of metals gradually increase from M8 to M5, highest at stations M5 and M4 and then decrease from M4 to M1 (Fig. 6). The causes for the concentration of these metals in SPM, close to the meandering of the river and junction point of the canal to the river channel (see Fig. 1 for locations of M4 and M5) are not known. It is likely that these metal ions are quickly adsorbed onto oxyhydroxides and silicates with slight increase in salinity and less intense water flow into the channel, because the river waters are partitioned into two channels. Organic-rich clays are, however, characteristic in bottom sediments of this region. The metals released from reductive diagenesis of sediments might have diffused into the water column and reprecipitated onto particulates at the sediment-water interface. Resuspension of these particles under relatively high-energy conditions (one would expect at the confluence of canal) should cause the high metal/Al ratios. Shynu et al. (2012) also reported higher M/Al ratios of trace metals at M4 and M5 stations during the monsoon.

Channel stations of Zuari exhibit MREE- and LREE-enriched REE patterns. Smectite increases from Z7 to Z4. Sanvordem Formations in the low plain of Zuari may have contributed these REEs and clays rich in smectite. Although one would expect seaward decrease of total-REEs Σ REE increased from Z7 to Z4 and, station Z4 is characterized by high MREE- and near equal values of (LREE)_n and (HREE)_n (Table 2; Fig. 7). The REE patterns at Z4 in Zuari and M1 in Mandovi are similar (M1 and Z4 are sea-end stations of the channels in respective rivers). Therefore the increase in smectite, Σ REE and (HREE)_n at Z4 indicate that the SPM comprises of particulates from the ore dust (rich in MREE- and HREEs) and smectite-rich clays. The M/Al ratios of trace metals at the river-end stations (Z7-Z5) of Zuari are much higher than those of the World River average SPM (see Table 2; Viers et al. 2009). Higher concentrations of trace metals could be due to the anthropogenic contamination because of the ship-building industry and Fe-pellet making factory located on the shore either side of the river at stations between Z7 and Z6. Chipping and welding works and anti-fouling painting works are being carried out at the ship-building unit. Cr, Cu, Pb and Zn have been used in anti-fouling paints, and Ni and Zn in welding materials, galvanizing and metal plating (Sutherland 2000; Buggy and Tobin 2008; Shynu et al. 2012). Therefore, one would expect flushing of trace metals into the channel during heavy monsoon rains and increase their concentrations in SPM. Sharp decrease in trace metal concentrations

at bay stations of Zuari (Fig. 6) might be due to the aggregation and coagulation of the metal-bearing particles and their deposition to the bottom in response to the increase in salinity.

Sources of SPM at bay stations (Z3 to Z0)

The average concentrations of SPM, Al, Mg, Fe, Σ REE and (HREE)_n were higher at bay stations (17.2 mg/l, 5.3%, 1.3%, 7.9%, 124.1 μ g/g, 2.59, respectively) than at channel stations (15.8 mg/l, 3.7%, 0.7%, 8%, 101.8 μ g/g, 2.03, respectively) (Table 2; Figs. 5 and 7). Higher concentrations of SPM and other elements at bay stations were associated with increased salinity from 0.4 to 10 (Fig. 3). Sholkovitz (1995) and Hoyle et al. (1994) reported 60-90% of the REEs carried by the rivers are removed in estuaries and, about 70% of total REEs are removed at salinities <5 during estuarine mixing. Despite increased salinities high SPM, Σ REE and (HREE)_n occur at bay stations suggesting resuspension of bottom sediments must have supplied particulates associated with HREE to the water column. The funnel-shaped bay favours enhancement of physical processes. For example, strong, westerly to southwesterly winds with speeds of 4-7 ms⁻¹ prevailing during the monsoon (Shetye et al. 2007) not only generate waves but also reinforce currents. As wind is directed landward during the monsoon the magnitude of the effect of winds on currents is expected to be more towards narrow end of the bay. The funneling effect of the water enhances energy conditions as the tide level increases towards narrow end of the bay. The enhanced energy conditions lead to increased turbulence and resuspension of bottom sediments. Several investigators reported increased turbidity and resuspension of bottom sediments due to the funneling effect at the mouth of the estuaries (Nichols and Poor 1967; Allen and Castaing 1973; Collins 1983; Scully and Friedrichs 2007; Manning et al. 2010). In other words, physical processes modulated by the geometry of the bay favoured resuspension leading to high SPM.

The REE patterns at bay stations further show dominant positive Eu anomaly and no Ce anomaly. The positive Eu anomaly may have been associated with Fe, Mn-particulates and its presence in the SPM of bay simply reflects contribution from these particulates and stability of Eu at low salinities (0.4 to 10). Positive Ce anomaly in Fe, Mn ores may be due to Ce oxidation at their oxyhydroxide surfaces (De Carlo et al. 1998; Bau 1999). Absence of Ce anomaly in three of the four stations in the bay (Fig. 7) can be explained due to the oxidative scavenging of Ce (IV) by Mn and Fe-oxyhydroxides and its subsequent removal to sediments. The oxidative scavenging of Ce (IV) is also controlled by the type of organic matter and complexation with carbonates. Relative increase in salinity and marine organic matter (see $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values at bay stations in Table 3 and discussion on

sources of organic matter below) may have also favoured preferential adsorption of Ce (IV) onto organic substances (see Pouret et al. 2008) and scavenging these particles to the bottom sediments results in the absence of Ce anomaly.

Sources of SPM in Cumbarjua Canal (C3 to C0)

Clay minerals at stations on either side of the canal resemble those of nearby stations in the channels of the respective estuaries (compare C3 with Z4 and, C0 with M5 in Fig. 4) and suggest the influence of both estuaries on SPM compositions in the canal. As smectite is a minor component at central stations (C1 and C2) the direction of transport through the canal is not clear from the mineralogy. The MREE- and HREE-enriched patterns with strong Eu and Ce anomalies at C1 and C2 differ from those at C0 which contains MREE- and LREE-enriched patterns. They also differ from C3 which contains small Ce anomaly that increases from C3 to C1 (Fig. 7). As discussed above Ce may have been affected by removal processes. On the other hand, Fe and Mn concentrations are highest at C1 and C2 than those at C3 and C0 (Table 1). The metal oxides accumulated locally could have contributed to the REE patterns. Further, the high M/Al ratios of trace metals at stations M4 and M5 of Mandovi and at station C0 of Cumbarjua canal and their decrease towards C3 (Fig. 6) point out that the suspended material from Mandovi estuary is transported into the canal. This is possible, because the runoff from Mandovi River is much high and nearly double that of Zuari during the monsoon (see study area). Nagaraj and Raghuram (2005) reported that more than 50% of the ore carried through the Mandovi is diverted to the port through this canal during the monsoon. Highest concentrations of Fe, Cr, Ni, Cu and Σ REE in canal stations could be due to the heavy traffic of ore-filled barges through the canal and spilled-over ore material from the barges into the canal. Resuspension of bottom sediment could be an important process because of the narrow width of the canal and heavy traffic of barges that create turbulence and supply metal-rich bottom sediment to the water column.

Contamination and pollution of metals

Salinity of the surface waters at channel stations of both estuaries and canal is <1 (Fig. 3), suggesting that the SPM from fluvial sources could be the dominant source of metals. As discussed above flushing of Fe, Mn ores stored on the shore during monsoon, weathering of hinterland rocks and resuspension of bottom sediments locally contributed these metals. Shynu et al. (2012) reported strong inter-relationship among trace metals and their moderate correlation with Fe from the Mandovi estuary. Ship-building industries on the shores of both rivers may have contributed to the trace metals. It is likely that the metal-bound clays may have been washed into the estuary during heavy monsoon rains.

Resuspension of bottom sediment is important at stations in the bay, Cumbarjua canal and stations where canal joining the Mandovi estuary. The combined sources of SPM lead to increase the concentration levels of major and trace metals to moderate pollution (Fig. 8). Significant pollution of Mn compared to the moderate pollution of other metals (Fe, Cr, Co, Cu, Ni, and Zn-Fig. 8) could be due to its lower reactivity to oxidation (Sholkovitz 1978; Zhou et al. 2003).

Sources of organic matter

The total organic carbon (OC) and OC/TN ratio decrease seaward in the Mandovi estuary (Figs. 9A, 9E). The gradual decrease in OC/TN from 12.5 to 6.4 indicates seaward depletion of terrestrial organic matter. Ogrinc et al. (2005) suggested that the C/N ratios range from 13.7 to 8.3 for terrestrial organic matter and 7.0 ± 1.5 for marine organic matter in the sediments of the Gulf of Trieste, Adriatic Sea. The OC and OC/TN ratios in Zuari estuary decrease seaward in channel stations but maintained near similar values at bay stations (Fig. 9B, 9F) suggesting that the organic matter in the bay may be of reworked type (see below).

The $\delta^{13}\text{C}$ values at the river-end stations of both estuaries (-26.6‰ and -25.68‰ ; Table 3) are close to that of terrestrial organic matter reported by Wada et al. (1987; -26.5‰), Thornton and McManus (1994; -25.4‰ to -28‰), Peters et al. (1978; -26‰), Ogrinc et al. (2005; $-26.6 \pm 0.4\text{‰}$), Zhang et al. (2007; $-22.4 \pm 3.5\text{‰}$), Sarma et al. (2012; $-27.2 \pm 0.7\text{‰}$), Fernandes (2011; -32.1‰ to -25.1‰) and Maya et al. (2011; $-24.8 \pm 0.5\text{‰}$) and indicate terrestrial organic matter to be the dominant component. The seaward increase of $\delta^{13}\text{C}$ from -26.6‰ to -24.6‰ in Mandovi, and from -25.7‰ to -24.0‰ in Zuari estuary indicates depletion of terrigenous material and enrichment of marine organic matter. The $\delta^{13}\text{C}$ values at sea-end stations of both estuaries (-24.6‰ , -24.0‰) are close to that of marine organic matter reported by Salmons and Mook (1981; -25.4‰) and Dehairs et al. (2000; -24.16‰ to -22.8‰), but are slightly lower than in marine plankton ($-23 \pm 0.1\text{‰}$; Dehairs et al. 2000). Zhang et al. (2007) reported $\delta^{13}\text{C}$ values of -23‰ to -24‰ for estuarine mixing. Ramaswamy et al. (2010) reported an average $\delta^{13}\text{C}$ of -26.8‰ for terrigenous organic matter and -24.2‰ for organic matter in estuarine sediments of the Mandovi and Zuari. Strong negative correlation ($r = -0.92$) between OC/TN and $\delta^{13}\text{C}$ in Mandovi (Fig. 9G) also indicates seaward increase of marine organic matter.

The $\delta^{15}\text{N}$ values of Mandovi (1.5 to 2.5‰; Table 3) are within the range of values for terrestrial organic matter ($\sim 1.5\text{‰}$ – Mariotti et al. 1984; $2.3 \pm 0.9\text{‰}$ – Owens and Law 1989). On the other hand, the gradual increase in $\delta^{15}\text{N}$ values, especially in the bay stations of Zuari (4.2 to 5.9‰) and, strong

correlation of $\delta^{13}\text{C}$ with $\delta^{15}\text{N}$ ($r=0.67$; Fig. 9H) suggest seaward increase of marine organic matter. However, small variations in OC/TN ratio between river-end and sea-end stations of Zuari (Fig. 9F) and, near equal OC/TN ratios at bay stations, despite gradual increase in $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ (Figs. 9B and 9D) suggest addition of non-labile (inert) type organic matter that could have resuspended from bottom sediments. SPM concentrations, mineralogy and geochemistry of SPM at bay stations indeed support resuspension of bottom sediments. In other words, the OC/TN ratios indicate that the organic matter at bay stations may be marine and altered-type.

As $\delta^{13}\text{C}$ values are distinct for terrestrial and marine organic matter in both estuaries the contribution of terrestrial organic carbon (TOC) discharged into the coastal system was calculated, following the equation of Schultz and Calder (1976),

$$\text{Percentage of TOC} = [(\delta^{13}\text{C}_{\text{marine}} - \delta^{13}\text{C}_{\text{sample}}) / (\delta^{13}\text{C}_{\text{marine}} - \delta^{13}\text{C}_{\text{terrestrial}})] \times 100$$

This equation requires end-member values for marine and terrestrial organic matter. We have analyzed $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ of organic matter for several samples along transect of the Mandovi and Zuari River estuaries in different seasons and found that -28.6‰ is the lowest $\delta^{13}\text{C}$ value for terrestrial organic carbon at river-end stations (Rao et al. communicated). The $\delta^{13}\text{C}$ of marine plankton is -23.1‰ (Dehairs et al. 2000). Using end member $\delta^{13}\text{C}$ values, -28.6‰ and -23.1‰ for terrestrial and marine organic matter, respectively, we found that the organic matter is a mixture of 43% terrestrial and 57% marine organic matter at sea-end stations of the Mandovi estuary and, 26% terrestrial and 74% marine organic matter at the mouth of the bay in Zuari estuary.

The difference in $\delta^{13}\text{C}$ values between river-end and sea-end stations is smaller in the Zuari estuary (1.68‰) than in Mandovi (2‰). It is likely that the terrigenous organic matter in Zuari is effectively diluted by the organic matter transported from the bay to the channel. The tidal and wind-induced currents enhanced by the narrowing bay conditions in Zuari may have effectively pushed particulate organic matter from bay to the channel. Even in Mandovi, the $\delta^{13}\text{C}$ values at sea-end stations (M1-M3) of the estuary are nearly similar and affected by dilution of marine organic matter. Distribution of smectite and REE/HREE in Zuari and, Fe, Mn and REE/HREE in Mandovi also argue in favour of landward advection of suspended matter from bay to the channel in both estuaries. This landward advection is happening because of the breaks in the monsoon rainfall. During heavy rainfall the river flow dominates the strength of the flow derived from the tidal and wind-induced currents and SPM moves seaward of the estuary. However, during the lull periods in monsoon rains the combined

strength of tidal and wind-induced currents regulated by the geometry of the bay dominates river flow. As a consequence the particulates resuspended from the bottom sediments are transported from bay to the channel. The present study documents this process. Similar process of landward transport of particulates was also reported in these estuaries during the pre-monsoon when the river discharge was negligible (Rao et al. 2011).

Summary

The concentrations and composition of SPM for each estuary is summarized below:

Concentrations of SPM decrease seaward in the Mandovi estuary. Concentrations of Fe, Mn, Al, Mg and Σ REE are high at the upstream stations, decreased to low at mid-stations and then increase seaward of the estuary. MREE and HREE-enriched REE patterns occur at extreme stations on either side of the estuary and MREE- and LREE-enriched REE patterns at mid-stations. These observations indicate SPM at extreme stations is dominated by ore dust and to minor extent clay. Kaolinite is dominant at upstream station while smectite increases seaward. Concentrations and composition of SPM at sea-end stations of the estuary demonstrate that the SPM resuspended from the bottom of the bay is advected into the channel.

In Zuari estuary SPM decreases seaward in channel stations but is high at bay stations. SPM at upstream stations of the channel is dominated by kaolinite and is MREE- and LREE-enriched. While at bay stations it is dominated by smectite and is MREE- and HREE-enriched. Resuspension is an important process in the bay and resuspended sediment characteristic of ore dust and clay are transported into the channel. Further, high metal/Al ratios at upstream stations are probably anthropogenic, contributed by industries located on the shore.

Highest concentrations of major and trace metals in the Cumbarjua canal may be due to heavy traffic of ore-filled barges through the canal during which ore dust is spilled-over into the canal and particulates are resuspended into the water column. Gradual decrease in the concentrations of trace metals from Mandovi estuary to the canal documents the direction of flow in the canal during the monsoon.

Stable organic carbon and nitrogen isotopes in both estuaries indicate that the terrigenous organic matter is diluted seaward by marine organic matter. Organic matter at bay stations may be of altered-type and transported into the channel during the lull periods of monsoon.

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Figure captions

- Fig. 1. Location of stations in the Mandovi and Zuari estuaries and Cumbarjua canal. Rainfall (RF) measured at rain gauge stations on the day of sampling are also shown. Sampling was carried out from the upstream to downstream stations of the estuary. Insert figure shows tidal height during sampling period.
- Fig. 2. Photographs showing (A) Fe, Mn ore deposits stored on the shore of the Mandovi estuary and (B) loading of Fe, Mn ores into barges.
- Fig. 3. Histograms showing concentrations of suspended particulate matter (SPM) and salinity of surface water at stations in the Mandovi and Zuari estuaries and, Cumbarjua canal.
- Fig. 4. X-ray diffractograms of suspended particulate matter at each station. S- smectite, I- illite, K- kaolinite, Gi- gibbsite, Go- goethite.
- Fig. 5. Histograms showing concentrations of Fe, Mn, Al, Mg and Σ REEs in suspended particulate matter at each station.
- Fig. 6. Histograms showing Metal/Al ratios in the suspended matter at each station. Horizontal dashed line is metal/Al ratio in the World River average suspended particulate matter.
- Fig. 7. Post-Archaean average Australian Shale (PAAS)-normalized REE patterns at each station in the estuaries and canal. Normalized REE pattern of Fe, Mn ores is also shown along with 'ore stations'.
- Fig. 8. Enrichment factor of metals from different domains of the estuaries and canal. Categories of pollution based on the enrichment factor of metals, adopted from Sutherland (2000) are also shown.
- Fig. 9. Variations in total organic carbon (OC), total nitrogen (TN), OC/TN, $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ of suspended matter at different stations (A-F). The plots showing correlation between OC/TN and $\delta^{13}\text{C}$ (G) and, between $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ (H) in the Mandovi and Zuari estuaries are also shown.

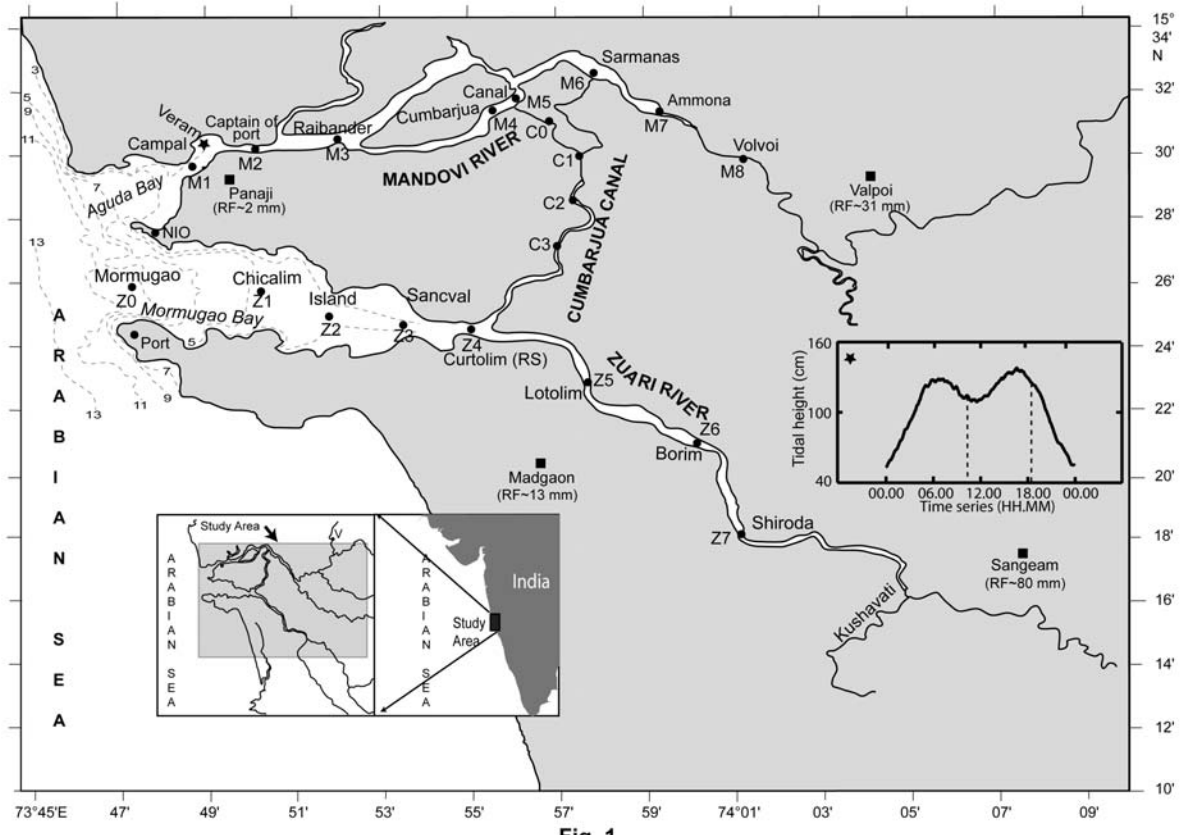


Fig. 1



Fig. 2

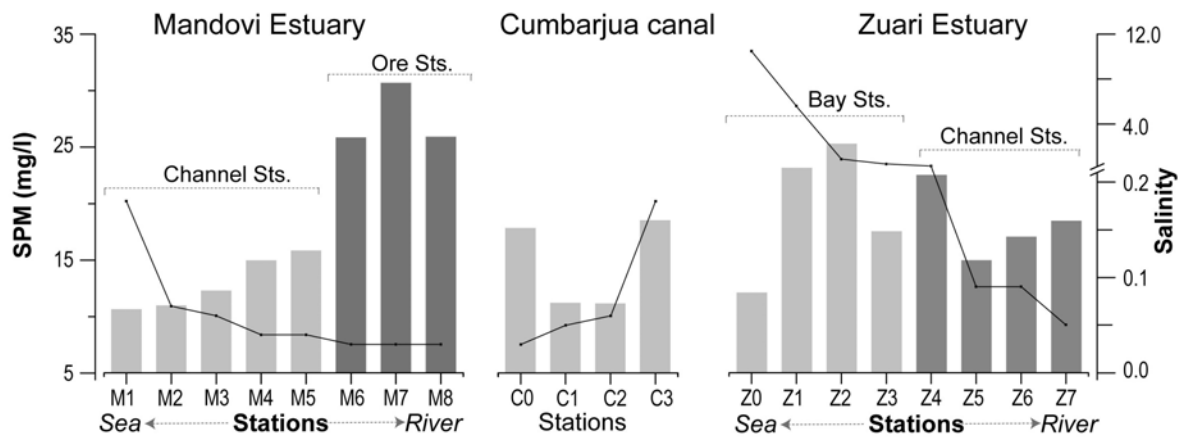


Fig. 3

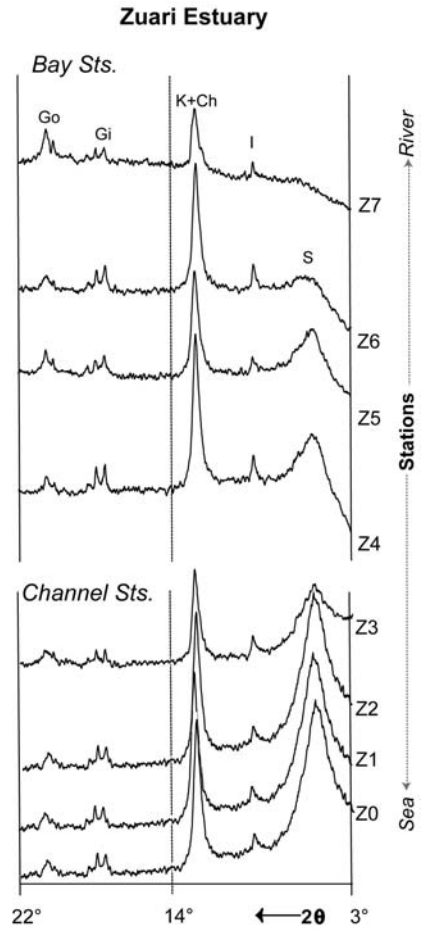
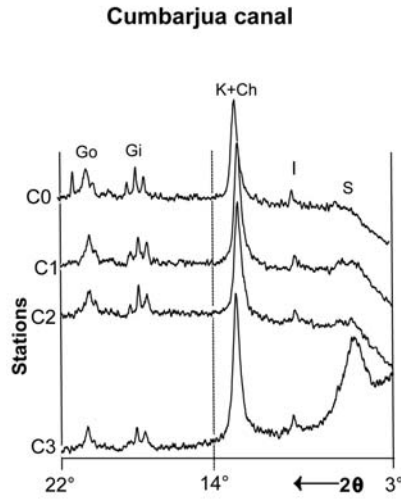
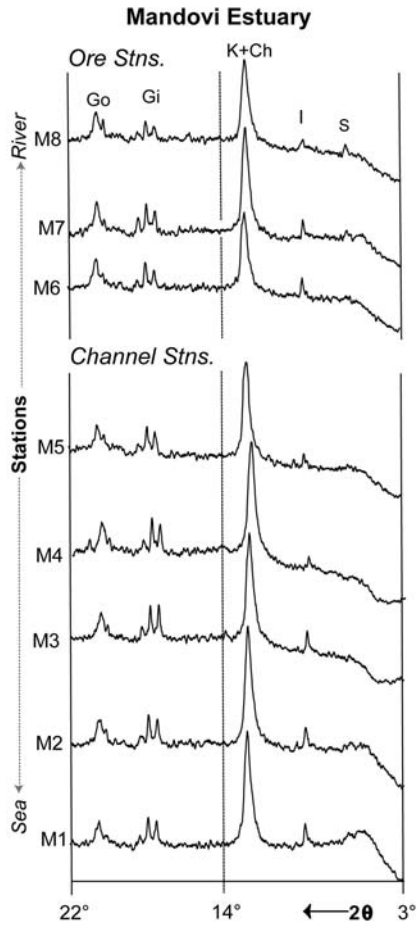


Fig. 4

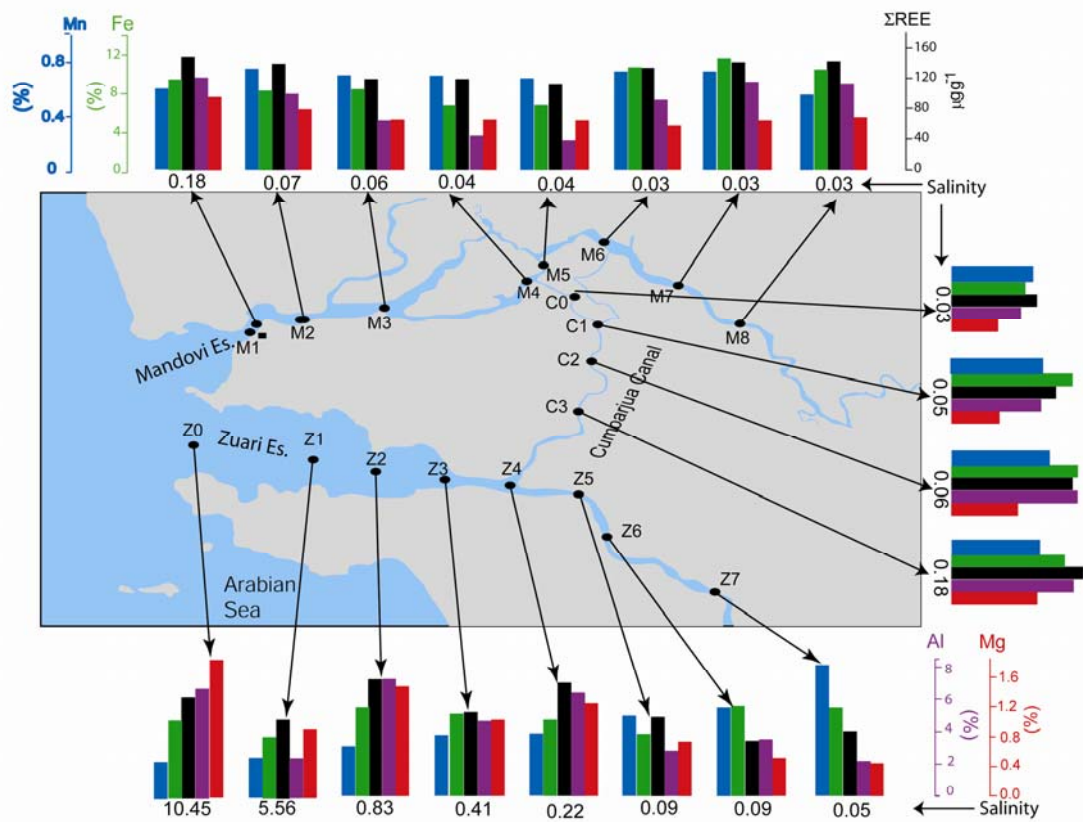


Fig. 5

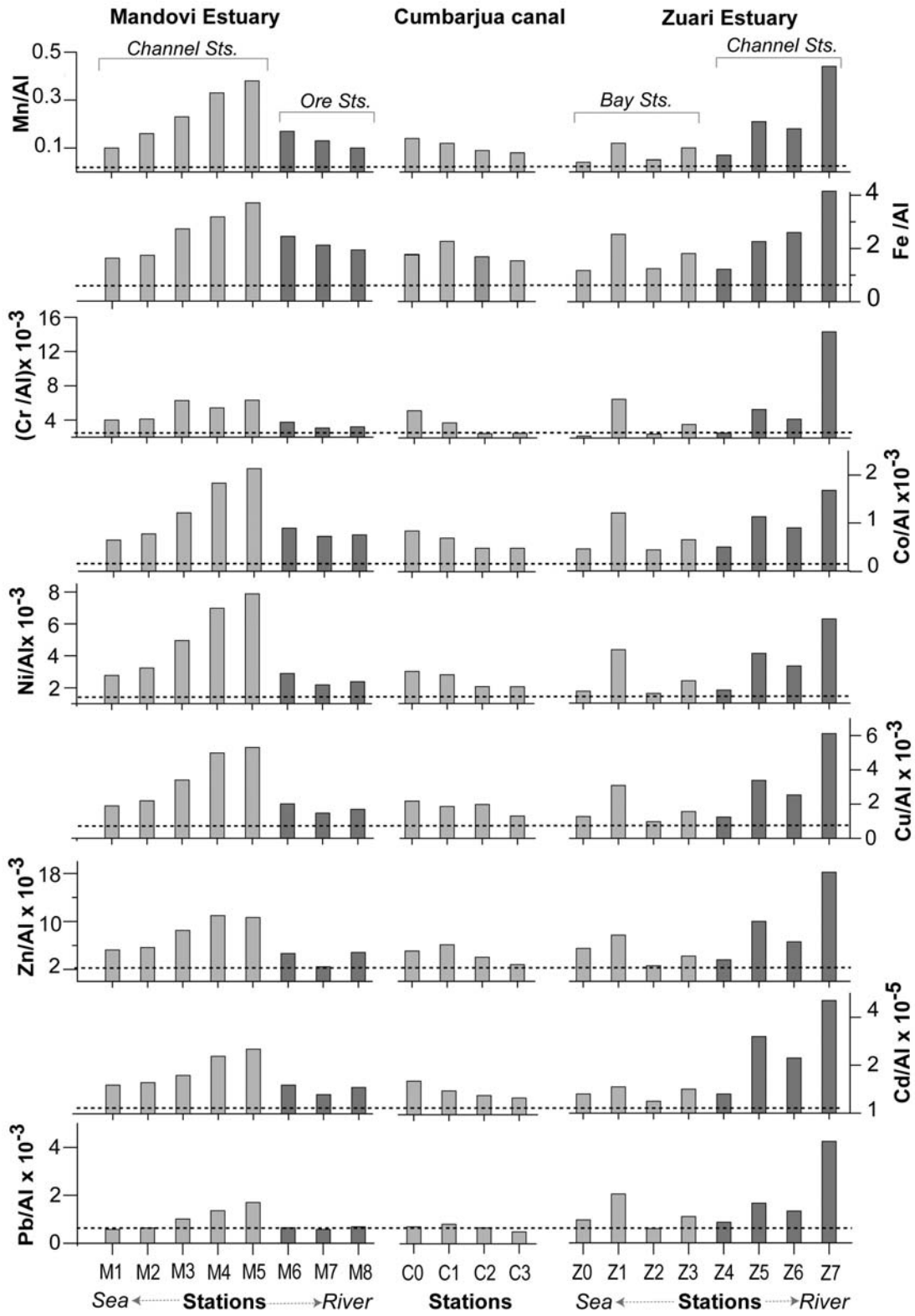
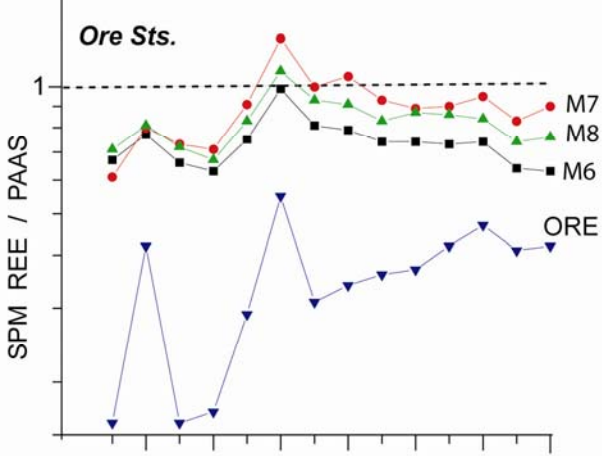
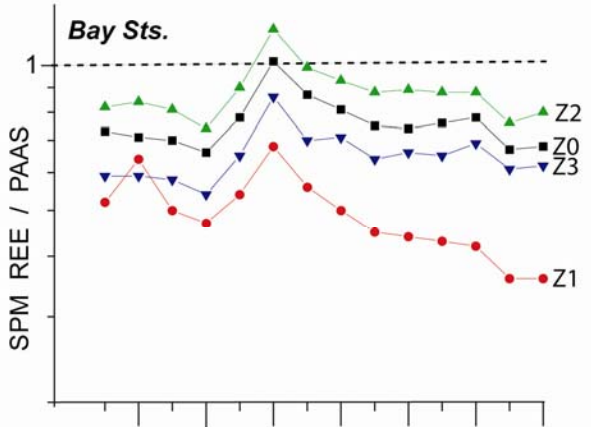
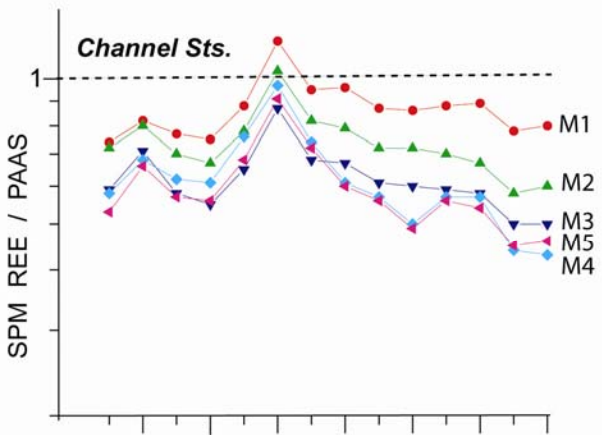


Fig. 6

Mandovi Estuary



Zuari Estuary



Cumbarjua canal

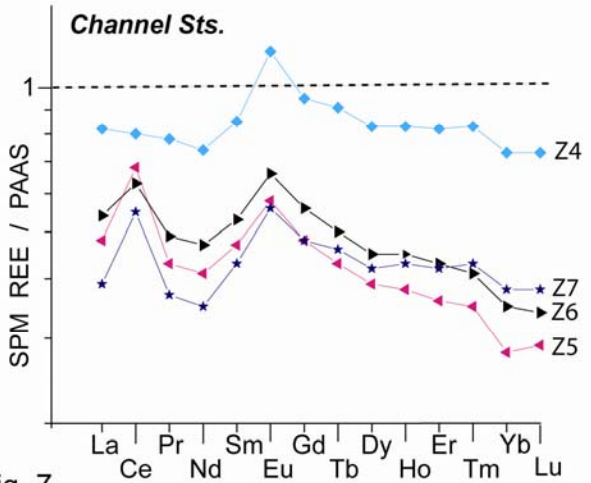
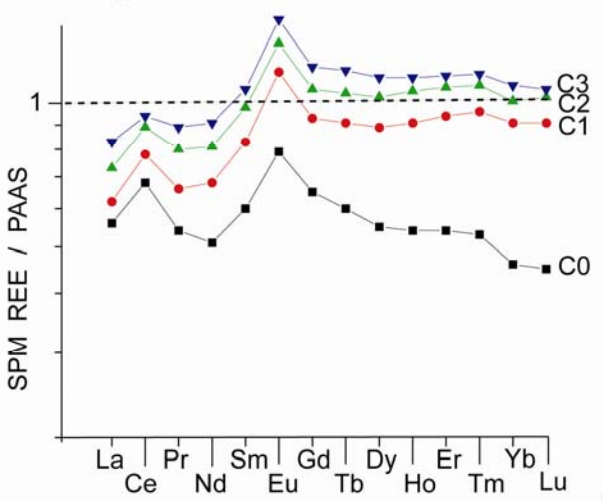


Fig. 7

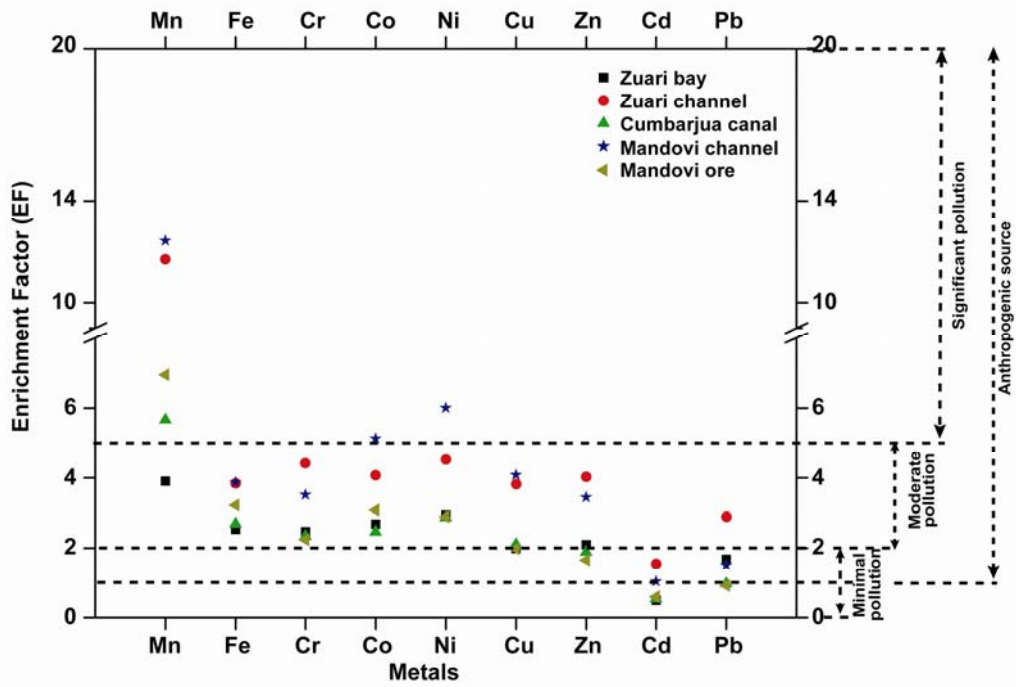


Fig. 8

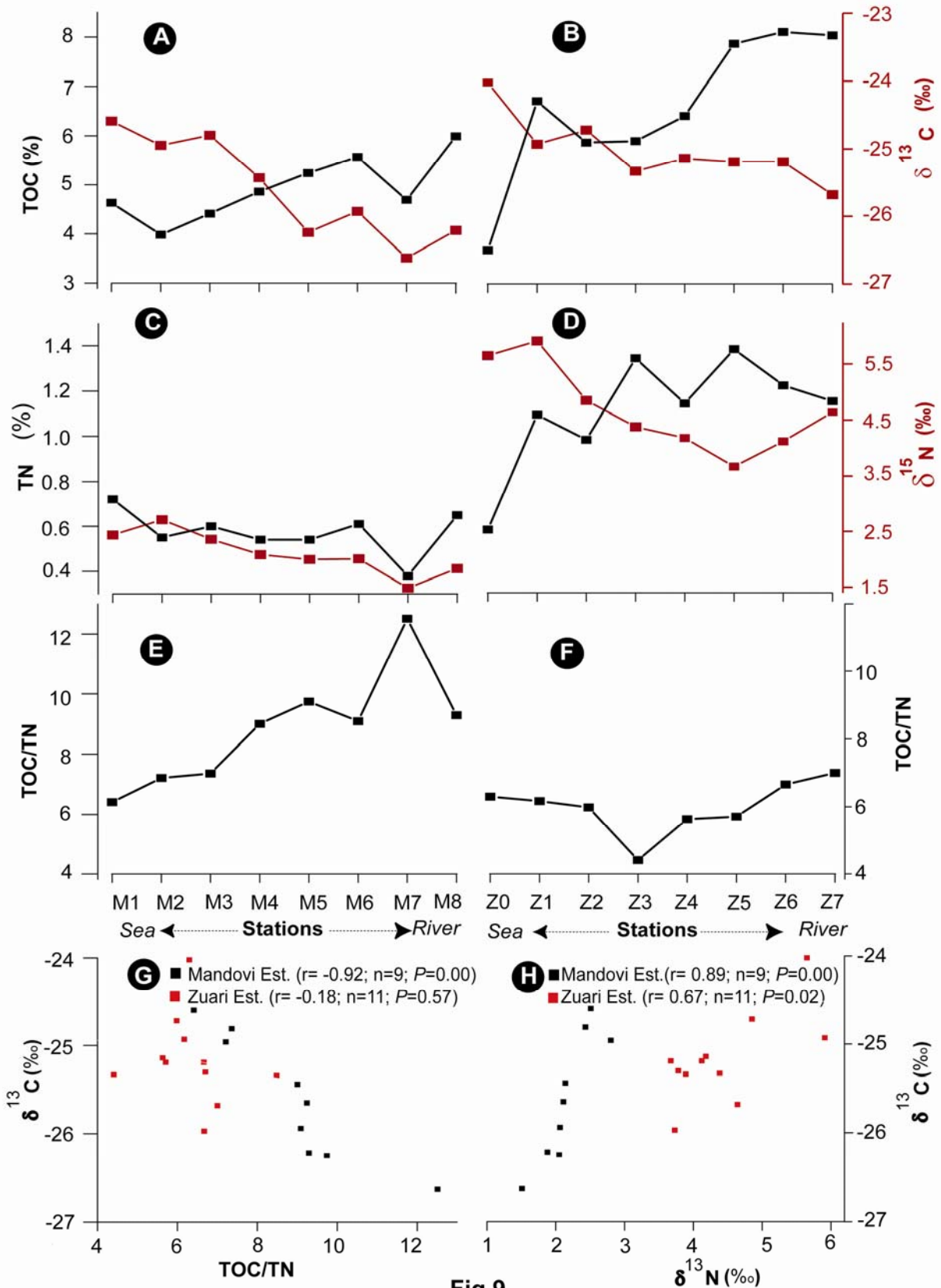


Fig.9

Table. 1
SPM Concentrations, salinity, tidal height and wind speed during sampling.

Estuary	Station No	Sampling time (hrs)	SPM* (mg/l)	Salinity	tidal ht [#] (cm)	Wind speed ^{\$} (m/s)
Mandovi Es.	M8	1139	25.97	0.03	132.8	4
	M7	1227	30.75	0.03	137.7	1.9
	M6	1254	25.90	0.03	138.5	1.9
	M5	1340	15.89	0.04	148.0	3.6
	M4	1444	15.03	0.04	158.0	2.7
	M3	1553	12.35	0.06	164.9	3.1
	M2	1717	11.04	0.07	167.0	1.6
	M1	1756	10.71	0.18	159.8	4.5
Zuari Es.	Z7	1022	16.02	0.05	138.9	3.3
	Z6	1105	14.40	0.09	134.2	3.7
	Z5	1207	12.01	0.09	136.2	4.6
	Z4	1616	20.70	0.02	166.4	1.3
	Z3	1658	14.95	0.41	166.4	2.7
	Z2	1725	23.86	0.83	166.4	3.1
	Z1	1748	21.42	5.56	160.5	4.5
	Z0	1826	8.72	10.45	154.0	2
Cumbarjua canal	C3	1530	18.57	0.03	165.4	3.3
	C2	1435	11.22	0.05	157.4	2.7
	C1	1400	11.27	0.06	155.2	3.9
	C0	1420	17.89	0.18	152.4	3.2

* Suspended Particulate Matter. [#] At tide gauge station (Verem). ^{\$} At AWS (NIO).

Table. 2
Concentrations of major elements (%) and trace metals ($\mu\text{g g}^{-1}$) in the suspended particulate matter (SPM).

St.No.	Al%	Mg%	Mn%	Fe%	Cr	Co	Ni	Cu	Zn	Cd	Pb	$\Sigma\text{REE}(\text{LREE})_n$	$(\text{MREE})_n$	$(\text{HREE})_n$	$(\text{L/M})_n$	$(\text{L/H})_n$	Ce/Ce*	Eu/Eu*	
Mandovi ore stations.																			
M8	5.3	0.7	0.5	10.2	169.45	40.33	126.03	89.20	255.54	0.59	36.50	141.2	2.90	5.46	3.19	0.53	0.91	1.16	1.25
M7	5.4	0.7	0.7	11.3	165.34	39.17	117.62	79.20	130.90	0.42	31.46	139.9	2.84	6.10	3.58	0.46	0.79	1.24	1.36
M6	4.3	0.6	0.7	10.4	160.46	38.33	123.65	86.00	198.94	0.52	27.78	132.5	2.73	4.82	2.74	0.57	1.00	1.18	1.28
Mean	5.0	0.6	0.7	10.6	165.08	39.28	122.43	84.80	195.13	0.51	31.91	137.9	2.82	5.46	3.17	0.52	0.90	1.20	1.29
Mandovi channel stations.																			
M5	1.8	0.7	0.7	6.5	110.84	37.49	138.23	93.07	187.17	0.47	29.92	111.5	2.32	3.96	2.01	0.59	1.15	1.22	1.30
M4	2.0	0.7	0.7	6.4	110.45	37.51	142.16	101.44	223.82	0.49	27.60	117.8	2.48	4.15	2.01	0.60	1.24	1.15	1.29
M3	3.0	0.7	0.7	8.1	188.02	36.41	148.57	101.88	254.89	0.49	30.10	118.0	2.43	4.08	2.18	0.60	1.12	1.24	1.31
M2	4.6	0.8	0.7	8.0	190.53	36.16	149.98	101.59	262.24	0.61	29.81	138.1	2.88	4.87	2.54	0.59	1.13	1.15	1.29
M1	5.7	1.0	0.6	9.2	227.34	36.90	157.56	107.36	298.01	0.71	32.87	147.7	3.08	5.72	3.35	0.54	0.92	1.11	1.32
Mean	3.4	0.8	0.7	7.6	165.43	36.89	147.30	101.07	245.22	0.55	30.06	126.6	2.64	4.55	2.42	0.58	1.11	1.17	1.30
Zuari channel stations.																			
Z8	2.2	0.4	0.9	8.9	307.44	36.12	135.04	132.11	392.18	1.00	91.40	84.5	1.67	2.77	1.61	0.60	1.03	1.46	1.24
Z7	3.5	0.5	0.9	9.3	183.24	34.84	120.99	114.44	279.38	1.07	66.21	125.6	2.54	4.67	2.97	0.54	0.85	1.28	1.27
Z6	3.5	0.5	0.6	9.1	146.42	31.33	116.49	89.05	230.77	0.81	46.60	72.0	1.48	2.78	1.87	0.53	0.79	1.11	1.23
Z5	2.8	0.7	0.6	6.3	147.93	31.60	115.05	94.76	279.15	0.88	46.40	103.0	2.14	3.14	1.54	0.68	1.39	1.23	1.22
Z4	6.4	1.2	0.5	7.7	164.09	31.53	115.55	79.18	228.38	0.49	54.54	147.7	3.14	5.56	3.11	0.56	1.01	1.01	1.32
Mean	3.7	0.7	0.7	8.3	189.82	33.08	120.62	101.91	281.97	0.85	61.03	106.6	2.19	3.79	2.22	0.58	1.01	1.22	1.26
Zuari bay stations.																			
Z3	4.6	1.0	0.4	8.3	164.25	29.89	110.59	72.35	194.23	0.47	50.71	109.2	2.31	4.21	2.57	0.55	0.90	1.03	1.28
Z2	7.2	1.5	0.4	9.0	177.32	31.92	116.18	70.50	186.75	0.35	43.14	152.3	3.21	5.76	3.33	0.56	0.96	1.06	1.26
Z1	2.5	0.9	0.3	6.3	160.07	29.87	107.55	76.43	190.44	0.28	50.55	103.2	2.13	3.17	1.57	0.67	1.36	1.28	1.25
Z0	6.8	1.8	0.3	7.9	151.90	31.42	118.41	86.46	371.77	0.57	65.00	131.8	2.80	4.96	2.90	0.56	0.97	1.01	1.24
Mean	5.3	1.3	0.3	7.9	163.38	30.78	113.18	76.44	235.80	0.42	52.35	124.1	2.61	4.53	2.59	0.58	1.05	1.09	1.26
Cumbarjua canal stations.																			
C3	7.5	1.2	0.6	11.5	191.11	37.12	153.38	98.44	211.46	0.51	37.58	172.8	3.57	7.17	4.45	0.50	0.80	1.09	1.32
C2	7.8	0.9	0.7	12.8	195.64	38.42	159.72	153.72	312.57	0.62	52.50	158.2	3.22	6.52	4.22	0.49	0.76	1.17	1.31
C1	5.5	0.6	0.7	12.3	206.44	38.64	153.82	103.17	336.88	0.54	45.33	136.2	2.73	5.63	3.73	0.49	0.73	1.22	1.32
C0	4.3	0.6	0.6	7.5	220.21	36.27	128.03	93.32	216.35	0.59	30.38	111.4	2.29	3.73	1.98	0.61	1.16	1.24	1.27
Mean	6.3	0.8	0.7	11.0	203.35	37.61	148.73	112.16	269.32	0.57	41.45	144.6	2.95	5.76	3.60	0.51	0.86	1.18	1.30
WRSPM	8.72	1.26	0.16	5.81	130	22.5	74.5	75.9	208	1.55	61.1	174.6	3.74	6.28	3.29	0.59	1.13	0.95	1.07
PASS	10	0.08	4.54	110	23	55	50	85	20	184.7									

^a L/H= LREE/HREE, ^b L/M= LREE/MREE; LREE are La to Nd and HREE are Er to Lu and MREE are Sm to Ho (Rollinson, 1993);
Eu*, Ce* anomalies were calculated using this equations of Taylor and Mc Lennan (1985), $\text{Ce}/\text{Ce}^* = 3\text{Ce}_{\text{CN}} / (2\text{La}_{\text{CN}} + \text{Nd}_{\text{CN}})$, $\text{Eu}/\text{Eu}^* = \text{Eu}_{\text{CN}} / (\text{Sm}_{\text{CN}} \times \text{Gd}_{\text{CN}})^{0.5}$
^c 'CN' denote concentration normalized with respect to shale.
^d World river average suspended particulate matter (Viers et al, 2009), ^d Post-Archaean average Australian sedimentary rock (McLennan, 1989)

Table. 3
Organic carbon(OC), Total nitrogen (TN) and their isotopes
in the suspended particulate matter.

St.No.	OC (%)	TN (%)	OC/TN	$\delta^{13}\text{C}$ (‰)	$\delta^{15}\text{N}$ (‰)
Mandovi ore stations.					
M8	5.99	0.65	9.29	-26.22	1.88
M7	4.69	0.38	12.51	-26.63	1.51
M6	5.57	0.61	9.09	-25.94	2.06
Mandovi channel stations.					
M5	5.24	0.54	9.74	-26.25	2.05
M4	4.86	0.54	9.00	-25.44	2.14
M3	4.41	0.60	7.36	-24.81	2.43
M2	3.98	0.55	7.21	-24.96	2.80
M1	4.63	0.72	6.41	-24.60	2.51
Zuari channel stations.					
Z7	8.05	1.15	7.00	-25.68	4.64
Z6	8.12	1.22	6.66	-25.19	4.12
Z5	7.88	1.38	5.71	-25.19	3.67
Z4	6.42	1.14	5.63	-25.14	4.18
Zuari bay stations.					
Z3	5.91	1.34	4.41	-25.33	4.38
Z2	5.88	0.98	5.98	-24.72	4.85
Z1	6.72	1.09	6.17	-24.93	5.91
Z0	3.68	0.58	6.30	-24.02	5.65
Cumbarjua canal stations.					
C3	2.83	0.56	5.04	-24.84	2.43
C2	3.48	0.43	8.07	-25.53	1.58
C1	3.97	0.52	7.62	-24.89	2.78
C0	7.17	0.89	8.03	-25.82	2.19