

Variations in some environmental characteristics including C and N stable isotopic composition of suspended organic matter in the Mandovi estuary

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Abstract

Chemical and isotopic ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$) investigation of the Mandovi estuary along the Indian west coast affected strongly by the seasonal monsoon cycle, were carried out. The Mandovi estuary is a major waterway for Goa and extensively used for transportation of iron and manganese ore. In addition, with large population centers as well as agricultural fields located on its shores, the estuary is assumed to have been influenced by human activities. Measurements of chemical and isotopic parameters made in the lower part of the estuary during the SW (southwest) monsoon and post monsoon seasons reveal distinct changes and it is observed that despite considerable enrichments of macronutrients during the SW monsoon, productivity of the estuary (phytoplankton biomass), as inferred from the Chlorophyll-*a* content, is not as high as expected. This is due to occurrences of high turbidity and ambient cloud cover that limits photosynthetic productivity. The isotopic characterization (C and N isotopes) of suspended organic matter produced/transported during the monsoon and post monsoon seasons of year 2007 provides a baseline dataset for future isotopic studies in such type of tropical estuaries.

Keywords: Mandovi estuary, West coast of India, Nutrients, Chlorophyll, Carbon and Nitrogen isotopes

1. Introduction

The Mandovi is a tropical estuary located on the west coast of India draining into the Arabian Sea, known to respond to seasonal monsoonal changes quite significantly. In addition, increasing human interferences since the beginning of industrial revolution also affects such coastal bodies. As the continental runoff is also a manifestation of monsoonal cycle inventory, of anthropogenically added components are also assumed to be strongly modulated by natural (monsoonal) forcing. Therefore, delineation between natural versus anthropogenic inputs to coastal bodies such as the Mandovi estuary is not straightforward by conventional means.

In this paper, we report the changes in nutrient and isotopic composition of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ in the Mandovi estuary during two seasons (SW monsoon and post monsoon of 2007). The post monsoon observations also sought to understand the effect of tides on the distribution of the various biochemical parameters in the estuary. We have also made a comparative study of the nutrients reported in literature with our study to see if there was any noticeable increase in nutrient concentrations over the past several years. While in some coastal environments the impact of anthropogenic modification is evident and can be traced back to the beginning of the Industrial Revolution (e.g. over the Louisiana shelf - Eadie et al. 1994; in Chesapeake Bay - Bratton et al. 2003; and in the Long Island Sound - Altabet 2007), the biogeochemical imprints of anthropogenic perturbation are not so obvious in other areas. For example, along the west coast of India, distinction via biomarkers between human-induced changes from natural variability continues to be a challenging task (Kurian et al. 2009). This is because of the strong monsoonal influence exerted on coastal processes. As the land runoff is directly related to monsoonal precipitation, fluxes of anthropogenically-generated materials are also strongly modulated by natural forcing.

2. Study area

The Mandovi is one of the major rivers of Goa that drains into the eastern Arabian Sea. The estuarine region is endowed with thick mangrove vegetation and several smaller streams carrying weathered material from the Western Ghats drain into the estuarine region. The Western Ghats that run parallel to the west coast with an average elevation of ~ 1 km, force strong rainfall during the SW monsoon over the western coastal plains in the states of Maharashtra, Goa, Karnataka and Kerala. The bulk of the annual precipitation ($\sim 90\%$) occurs from June to September resulting in heavy continental runoff to the Arabian Sea during this period. As a result, the estuarine regions of the rivers experience extreme seasonal variability with nearly freshwater conditions prevailing during the SW monsoon and almost marine conditions during the non-SW monsoon periods (Qasim and Sen Gupta 1981).

The Mandovi estuary, is about ~ 50 km long and ~ 5 m deep, covering an area of ~ 29 km² (Alagarsamy 2006; Shetye et al. 2007a). The shallow depth generally results in well-mixed conditions except at the estuarine mouth where a salt wedge exists during the SW monsoon (Qasim and Sen Gupta 1981). Based on geographical features the Mandovi estuary can be divided into two regions i.e. the bay and the channel (Shetye et al. 2007a). The bay portion, known as the Aguada Bay is much wider (~ 4 km) compared to the

channel giving the estuary a wineglass like appearance. The city of Panjim is located on banks of the Aguada Bay and the river passing through land area is intensely used for both industrial and agricultural activities. The Mandovi estuary thus receives municipal, industrial and agricultural wastes from adjacent areas. Other prominent human activities in the Mandovi estuary include navigation by fishing trawlers, barges carrying iron and manganese ore, and passenger ferries; and recreational activities like boat cruises for tourists. Though treated sewage from Panjim city is discharged near the bottom at a location 3.93 km upstream from the estuarine mouth (Figure 1), both the channel and bay regions receive untreated sewage as well. The present study focuses on the lower part of the Mandovi estuary to get integrated signatures of the human activities in the upstream region where the discharge point of treated sewage from Panjim city is located.

3. Materials and methods

A total of eight sites were selected for sampling (Figure 1) located both in the bay region (stations S0 to S4) and the channel region (S5 to S7). Water samples for various hydrographic and biogeochemical parameters were collected during the peak SW monsoon season (August 2007) and post monsoon season (December, 2007). As the tides are the major determinants of estuarine mixing during the post monsoon season, sampling was done during both high and low tide periods on two different days (17/12/2007 and 24/12/2007). The difference between the high and low tides was minimal on 17/12/07 and maximal at the time of second sampling a week later.

Sampling was done on a fishing trawler using Niskin water samplers (5 liter capacity), fitted with a protected reversible thermometer which is used in oceanographic studies for measuring seawater temperature. The thermometer is lowered to a particular depth along with the Niskin sampler in a reversing manner and at the desired depth it is flipped back to upright position, this breaks the mercury column and the actual in-situ temperature is recorded. The main advantage of the reversing thermometer is that the in-situ temperature measured at a particular depth is corrected for pressure effects and can be read later on the deck (Keyte 1965). The parameters measured were salinity, temperature (Table 1), dissolved oxygen (DO), nutrients [nitrate (NO_3^-), nitrite (NO_2^-), silicate ($\text{Si}(\text{OH})_4$), phosphate (PO_4^{3-}), and ammonium (NH_4^+)], dissolved organic carbon (DOC), dissolved organic nitrogen (DON), Chlorophyll *a* (Table 2 and 3) and suspended particulate organic matter (SPOM) for its C and N isotopes (Figures 3, 4 and 5). Dissolved oxygen was estimated following the Winkler method (Grasshoff et al. 1983). Nutrients were analyzed using a SKALAR analyzer following standard procedures (Grasshoff et al. 1983). Samples for Chlorophyll *a* were filtered immediately through Whatman GF/F filters and the filter papers were soaked in 90% acetone and stored at -20°C in the dark. Quantitative estimation of Chlorophyll *a* was done after 24 hours following the spectrofluorometric technique. Samples for SPOM were filtered through precombusted $0.4\ \mu\text{m}$ Whatman GF/F filter papers. All SPOM samples were decalcified by exposing them to HCl fumes and later analyzed using isotopic ratio mass spectrometer (IRMS) (Delta V plus; Thermo) coupled with an Elemental Analyzer (Owens and Rees 1989). Salinity was measured using an AUTOSAL Salinometer. Sub-samples for DOC and DON were filtered

through 0.4 μm filters and collected in pre-combusted 40-mL EPA vials and analyzed by the high temperature combustion technique using a Shimadzu TOC analyzer (Sugimura and Suzuki 1988; Cauwet 1994).

4. Results and discussion

4.1 Hydrographic features

The hydrographic conditions in the Mandovi estuary are significantly different during the dry and wet season (Table 1). During the SW monsoon period/wet season, the mean water temperature was 26.9°C, slightly lower than that observed during the post monsoon period (27.9°C). As expected, salinity showed large seasonality with the mean values for the SW monsoon and post monsoon periods being 10.4 and 29.3, respectively. Maximum variation in salinity (16.1) was seen at station S5 between the surface and bottom waters. This is evidently due to the dilution effect on the water column by heavy rainfall and runoff during the SW monsoon that makes the water column vertically stratified, leading to formation of a salt wedge in the estuary (Qasim and Sen Gupta 1981). Salinity distribution at the surface also showed a horizontal gradient from the most downstream station (S1) to the most upstream station (S6) showing a difference of ~ 7 . After the withdrawal of the SW monsoon, the estuary changes from a stratified system to a partially mixed system and its circulation is governed by tides (Shetye et al. 1995). This change is reflected in the salinity distribution, which did not show much difference between the surface and bottom waters (maximum 3.9, with an average of < 2).

During the post monsoon/dry season vertical variation in salinity depends on the tide. Strong tidal currents result in a well-mixed water column, whereas when the tidal currents weaken the magnitude of stratification increases (Shetye et al. 2007b). Tides are thus a dominant factor in controlling estuarine circulation and water column stratification during the post monsoon season, propagating at an average speed of about 6 m s^{-1} from the mouth of estuary to about 50 km upstream (Shetye et al. 1995; Unnikrishnan et al. 1997; Sundar et al. 2005). Observations during the high and low tides carried out during the post monsoon period revealed an increase in temperature by 0.9°C and a decrease in salinity by 5 during low tide. Thus, hydrography of the Mandovi estuary demonstrates typical features of most west coast tropical estuaries such as the Kochi estuary of Kerala state, Narmada and Tapti estuaries of Gujarat state and Mahi estuary in the Maharashtra state.

4.2 Dissolved oxygen (DO)

The estuarine water column was well oxygenated during the periods of the study, especially during the SW monsoon, with an average DO concentration of $233 \pm 38 \mu\text{M}$ ($n=12$). Values during the post monsoon season were slightly lower ($174 \pm 17 \mu\text{M}$, $n=16$) most likely owing to salinity (solubility) effect. Observations made during the high and low tides yielded average DO concentrations of $161 \pm 7 \mu\text{M}$ ($n=16$) and $193 \pm 16 \mu\text{M}$ ($n=16$) respectively, again reflecting the salinity effect. Oxygen saturation did not fall below 70% during the two

seasons. Figure 2a presents a plot of DO versus salinity, which reveals an inverse correlation confirming that, DO is primarily controlled by salinity as reported previously by De Souza and Sen Gupta (1986).

4.3 Nutrients

Nutrient inventories in the estuaries are controlled by supply through runoff, sewage and industrial discharges, and atmospheric deposition (including N₂ fixation), exchanges with sediments and open ocean, and removal through phytoplankton uptake. Processes such as nitrification, denitrification and anaerobic ammonium oxidation (anammox) are important for intrinsic nitrogen cycling with denitrification and anammox responsible for the loss of combined nitrogen, mainly in sediments (Codispoti 1995; Codispoti et al. 2001; Thamdrup and Daalgaard 2002). Variations in nutrients during the two seasons and with the tide during the post-monsoon season are discussed in the following sections.

4.3.1 Nitrate

The average NO₃⁻ concentrations were 9.7±1.5 μM during the SW monsoon and 0.61±0.7 μM during the post monsoon season (Figure 2b). The high NO₃⁻ levels during SW monsoon could be due to several sources viz. atmospheric dry/wet deposition, runoff from agricultural fields and other industrial sources (e.g. mining). Freshwater runoff could play a major role in controlling NO₃⁻ concentrations in the bay area and as ~90% of the total freshwater discharge occurs during the SW monsoon (Suprit and Shankar 2008), thereby concentrations are the highest during this season.

In order to investigate the role of freshwater inputs on NO₃⁻ distribution in the estuary, we plotted NO₃⁻ against salinity (Figure 2b). The plotted data showed a significant inverse relation ($r^2 = 0.79$; $n=60$) strongly indicating that most of the NO₃⁻ is from fresh water runoff during the SW monsoon period. Atmospheric deposition of reactive N is another important pathway that has been greatly enhanced by human activities (Galloway et al. 2004). Our measurements of NO₃⁻ in rainwater in the NIO premises yielded concentrations ranging from 6 to 12 μM. NO₃⁻ measurements carried out during the post monsoon season did not show significant variability with tide; the mean concentrations (± standard deviation, sd) were 2.5±0.2 μM ($n=16$) during high tide and 2.3±0.5 μM ($n=16$) during low tide. NO₃⁻ accounted for the bulk (about 73% on the average) of the dissolved inorganic nitrogen (DIN) load during the SW monsoon season and about 44% during the post monsoon season. This indicates that sedimentary inputs of NH₄⁺ are relatively more important during the non-monsoon seasons. NO₃⁻ concentrations in the Mandovi estuary observed by us (~10 μM), although elevated relative to the post monsoon season, are substantially lower than those reported from other anthropogenically impacted systems. For example, in the Jiaozhou Bay, a shallow subtropical estuary in North China, concentrations up to 40 μM have been reported (Liu et al. 2005). Even higher values, on the order of 100 μM, are encountered in the Mississippi river that feeds the famous “Dead Zone” of the Gulf of Mexico (Dagg et al. 2004). Most of the DIN inputs to the coastal ocean are believed to occur through fertilizer runoff. Employing a model that uses fertilizer consumption as the key input parameter, Seitzinger et al. (2002)

estimated that DIN flux to the North Indian Ocean from the South Asian rivers was 4.2 TgN y^{-1} in 1990. The observed DIN concentrations in the Mandovi estuary are well below those expected from this model.

4.3.2 Nitrite

Unlike NO_3^- the distribution of nitrite (NO_2^-) in the Mandovi estuary does not seem to be controlled by freshwater runoff/precipitation as evident from the plot of NO_2^- versus salinity (Figure 2c; $r^2=0.37$; $n=60$). The mean (\pm sd) NO_2^- concentrations during the SW monsoon and post-monsoon seasons were $0.3\pm 0.3 \mu\text{M}$ ($n=12$) and $0.7\pm 0.3\mu\text{M}$ ($n=16$), respectively. As the water column is well oxygenated in the estuary ($\sim 98\%$ saturation), the main pathway of NO_2^- production is probably assimilatory reduction of NO_3^- by phytoplankton (Naqvi et al. 2006a;b). Thus, the lower NO_2^- during the SW monsoon can be explained by a decrease in assimilatory nitrate reduction by phytoplankton biomass that is considerably lower during SW monsoon compared to post monsoon, as will be discussed in Section 4.5.

During the post-monsoon period, NO_2^- concentration showed marginal variation with the tide with mean values for high and low tide periods being $1.0\pm 0.1 \mu\text{M}$ and $0.8\pm 0.08 \mu\text{M}$, respectively. While rainwater collected in NIO premises contained negligible amounts of NO_2^- ($0.05\text{-}0.08 \mu\text{M}$), it appears that in-situ NO_2^- concentrations in the Mandovi estuary are largely controlled by internal cycling (mostly phytoplankton production) rather than external sources such as precipitation and freshwater runoff. Estimated NO_2^- contribution to the DIN pool during the SW monsoon period was only 2.5% as most of the DIN came along with fresh water as NO_3^- , but during the post-monsoon period, NO_2^- accounted for as much as 48% of the total DIN.

4.3.3 Ammonium

Dissolved NH_4^+ in the estuary exhibited a behavior similar to that of NO_3^- . Plot of NH_4^+ versus salinity (Figure 2d) shows a statistically significant correlation ($r^2=0.78$; $n=60$). Significantly high concentrations of NH_4^+ ($3.3 \pm 1.3 \mu\text{M}$; $n=12$) were observed only during the SW monsoon, indicating that bulk of the NH_4^+ is derived from runoff and precipitation which had NH_4^+ levels ranging from ~ 2 to $9 \mu\text{M}$ (unpublished data). During the post monsoon season, NH_4^+ concentrations were much lower ($0.1\pm 0.1 \mu\text{M}$, $n=16$), being marginally higher during the high tide ($0.2\pm 0.2 \mu\text{M}$, $n=16$) than during the low tide ($0.04\pm 0.07 \mu\text{M}$, $n=16$). NH_4^+ contribution to the DIN pool during the SW monsoon was 25% whereas during the post monsoon season it was only 8%. These results indicate that like NO_3^- , NH_4^+ is also available in excess in the estuary during the SW monsoon, and productivity during this season is not nutrient-limited.

4.3.4 Phosphate

Average PO_4^{3-} concentration observed during the SW monsoon and post monsoon seasons are $0.9 \pm 0.3 \mu\text{M}$ and $0.3 \pm 0.1 \mu\text{M}$ respectively. Plot of PO_4^{3-} versus salinity shows considerable scatter ($r^2=0.45$; $n=60$) when all data are considered (Figure 2d). However, during the SW monsoon period the two parameters

appear to exhibit significant positive correlation ($r^2 = 0.63$; $n=12$) (Figure 2e; broken line), pointing to a marine source. The SW monsoon forces upwelling along the west coast of India, which causes the development of intense water column suboxia over the inner and mid-shelf regions (Banse 1959; 1968; Naqvi et al. 2000; 2006a). Following complete denitrification, PO_4^{-3} concentrations in sub-pycnocline waters reach up to $6 \mu\text{M}$ (Naqvi et al. 2000). While some of the PO_4^{-3} build-up is due to regeneration from organic matter, release from iron-oxyhydroxo-phosphate complex in anoxic waters appears to be another important contributing process (Naqvi et al. 2006a). As this water intrudes into the estuary during the SW monsoon, the DO gets replenished through aeration but the signature of high PO_4^{-3} is retained. PO_4^{-3} concentrations during the high and low tide periods during the post monsoon season did not show much variability ($\sim 0.4\text{-}0.5 \mu\text{M}$) (Figure 2e) due to well mixed nature of estuarine waters.

4.3.5 Silicate

In some estuaries like the sub tropical estuary in Taiwan and the Jiaozhou Bay in North China, silicate is observed to be the limiting nutrient for phytoplankton growth (Jiunn-Tzong et al. 2003; Liu et al. 2005).

Plot of $\text{Si}(\text{OH})_4$ against salinity (Figure 2f) shows an excellent negative correlation ($r^2=0.92$; $n=60$). During the SW monsoon the $\text{Si}(\text{OH})_4$ concentration averaged $86.6 \pm 13.5 \mu\text{M}$ ($n=12$) an order of magnitude higher than the post monsoon levels ($8.2 \pm 2.2 \mu\text{M}$, $n=16$). Some variability in $\text{Si}(\text{OH})_4$ concentrations was associated with tidal changes with the high tide values ($10.3 \pm 1.2 \mu\text{M}$, $n=16$) being lower than those ($16.3 \pm 2.3 \mu\text{M}$, $n=16$) during the low tide. Thus, in contrast to the case of PO_4^{-3} , $\text{Si}(\text{OH})_4$ appears to be supplied by the river runoff.

4.4 Dissolved organic carbon (DOC) and dissolved organic nitrogen (DON)

DOC and DON concentrations did not show any significant seasonal variations. Plots of DOC and DON versus salinity are shown in (Figure 2g and 2h). Mean (\pm sd) DOC concentrations are $81 \pm 23 \mu\text{M}$ ($n=12$) during the SW monsoon and $116 \pm 31 \mu\text{M}$ ($n=16$) during the post monsoon season. The corresponding DON values are $7 \pm 4 \mu\text{M}$ ($n=12$) and $13 \pm 9 \mu\text{M}$ ($n=16$). Although the estuary receives large amounts of organic matter from the surrounding mangrove forests and also municipal wastes, the observed DOC and DON concentrations are not abnormally high even at stations located close to the point of sewage discharge from the city of Panjim. This may be because the organic matter is mostly labile and the high temperature facilitates its rapid decomposition. However, DOC does not appear to be related to the apparent oxygen utilization (AOU) (Figure 2i), which is probably due to shallow water depths that ensure maintenance of well-oxygenated conditions. High inputs of nutrients and terrestrial matter are known to increase DOC concentrations in coastal waters (Kemp et al. 1997). But, DOC concentrations in the Mandovi estuary are much lower than those reported from other anthropogenically-impacted systems. For examples, in another subtropical mangrove-dominated estuary in southwest Florida DOC concentration were found to range from 318 to 2043 μM (Jaffe et al. 2004).

4.5 Chlorophyll-*a*

Phytoplankton biomass as indicated by Chlorophyll-*a* concentration was relatively low during the SW monsoon, with an average of $1.4 \pm 0.6 \text{ mg m}^{-3}$ ($n=12$). During the post monsoon season, the biomass content (mean \pm = $1.6 \pm 0.4 \text{ mg m}^{-3}$, $n=16$) was slightly higher despite lower nutrient levels. Figure 2j, which shows the relationship between chlorophyll and salinity, also reflects low chlorophyll-*a* during the SW monsoon season. Light inhibition due to cloud cover and high water column turbidity resulting from resuspension of fine sedimentary material controls phytoplankton productivity. During SW monsoon the water column turbidity ranged from 19-22 NTU. Plots of dissolved inorganic nitrogen (DIN) vs chlorophyll (Figure 2k) and phosphate vs chlorophyll (Figure 2l) did not show any significant correlation. This shows that primary production in the Mandovi estuary is not limited by either of these macronutrients, contrary to what has been reported from several other estuaries such as the Darwin harbour, Gulf of Papua, Jiaozhou Bay where these nutrients are limiting the productivity (Burford et al. 2008; Davis 2004; Liu et al. 2005; Neill 2005). Primary productivity measurements reported by Pradeep Ram et al (2003) show that there is a seasonal shift in net ecosystem productivity where in the estuarine environment changes from being net heterotrophic to net autotrophic after the cessation of the SW monsoons. They report an integrated primary production as low as $23 \text{ mmol C m}^{-2} \text{ d}^{-1}$ during SW monsoons and $100.4 \text{ mmol C m}^{-2} \text{ d}^{-1}$ during the post monsoon season. This is in agreement with our results where we do not see high Chlorophyll-*a* biomass with increase in nutrient loading.

4.6 Isotopic composition of SPOM ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$)

We also measured isotopic composition ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$) of suspended particulate organic matter (SPOM) in the Mandovi estuary for the first time from a west coast Indian estuary. Hence, it is expected to provide baseline data for further isotopic studies in this region.

Global freshwater and estuarine particulate organic nitrogen has average $\delta^{15}\text{N}$ values of $4.3 \pm 2.7\text{‰}$ and $4.6 \pm 2.0\text{‰}$, respectively (Owens 1987; Kao and Liu 2000). In the Mandovi estuary, the $\delta^{15}\text{N}$ of SPOM showed distinct seasonality. During the SW monsoon and post monsoon seasons the mean $\delta^{15}\text{N}$ values (\pm sd) were $2.4 \pm 0.7\text{‰}$ ($n=7$) and $4.8 \pm 0.7\text{‰}$ ($n=13$), respectively (Figure 3a). The effect of tide on the nitrogen isotopic composition of SPOM was small: $\delta^{15}\text{N}$ of SPOM during the high tide ($3.30 \pm 0.85\text{‰}$, $n=12$) was slightly lower than that ($4.65 \pm 1.25\text{‰}$, $n=14$) during the low tide (Figure 3b). This is in contrary to normal behavior because the concentration of isotopically lighter terrestrial matter should increase during the low tide. At a first glance, the observed lower $\delta^{15}\text{N}$ of SPOM during the SW monsoon season could be ascribed to enhanced inputs of terrestrial organic matter. The terrestrial inputs should also deplete the $\delta^{13}\text{C}$ of SPOM. Indeed, the $\delta^{13}\text{C}$ values also show distinct variation between the two seasons with lower $\delta^{13}\text{C}_{\text{org}}$ ($-24.8 \pm 0.5\text{‰}$, $n=8$) occurring during the SW monsoon as compared to the post monsoon period ($-22.4 \pm 0.4\text{‰}$, $n=14$). However, an additional mechanism of depletion of ^{15}N in SPOM during the SW monsoon could be preferential utilization of $^{14}\text{NO}_3^-$ by phytoplankton, as has been observed in other NO_3^- -replete areas (e.g. Altabet and Francois 1994). This

effect may arise from the aforementioned light limitation of primary productivity. Our data do not allow us to assess the relative importance of the two processes.

The $\delta^{13}\text{C}_{\text{org}}$ of SPOM showed distinct variation with the tide during the post-monsoon season: $\delta^{13}\text{C}_{\text{org}}$ during the high tide ($-22.5 \pm 0.7\text{‰}$, $n=14$) was substantially lower than the corresponding value ($-24.0 \pm 0.15\text{‰}$, $n=15$) during the low tide, consistent with expected inputs of terrestrial carbon. The fact that the mean low-tide value during the post-monsoon period is so close to the mean value during the SW monsoon, suggests that the inputs of terrestrial material through runoff is not excessively large as one would expect for rivers originating in the thickly forested Western Ghats. Intrusion of water with $\delta^{13}\text{C}_{\text{org}}$ of SPOM approaching typically marine values is clearly evident from our data. This is also supported by isotopic data collected during the pre monsoon period (March 2007), which reveal a gradient of $\delta^{13}\text{C}_{\text{org}}$ of SPOM from the estuarine end (-26‰) to the river end (-30‰) (Figure 5). A similar increasing trend is not observed for $\delta^{15}\text{N}$. In agreement with results from other similar environments such as the Chesapeake Bay (Bratton et al., 2003), it appears that while $\delta^{13}\text{C}_{\text{org}}$ of SPOM in the Mandovi estuary is a good proxy for source characterization, while $\delta^{15}\text{N}$ of SPOM seems to be determined by in-situ nitrogen cycling. Plot of $\delta^{13}\text{C}$ vs salinity (Figure 4) gives a good correlation ($r^2=0.6$) providing further evidence to the above statement.

We also measured $\delta^{13}\text{C}_{\text{org}}$ and $\delta^{15}\text{N}$ of effluent from the sewage treatment plant that is disposed into the estuary (Figure 1). The isotopic values ($\delta^{13}\text{C}_{\text{org}}=-24.76\text{‰}$ and $\delta^{15}\text{N}=5.23\text{‰}$) are only slightly different from those observed in the SPOM. However, the absence of any abnormal values of bulk parameters described above in the vicinity of the sewage disposal point indicates that the discharged effluent gets well dispersed and does not leave a discernible imprint.

5. Variability of nutrients from the Mandovi in historical perspective

The available data on nutrients from the Mandovi estuary over the past 36 years are summarized in Table 4. It may be noted that these data do not include DON given that urea is an important nitrogenous nutrient applied to the agricultural fields, absence of these data introduces some uncertainty. Nevertheless, it is obvious that nutrient concentrations have always been high during the SW monsoon with one exception (1999), and while the most recent DIN data is marginally elevated, the increasing trend expected from the large ongoing rise in fertilizer consumption is not seen. This indicates that the Mandovi estuary may have a self-regulating mechanism by which the intrinsic cycling is significantly modulating anthropogenic forcing. While the concentrations of DON in the estuary (which is believed to contribute significantly to phytoplankton productivity, Bronk et al. 2007) are not unusually high, the possibility that levels of both DON in estuarine water and DIN in rainwater have risen significantly cannot be ruled out. There are no previous data on rainwater DIN and seawater DON with which to compare our results, so further time series investigations need to be carried out to ascertain the role of anthropogenic inputs on DON and rain water DIN levels.

6. Summary and Conclusion

The Mandovi estuary exhibits strong seasonality of hydro-chemical changes, dominantly controlled by the SW monsoon precipitation and river runoff, which greatly impacts nutrient and isotopic characteristics. Despite high anthropogenic influence the estuarine environment does not show signs of eutrophication and hypoxia: nutrient levels are only moderately high during the SW monsoon and the waters remain well oxygenated throughout the year. The DON and DOC concentrations in the estuary are also not unusually high.

Phytoplankton biomass in the estuary during the SW monsoon remains well below expectation given copious macronutrients, most likely owing to light limitation of photosynthetic productivity arising from cloud cover and high water column turbidity. It is reasonable to assume that similar conditions also prevail in numerous other estuaries that lie along the west coast of India. One important implication of such a limitation is that nutrients (especially NO_3^-) are exported from the estuaries to coastal waters, promoting primary production and contributing to the formation of seasonal anoxia in the inner and mid-shelf regions. Partial nutrient utilization seems to produce organic matter having lighter $\delta^{15}\text{N}$ values, in addition to the terrestrial supply that also lowers $\delta^{15}\text{N}$ of SPOM. $\delta^{13}\text{C}$ of SPOM can be used as a good proxy for source characterization as there is a clear demarcation between the marine and riverine end members (Figure 4).

Comparison of our measurements with the historical data does not support very large increases in estuarine inorganic macronutrient loads over the past three decades or so. However, it is possible that the fixed nitrogen deposition from the atmosphere and concentrations of DON (including urea, a major fertilizer used in India) in estuarine waters has been rising and these may contribute to the observed intensification of anoxia along the Indian west coast as reported by Naqvi et al. (2000).

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Figure Captions

Figure 1: Area map showing sampling locations in the Mandovi estuary.

Figure 2a: Variations of DO versus salinity during (SW) monsoon- post monsoon and low tide-high tide periods during post monsoon season of year 2007.

Figure 2b: Variations of NO_3^- versus salinity during (SW) monsoon- post monsoon and low tide-high tide periods during post monsoon season of year 2007.

Figure 2c: Variations of NO_2^- versus salinity during (SW) monsoon- post monsoon and low tide-high tide periods during post monsoon season of year 2007.

Figure 2d: Variations of NH_4^+ versus salinity during (SW) monsoon- post monsoon and low tide-high tide periods during post monsoon season of year 2007.

Figure 2e: Variations of PO_4^{3-} versus salinity during (SW) monsoon- post monsoon and low tide-high tide periods during post monsoon season of year 2007.

Figure 2f: Variations of Si(OH)_4 versus salinity during (SW) monsoon- post monsoon and low tide-high tide periods during post monsoon season of year 2007.

Figure 2g: Variations of DOC versus salinity during (SW) monsoon- post monsoon and low tide-high tide periods during post monsoon season of year 2007.

Figure 2h: Variations of DON versus salinity during (SW) monsoon- post monsoon and low tide-high tide periods during post monsoon season of year 2007.

Figure 2i: Variations of DOC versus AOU during (SW) monsoon- post monsoon and low tide-high tide periods during post monsoon season of year 2007.

Figure 2j: Variations of Chlorophyll-a versus salinity during (SW) monsoon- post monsoon and low tide-high tide periods during post monsoon season of year 2007.

Figure 2k: Variations of DIN versus Chlorophyll-a during (SW) monsoon- post monsoon and low tide-high tide periods during post monsoon season of year 2007.

Figure 2l: Variations of PO_4^{3-} versus Chlorophyll-a. during (SW) monsoon- post monsoon and low tide-high tide periods during post monsoon season of year 2007.

Figure 3a: Variations in $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ of SPOM during SW monsoon and post monsoon of year 2007.

Figure 3b: Variations in $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ of SPOM during high tide and low tide year 2007.

Figure 4: Variations of $\delta^{13}\text{C}$ of SPOM versus salinity during (SW) monsoon- post monsoon and low tide-high tide periods during post monsoon season of year 2007.

Figure 5: $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ of SPOM during pre-monsoon season of year 2007 along the Mandovi estuary.

Figure 1

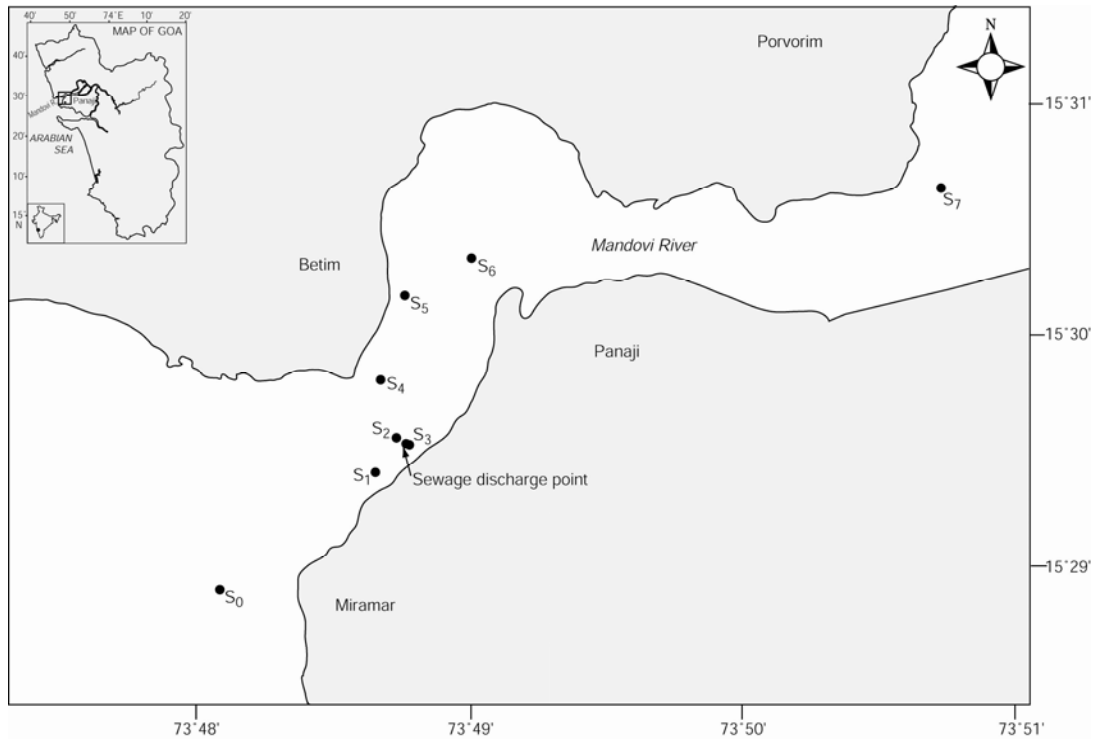


Figure 2

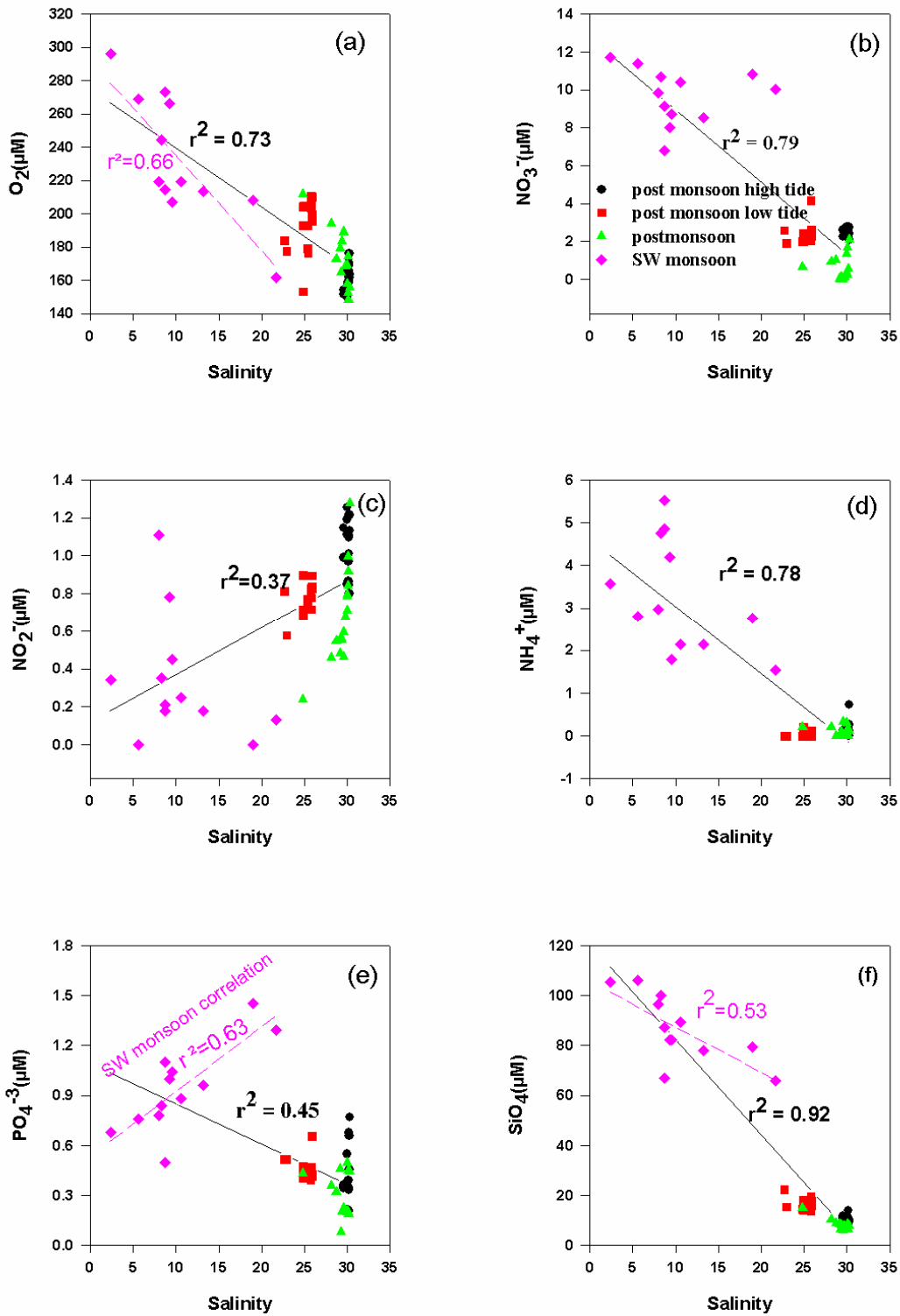


Figure 2

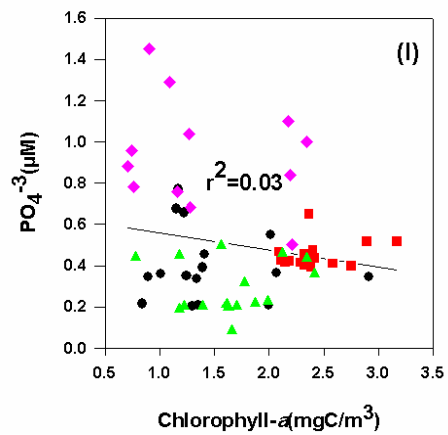
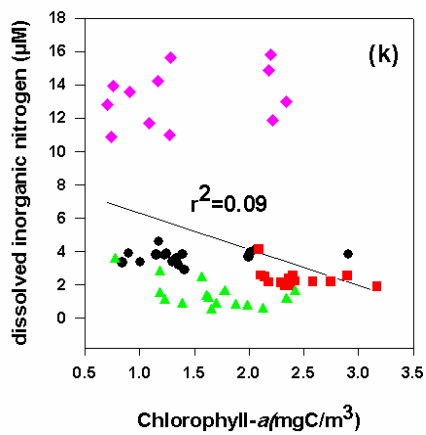
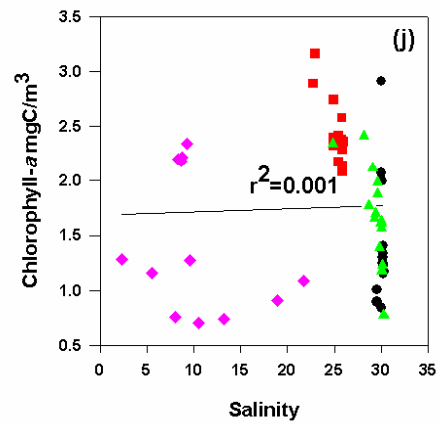
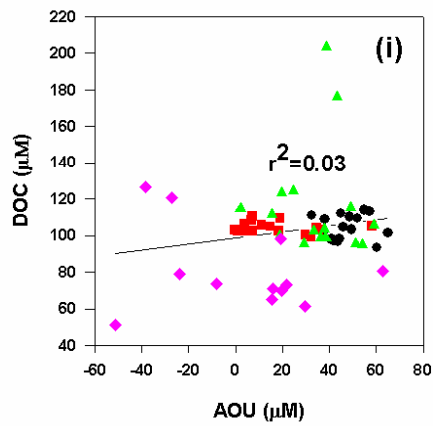
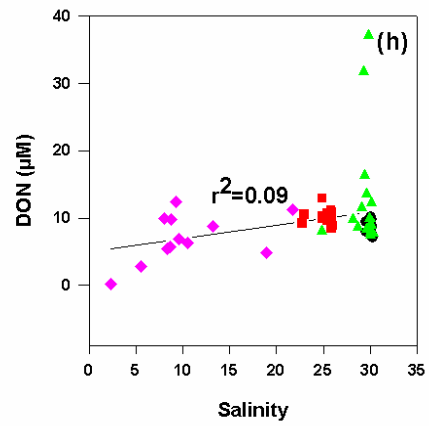
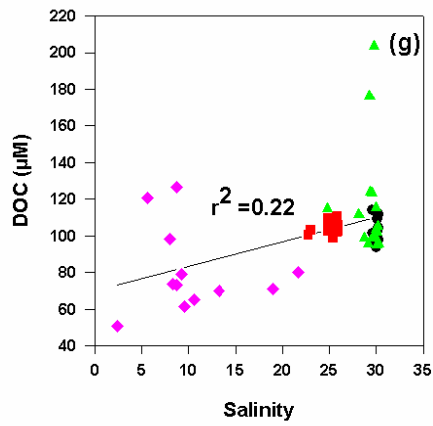


Figure 3

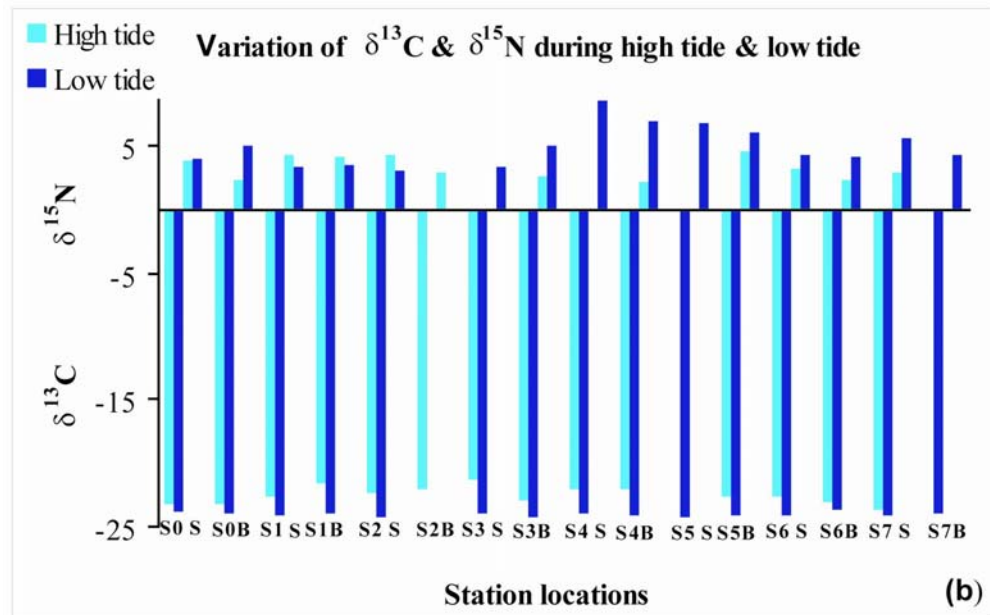
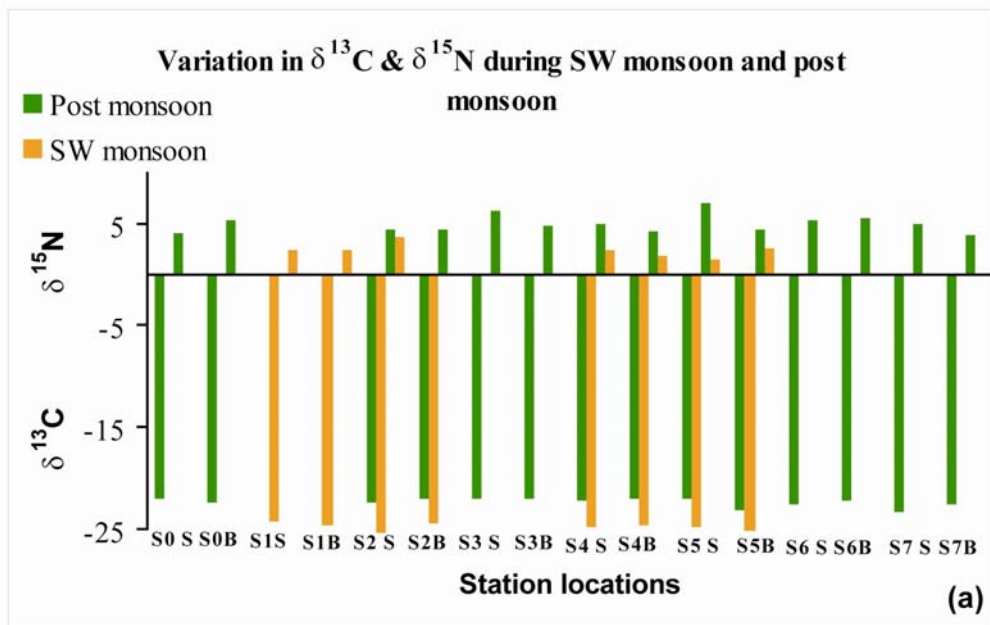


Figure 4

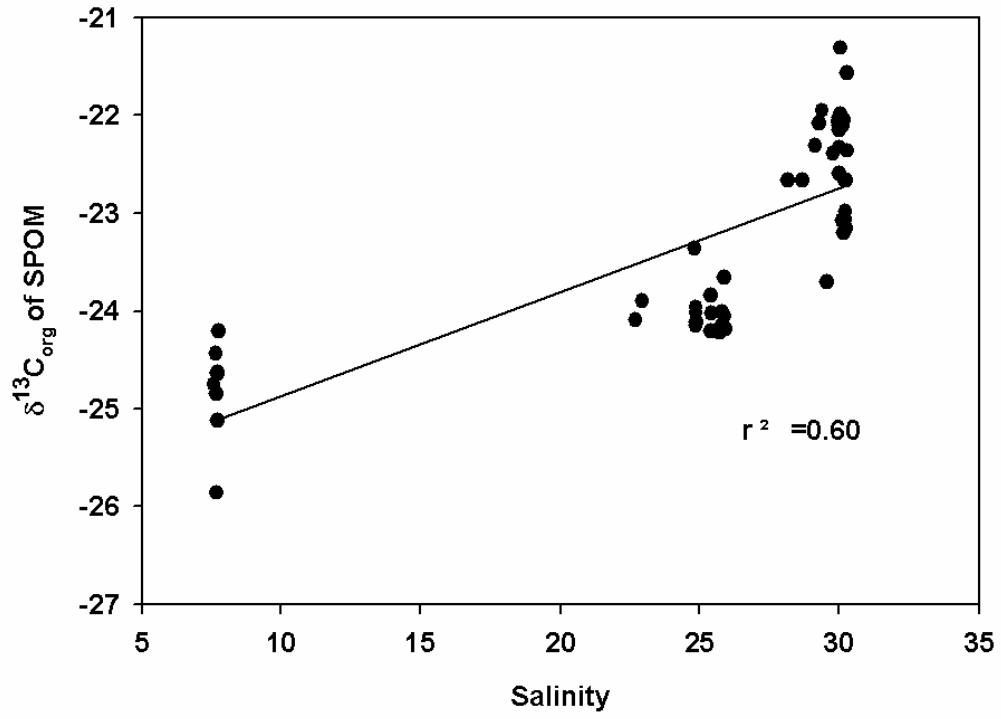


Figure 5

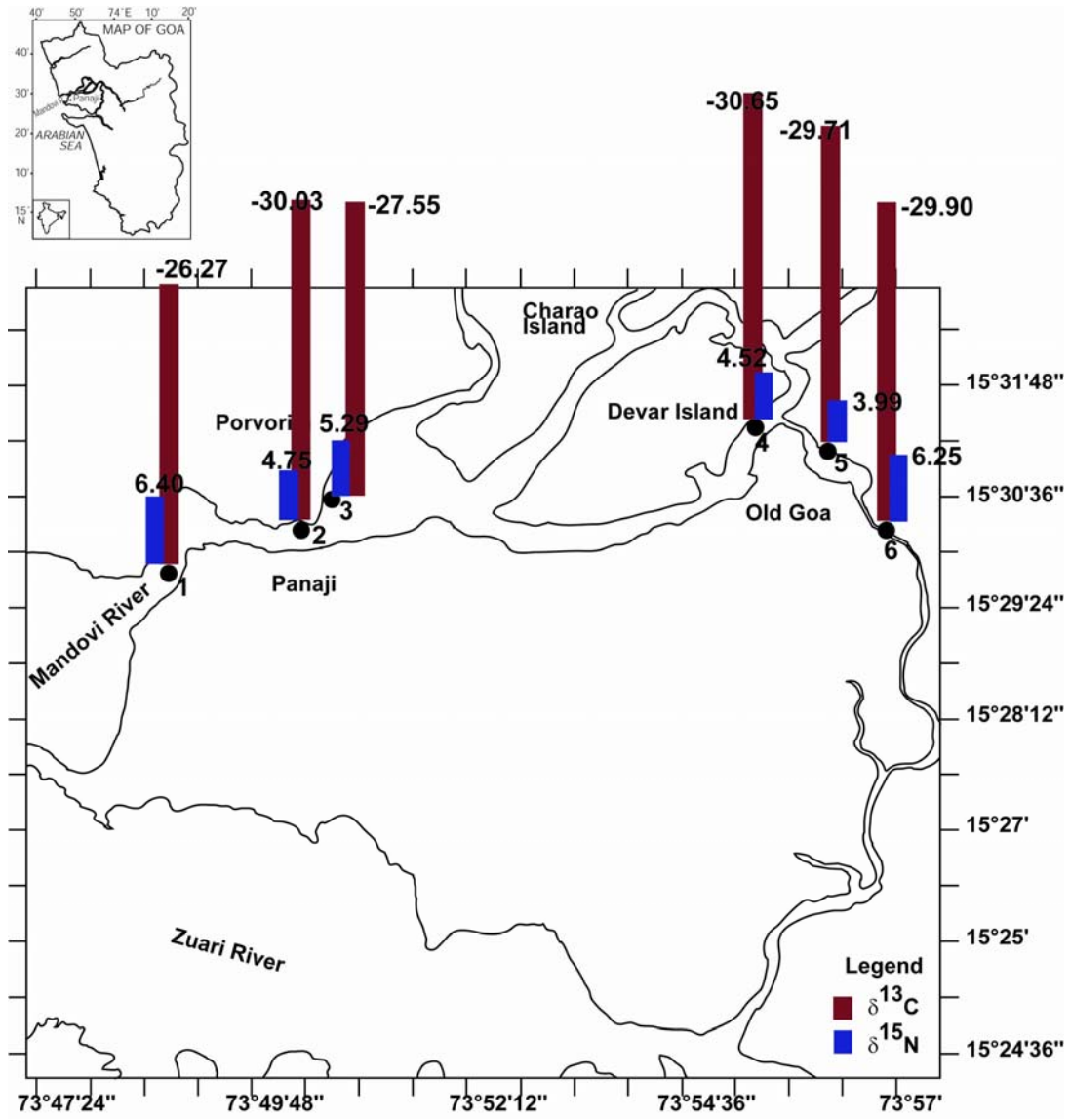


Table 1: *Temperature and salinity data of the Mandovi estuary .*

Station	Season				Tide			
	Monsoon		Post monsoon		High Tide		Low Tide	
	T(°C)	S(psu)	T(°C)	S(psu)	T(°C)	S(psu)	T(°C)	S(psu)
S0 S*	-	-	27.8	30.1	28.0	30.1	28.4	25.4
S0 B*	-	-	27.8	30.3	28.0	30.2	28.5	25.4
S1 S	25.6	9.3	27.8	29.6	27.7	30.0	28.4	24.9
S1 B	26.9	19.0	27.8	29.6	27.7	30.3	28.5	24.9
S2 S	27.6	8.7	28.0	29.8	27.0	30.0	28.4	25.4
S2 B	27.3	8.7	28.0	30.0	27.7	30.0	28.5	25.8
S3 S	27.4	8.3	27.8	29.4	27.1	30.1	28.5	25.8
S3 B	27.0	10.6	27.9	30.0	27.7	30.2	28.4	25.9
S4 S	26.8	9.5	27.9	29.1	27.6	30.0	28.5	24.9
S4 B	26.6	13.2	27.9	30.1	27.6	30.2	28.5	24.9
S5 S	27.0	5.6	28.0	29.3	27.6	30.1	28.5	25.7
S5 B	26.0	21.7	28.0	30.1	27.5	30.2	28.5	25.8
S6 S	27.2	2.3	27.8	28.2	27.7	30.2	28.4	25.9
S6 B	26.9	8.0	28.0	30.0	27.7	30.2	28.5	25.9
S7 S	-	-	27.8	24.8	27.6	29.6	28.6	22.7
S7 B	-	-	27.8	28.7		29.5	28.7	22.9

- 'S' – denotes surface
- 'B'- denotes bottom

Table 2: *Nutrients, DO, DOC, DON and Chlorophyll-a data during monsoon and post monsoon of the Mandovi estuary.*

Station No.	Season																		
	Monsoon									Post Monsoon									
	Nutrients					DO	DOC	DON	Chlorophyll	Nutrients					DO	DOC	DON	Chlorophyll	
	NO ₃	NO ₂	NH ₄	PO ₄	SiO ₄					NO ₃	NO ₂	NH ₄	PO ₄	SiO ₄					
	μM	μM	μM	μM	μM	μM	μM	μM	mg m ⁻³	μM	μM	μM	μM	μM	μM	μM	μM	μM	mg m ⁻³
S0S										1.68	1.00	0.13	0.45	8.67	174	102	8	1.18	
S0B										2.13	1.28	0.14	0.44	8.04	156	96	8	0.78	
S1S	8.02	0.78	4.19	1.00	82.10	266	79	12	2.34	0.00	0.47	0.34	0.22	6.25	189	123	14	1.88	
S1B	10.82	0.00	2.76	1.45	79.47	208	71	5	0.91	0.11	0.59	0.00	0.23	8.11	189	100	8	1.99	
S2S	6.82	0.18	4.86	0.50	66.88	273	127	10	2.21	0.14	0.68	0.00	0.20	6.95	168	203	37	1.39	
S2B	9.16	0.21	5.52	1.10	87.31	214	73	6	2.18	0.40	0.80	0.12	0.21	7.79	158	116	10	1.61	
S3S	10.69	0.35	4.76	0.84	100.05	244	74	5	2.20	0.17	0.55	0.12	0.20	8.26	184	124	16	1.70	
S3B	10.42	0.25	2.15	0.88	89.21	219	65	6	0.70	0.29	0.79	0.11	0.20	6.75	169	99	9	1.63	
S4S	8.74	0.45	1.79	1.04	82.34	207	61	7	1.27	0.04	0.48	0.00	0.46	8.74	179	96	12	2.12	
S4B	8.55	0.18	2.15	0.96	78.11	213	70	9	0.74	0.57	0.92	0.00	0.19	6.64	148	106	12	1.18	
S5S	11.40	0.00	2.81	0.76	106.20	269	121	3	1.16	0.00	0.57	0.00	0.08	6.64	165	176	32	1.66	
S5B	10.01	0.13	1.53	1.29	65.94	162	80	11	1.09	0.24	0.84	0.00	0.20	6.37	153	95	9	1.23	
S6S	11.71	0.34	3.58	0.68	105.33	296	51	0	1.28	0.92	0.46	0.21	0.36	10.36	194	112	10	2.42	
S6B	9.84	1.11	2.97	0.78	96.36	219	98	10	0.76	1.37	0.71	0.31	0.50	7.20	169	104	8	1.57	
S7S										0.66	0.24	0.22	0.44	15.04	212	115	8	2.34	
S7B										1.03	0.55	0.00	0.32	9.12	173	99	9	1.78	

Table 3: *Nutrients,DO,DOC,DON and Chlorophyll-a data during high tide and low tide of post monsson.*

Station No.	Tide																	
	High Tide									Low Tide								
	Nutrients					DO	DOC	DON	Chlorophyll	Nutrients					DO	DOC	DON	Chlorophyll
NO ₃	NO ₂	NH ₄	PO ₄	SiO ₄					NO ₃	NO ₂	NH ₄	PO ₄	SiO ₄					
μM	μM	μM	μM	μM	μM	μM	μM	μM	mg m ⁻³	μM	μM	μM	μM	μM	μM	μM	μM	mg m ⁻³
S0S	2.70	0.97	0.16	0.39	13.91	169	109	9	1.39	2.19	0.77	0.00	0.42	15.72	179	99	10	2.18
S0B	2.41	1.21	0.14	0.66	9.24	162	112	8	1.23	2.17	0.77	0.00	0.46	15.33	176	104	11	2.32
S1S	2.59	1.11	0.13	0.35	10.41	167	98	8	2.91	2.44	0.90	0.11	0.48	18.11	193	110	10	2.40
S1B	2.74	1.13	0.73	0.77	9.28	163	98	7	1.17	1.99	0.71	0.00	0.45	14.43	153	105	13	2.38
S2S	2.75	1.26	0.12	0.36	10.00	150	94	7	2.07	2.23	0.73	0.00	0.44	14.34	193	103	10	2.42
S2B	2.64	1.19	0.12	0.55	9.89	151	113	9	2.01	2.20	0.83	0.00	0.41	15.74	203	111	11	2.58
S3S	2.44	1.13	0.11	0.21	10.21	158	109	10	2.00	2.04	0.78	0.11	0.42	13.89	211	103	10	2.29
S3B	2.44	1.10	0.27	0.68	10.14	166	97	7	1.15	2.29	0.84	0.12	0.65	15.87	199	106	9	2.36
S4S	2.35	0.85	0.12	0.21	9.44	165	97	8	0.84	2.00	0.68	0.00	0.41	14.27	204	103	10	2.32
S4B	2.42	0.85	0.11	0.20	9.57	170	102	9	1.30	1.98	0.72	0.22	0.40	14.99	205	109	10	2.75
S5S	2.35	0.86	0.00	0.21	10.03	159	103	9	1.35	2.20	0.80	0.00	0.39	15.76	206	102	10	2.38
S5B	2.09	0.80	0.00	0.45	9.42	176	111	10	1.41	4.15	0.72	0.00	0.47	19.69	207	107	9	2.09
S6S	2.63	1.11	0.11	0.35	11.00	159	110	9	1.24	2.60	0.82	0.00	0.43	17.84	210	103	10	2.11
S6B	2.42	1.01	0.12	0.33	9.42	162	105	8	1.34	2.52	0.89	0.00	0.42	17.34	195	105	11	2.14
S7S	2.60	1.15	0.12	0.35	11.81	154	114	9	0.90	2.58	0.81	0.00	0.52	22.44	184	101	9	2.89
S7B	2.25	0.99	0.11	0.36	10.91	151	102	8	1.01	1.91	0.58	0.00	0.52	15.42	178	103	11	3.17

Table 4: Nutrient data of the Mandovi estuary in realm of historical nutrient data.

Year	NO ₃ ⁻ (μM)	NO ₂ ⁻ (μM)	NH ₄ ⁺ (μM)	PO ₄ ³⁻ (μM)	Si(OH) ₄ (μM)	Reference
1971 monsoon	-	-	-	0.2-2.6	-	Dwivedi et al. (1974)
1972 monsoon	-	-	-	0.3-1.9	-	Sankaranarayanan et al. (1978)
1978 monsoon	6-11	-	-	0.4-2.5	90-150	Qasim and Sen Gupta (1981)
post monsoon	>2	-	-	0.7	>10	
1981 monsoon	7.3-9.8	-	-	0-0.5	62-138	De Souza ,S.N. (1983)
1996 post monsoon	0.2-0.4	0.1-0.2	0.8-2	0.1-0.3	-	COMAPS (1996)
1999 monsoon	0-1.3	0.02-0.07	0.4-11.5	0.1-0.8	-	Technical report (2000)
post monsoon	0-0.3	0.02-0.13	0.06-13.2	0.1-0.3	-	
2002 monsoon	>7	-	-	>1	-	Sardessai and Sundar (2007)
2002 post monsoon	0.08-1.3	0.4-0.6	-	0.05-0.8	2.7-9.6	COMAPS (2002)
2007 monsoon	7-12	0-1	1.5-5.5	0.5-1.5	66-106	Present study
post monsoon	0-4.15	0.24-1.3	0.08-0.5	0-0.7	6-16	