

Intra and inter seasonal variability of nutrients in a tropical monsoonal estuary (Zuari, India)

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Abstract

A study was conducted to understand the intra- and inter- seasonal variability of dissolved oxygen and nutrients in a tropical monsoon estuary (Zuari in Goa, India). We adopted a dual sampling approach with (a) daily or alternate day sampling at a fixed location in the mid estuarine zone and (b) longitudinal transect sampling from freshwater end to mouth during spring and neap tides of each month for about a year. Multivariate statistical analyses of oxygen and nutrients were carried out to evaluate the hypotheses (i) biogeochemical processes chiefly regulate their variability and (ii) anthropogenic inputs lead to material accumulation in the estuary. Multivariate statistical analyses helped identify the controlling factors of the oxygen and nutrient variability. Our results significantly revealed (i) physical forcings (freshwater discharge and tidal circulation, these also facilitate sedimentary releases) are more important than biogeochemical processes in determining oxygen and nutrient variability in the water column and (ii) the monsoon driven regular annual flushing makes the system resilient to human interference as the Zuari estuary returns to normalcy by postmonsoon every year. Our study identified the significance of subsurface discharges in transporting mining effluents from the river basin. Results also suggest that extrapolation of controlling factors of biogeochemical variables at a fixed location to the entire estuary is untenable since the relative dominance of forcings vary in time and space in the estuary.

Keywords: Zuari, nutrients, oxygen, monsoon, rainfall, resilience, nitrite maxima, controlling factors, tidal circulation

1. Introduction

When two natural waters of completely different compositions mix they create a unique environment - estuaries are one such unique ecosystems where fresh water from river mixes with rhythmically intruding seawater. Estuaries are major nutrient suppliers to coastal oceans, breeding grounds for marine organisms, nursery for juveniles and a potential fishery habitat. Sources of substances found in estuaries are land, river, ground water, sediments, sea, atmosphere and pollution. The materials undergo various biogeochemical transformations in the estuary before they are input into the sea. The extent of estuarine inputs of water, nutrients, organic material and sediments to the coastal ocean is determined by (i) geographic location and type of estuary (Edwards, 1973; Webb and Walling, 1985), (ii) the changes in the quantum of freshwater discharge (Schubel and Pritchard, 1986), (iii) tides (Griffiths, 1987; Balls, 1994) and (iv) processes occurring in the estuary (Billen et al., 1985; Froelich, 1988).

Indian subcontinent has a number of rivers draining into the Bay of Bengal and the Arabian Sea. These rivers are fed by melting of snow and monsoon rainfall. Rivers that originate in Himalayan mountain range have snow caps as source whereas the peninsular rivers are mostly fed by South West Monsoon (summer monsoon). Majority of the peninsular rivers originate in the western mountain range of India, known as the Western Ghats. This region receives maximal rainfall during the summer monsoon (June to September) that leads to peak river discharges (Shetye et al., 2007) and hence these rivers are referred as monsoon rivers. Monsoonal estuaries are highly unique in that they do not reach steady state at any time unlike the temperate estuarine systems (Vijith et al., 2009).

Zuari is a river flowing westward in Goa and is a part of the Mandovi-Zuari estuarine system (Fig. 1). It travels 70 km from the Western Ghats before reaching the Arabian Sea (Qasim and Sen Gupta, 1981). The Zuari estuary is completely flushed with freshwater during summer monsoon but remains a mere extension of the sea during non-monsoon months (Qasim and Sen Gupta, 1981; Vijith et al., 2009). There have been several studies (Dehadrai, 1969; DeSousa et al., 1981; Qasim and Sen Gupta, 1981; DeSousa, 1983; DeSousa and Sen Gupta, 1986; DeSousa, 1999; Ram et al., 2003; Sardessai and Sundar, 2007) on the Mandovi-Zuari estuarine complex in Goa but all are based on limited number of observations in space and time. With the classical notion of once a season (representing 3-4 months) transect sampling in an estuary it is not possible to understand the intra-seasonal variability. This is particularly important for monsoonal estuaries since breaks in monsoon rainfall do occur. More over, dissolved oxygen and nutrients have been studied in relation to biological and pollution aspects but no attempt has been made to understand the factors regulating their abundances

and distributions in the estuaries. In the present attempt dissolved oxygen and nutrient variability in Zuari estuary have been studied for a year through a high resolution sampling strategy (comprising daily or alternate day measurements at a fixed location in the mid-estuary region and a transect along the estuary during spring and neap tides every month). While aiming to understand (i) the intra and inter-seasonal variability of dissolved oxygen and nutrients, (ii) the relations among these properties (correlations) and (iii) factors regulating their levels and distributions (through Factor and Cluster statistical analyses) we attempted to test the hypotheses that (a) biogeochemical processes significantly modulate and control oxygen and nutrient distributions in the estuary and (b) nutrients anthropogenically discharged might remain (memory effect) and accumulate in estuarine waters. In this study the winter monsoon period (November-February) was considered as a part of the dry period (October-May) that comprises post- (October-January) and pre- (February-May) monsoon seasons.

2. Material and Methods

2.1 Study Area

Zuari covers the area between 14° 54' – 15° 30'N and 73° 44' – 74° 20'E (Fig. 1). The catchment area (calculated by using Globe Digital Elevation Model (DEM)) of the Zuari basin is nearly 1152 km² (Shetye et al., 2007). Width of the estuary increases from 0.05 km at the head to 5 km at the mouth. In the upstream region Uguem and Guloli rivulets join to form Sanguem. River Kushawathi joins Sanguem 4 km downstream from Sanvordem. These distributaries drain into the Zuari estuary. Zuari and Mandovi estuaries are joined by the Cumbarjua Canal 10 km from the mouth of Zuari estuary (Qasim and Sen Gupta, 1981; Shetye et al., 2007). The region receives maximal rainfall in the southwest monsoon at a seasonal average of 3000 mm y⁻¹. However, this region experiences active (period of intense spell of rain) and break (break in rainfall for a considerable number of days) phases of monsoon. Nearly 80% of the annual rainfall occurs during the active phase. The average annual runoff measured over the period 1981-1998 (before the Selaulim Dam was built), at the confluence of the Cumbarjua Canal, where it opens into Mormugao Bay (at 10 km upstream from Zuari mouth), is estimated to be about 2190x10⁶ m³. At present, the runoff (of 491x10⁶ m³; as reported in Shetye et al. (2007) by obtaining information from the Water Resources Department, Government of Goa) at the head of the estuary is partially controlled by Selaulim Dam on the Guloli river in monsoon (Fig. 1). The dam reservoir has a total storage capacity of 227x10⁶ m³. While this dam regulates discharge during dry period (post and premonsoon seasons) it is practically ineffective

during the summer monsoon; during active phases of monsoon the uncontrollable runoff spills over the dam. Therefore, the effect of dam on the discharge during monsoon is meagre.

In Goa, 52% of monsoon rainfall accounts for surface runoff while 16% for charging the ground water (Ghosh, 1985). Ground water discharge into estuary from the laterite laden terrain of Goa could be significant in the non-monsoon seasons. Laterite rock structures are known to contain water reservoirs in them that sustain several springs in Goa (Chachadi, 2009). Effluence of the leaky laterites has been found to sustain high discharges from rivers and tributaries of Goa all along their course, specifically in postmonsoon season (Subramaniam, 1981). Therefore, fresh water discharges from Selaulim dam (Shetye et al., 2007) and through subsurface flow (Subramaniam, 1981) could be expected into the Zuari estuarine system in dry seasons. In summer monsoon, when runoff is high in active phases, the estuary is completely filled with freshwater. When runoff is low (during onset, break phase or retreating phases of monsoon rain) the estuary becomes stratified; when seawater flows-in at the bottom and freshwater flows-out at the surface (salt-wedge circulation). After the monsoon the minimal freshwater inflow and tides facilitate well mixed water column. The effect of tides is found to reach upto Sanguem and even to 4 km upstream of Uguem (Shetye et al., 1999). Hence, in dry seasons the estuary transforms to an extended body of the sea.

2.2 Sampling Strategies

We have adopted a high resolution sampling strategy with a dual approach under ZUari MONsoon EXperiment (ZUMONEX). In the first, a location (Station 6, identified with a star in Fig. 1) in the middle of the estuary was regularly sampled at a fixed time (1100 hrs) for eleven months from 1 August 2008 to 24 June 2009. The sampling was done daily during monsoon but on alternate days during non-monsoon months. The above location was selected because it experiences maximal salinity variations in a year and also influenced by tides. The time of 1100 hrs was opted to maintain near uniform sunshine to enable day-to-day comparison. Our subsequent check on solar intensity variation at 1100 hrs everyday of the study period, measured at NIO, confirmed our assumption of near uniform intensity except for some days during monsoon due to cloud cover (Fig. 2). However, despite minor changes in solar intensity on some days of this study intra and inter seasonal variability in properties could be resolved since we have studied this location for 221 days in year. In the second strategy, longitudinal estuarine sampling was done from freshwater end to mouth at 10 locations along a transect (Fig. 1); twice in each monthly tidal cycle covering peak spring and neap tides from June 2008 to June 2009. Station details are furnished in Table 1. A total of 26 transect observations were made as detailed in Table 2. Only in monsoon season, due to rough weather conditions, a few

stations in the upstream (1 to 3) and mouth (10) regions could not be accessed (Table 2). Before 1 August 2008, station 6 was sampled only during the transect observations.

2.3 Sample collection and analyses

The daily rainfall data were obtained from the Indian Meteorological Department in Goa. Tide height (sea level) was measured by our institute using a tide gauge placed at Verem on the banks of the adjoining Mandovi estuary (Fig. 1). Tide height was measured at 5 minutes intervals. Solar intensity was measured using an automated weather station placed on the terrace of our institute (Fig.1). Real time measurements were made at 10 minutes intervals. For the present study, tide height and solar radiation data only of 1100 hrs, coinciding with fixed station (station 6) observations, were used. Vertical profiles of salinity, temperature and depth were obtained from Conductivity Temperature-Depth system (CTD; SBE 19 plus, Sea-Bird Electronics, USA). Salinity was computed from the conductivity through a built-in program in the system. Surface samples using a 5 l Niskin sampler, during daily (monsoon) or alternate day (post and premonsoon seasons) sampling, and both surface and bottom waters during transect sampling were collected for dissolved oxygen and dissolved inorganic nutrients (nitrate, nitrite, phosphate and silicate). Dissolved oxygen samples were sub-sampled into glass bottles while nutrient samples were collected in plastic containers and stored in an ice-box until reaching the laboratory. 2 l of the water was sub-sampled in separate containers for pigments only during select transect studies (23 October, 14 and 21 November, 14 and 19 December of 2008, and 12 January 2009). Sampling was done only at surface at station 6 with a focus on short-term variability. Both surface and bottom samples were collected during transect sampling to understand the longitudinal intrusion of salinity and the influence of lunar tides. Daily and alternate day samples were analyzed immediately after reaching the laboratory and transect samples within 48 hours of collection. Dissolved oxygen was analyzed by the Winkler method (Grasshoff et al., 1983), and nitrate, nitrite, phosphate and silicate were analyzed manually following the methods of Grasshoff et al. (1983). Errors in analyses in terms of standard deviations of replicates of samples were found to be ± 4 , ± 0.1 , ± 0.04 , ± 0.08 , and ± 0.4 μM , respectively. Percent oxygen saturation was calculated after estimating its saturation according to the formulation (shown below) given by Garcia and Gordon (1992) that uses measured temperature (T), salinity (S) and oxygen concentrations

$$\ln C_o^* = A_0 + A_1 T_S + A_2 T_S^2 + A_3 T_S^3 + A_4 T_S^4 + A_5 T_S^5 + S(B_0 + B_1 T_S + B_2 T_S^2 + B_3 T_S^3) + C_0 S^2$$

The constants A_0 to A_5 and B_0 to B_3 were obtained from Garcia and Gordon (1992). Data processing was done with Microsoft Office Excel software.

Seawater samples (1 l) were filtered through GF/F filters and analysed by HPLC for pigments (Wright et al., 1991; Bidigare and Charles, 2002). Prior to the HPLC analysis, the filters were immersed in 90 % acetone, extracted under cold and dark conditions overnight, sonicated and finally filtered through 0.2 μm (13 mm PTFE) filters. Aliquots of 1 ml of the pigment extract were then mixed with 0.3 ml of distilled water in a 2 ml amber vial and allowed to equilibrate for 5 minutes prior to injection into an HPLC (Agilent® 1100 series) equipped with a diode array detector. Pigments were separated using a C-18 reverse-phase column and the eluent gradient program of Wright et al. (1991) as adapted by Bidigare and Charles (2002) and detailed in Parab et al. (2006). Chlorophyll a and Pheophytin a were detected by their absorbance at 436 nm and identified by comparison with the retention times of standard pigments obtained from DHI® Water and Environment, Denmark.

2.4 Statistical Analyses

To understand the relationships among hydrological, physical and chemical properties multivariate statistical analysis (Correlation Analysis, Factor Analysis and Cluster Analysis) was carried out for fixed location (mid-estuary) and transect (total estuary) datasets separately by using SPSS statistical package (Windows Ver. 16). To check the suitability of our data sets for factor analysis, the entire data set was tested for KMO-A and Bartlett's test and the values are given in Table 3. Computations revealed KMO-A values to be higher than 0.5 in all seasons, except for transect observations in premonsoon season, for the large data sets we collected. Bartlett's significance was close to nil for all the seasons (Table 3). These results (KMO-A>0.5 and Bartlett's significance<0.05) confirmed the suitability of our seasonal data for Factor analysis. Another check for the suitability was carried out through Spearman's (not-normally distributed data) and Pearson's (normally distributed data) correlation tests. The correlation coefficients between the two (*Supplementary Table 1*) showed good agreement, in general, which confirms that our results of statistical analyses are reliable and sound. Factor analysis was then performed using R-mode to understand the factors controlling the observed variability in properties. The factors thus obtained were rotated using varimax rotation method to obtain the influence of variables on each factor. Data was standardized (to remove the differences in scales) and Hierarchical Cluster Analysis (HCA) was then performed to group the variables based on the clusters formed.

3. Results and Discussion

This section deals with the variability in properties (levels and distributions), relations (statistical) among them and factors controlling (Factor and Cluster analyses) their variability. Distribution and processes in the middle of the estuary (as observed at a fixed location, Station 6) have been dealt with first (Section 3.1) and those in the entire estuary (based on transect observations) in the second (Section 3.2).

3.1 Micro-scale variations and processes at a fixed location (Station 6) in the middle of the estuary

Daily and/or alternate day variability in properties at station 6 reflects changes due to physical and biogeochemical processes in the middle of the estuary. Variability of hydrological, physical and chemical properties at station 6 is shown in Fig. 2. Table 4 lists limits of variability observed in different seasons. The magnitudes of changes in daily, weekly and seasonal averages \pm SD (standard deviation) are shown in *Supplementary Table 2*.

3.1.1 Intra and Inter seasonal variability

3.1.1.1 Monsoon

Summer monsoon rainfall started early in June and continued till September 2008 (Fig. 2) and ranged from 0 to 169 mm d⁻¹ (Table 4). Thereafter the rain was rare until June 2009. Rainfall in summer monsoon 2008 occurred in three significant spells. The first was at the beginning (early June) of the monsoon period, the second in August and the last in September towards the end of monsoon (Fig. 2). Precipitation occurred at an average of 25 \pm 32 mm d⁻¹ (Table 4, see also *Supplementary Table 2*). Salinity variations at this location (Fig. 2) were largely governed by rainfall and the consequent discharges. Maximum variation was found during this season (0.04-33.06; Table 4). First spell of rain in June decreased the salinity from 33.06 to 4.55. The second spell in August brought down the salinity to near zero (0.04) levels. The breaks (lull periods) in rainfall during the first half of July and second half of August resulted in mid-monsoon salinity maxima as the seawater ingress occurred due to reduction in river discharge. Occupying one location facilitates the estimation of daily, weekly and seasonal variability in water column properties (*Supplementary Table 2*). With the data obtained in this study we estimated a mean \pm SD in daily salinity variability of 21.5 \pm 11.0. Its average weekly variability in a year ranged between 0.12 and 34.02 while the SD ranged from 0.2 to 7.9. The maximal variability (0.1 to 28.4 with SD from 0.2 to 7.9) in weekly averages occurred in summer monsoon seem to nearly account for the total weekly average

variability in a year. This trend agrees well with seasonal average \pm SD of 11.0 ± 9.2 , which is significantly lower than that of other seasons (Table 4). Surface water temperature (Fig. 2) varied significantly during the study period. Two periods of low temperature were found; one in August (with a minimum of 25.29°C) and the other in December/January (minimum of 26.73°C) coinciding with the summer and winter monsoons. Weekly average temperatures range was $25.9\text{-}31.88^{\circ}\text{C}$ (SD of $0.1\text{-}6.4^{\circ}\text{C}$) during the year. Seasonal average water temperature (Table 4) was cooler in summer monsoon ($28.0\pm 1.1^{\circ}\text{C}$) due to maximal rainfall and low air temperature aided by cloud coverage. Three dips in temperature occurred in monsoon 2008 in association with peaks in rainfall. The daily temperature variability in the year averaged to $29.0\pm 1.6^{\circ}\text{C}$ (*Supplementary Table 2*). Dissolved oxygen was high during August that coincided with high rainfall and low temperature. Like salinity, maximal change in dissolved oxygen ($100\text{-}246\ \mu\text{M}$) occurred during monsoon with a seasonal mean \pm SD of 191 ± 15 . The maximum value was associated with the peak in rainfall whereas the lowest value occurred during a lull period. Seasonally averaged dissolved oxygen in monsoon was more than the daily average ($171\pm 26\ \mu\text{M}$). Weekly averaged oxygen concentrations in monsoon ranged from 148 to $221\ \mu\text{M}$ (with SDs from $20\text{-}46\ \mu\text{M}$) that nearly accounted for those in a year (137 to $221\ \mu\text{M}$ and $3\text{-}46\ \mu\text{M}$, respectively). Oxygen saturation followed the same trend as in dissolved oxygen abundance. Fig. 2 reveals that during summer monsoon oxygen is undersaturated following its near saturation in August 2008. Ram et al. (2003) found the occurrence of net heterotrophy in the Mandovi-zuari estuarine system. Similar findings were also made by Thottathil et al. (2008) in Cochin estuary and by Sarma et al. (2009) in Godavari estuary. Net heterotrophy indicates dominance of respiration, in which bacterial decomposition of organic materials occur, over primary production. Bacterial respiration can be supported by dissolved and particulate organic materials supplied by river discharge (Sarma et al., 2009) or produced within the system. Estuaries of Goa are surrounded by wetland systems rich in mangroves. These systems lie mostly within the inter-tidal zones and hence significant quantities of organic materials can be drawn into estuarine waters by tides. The net heterotrophy supported by these organic materials (Ram et al., 2003) also contributed to pCO_2 supersaturation in the Mandovi-Zuari estuarine System besides the proton-exchange proposed by Sarma et al. (2001). Moreover, sediment resuspension or upward diffusion of interstitial waters due to tidal activity can lead to mixing of oxygen deficient pore fluids with overlying water that result in net oxygen undersaturation.

Dissolved inorganic nutrients (nitrate, phosphate and silicate; Fig. 2) peaked during monsoon except nitrite. Nutrient peaks were consistent with highs in rainfall and lows in salinity (Fig. 2). Average values of nutrients with minimum and maximum is shown in Table 4. Averages of nitrate, phosphate

and silicate in monsoon ($7.5 \pm 4.1 \mu\text{M}$, $1.50 \pm 0.80 \mu\text{M}$ and $80.0 \pm 33.0 \mu\text{M}$, respectively) were higher ($4.4 \pm 4.1 \mu\text{M}$, $1.21 \pm 0.57 \mu\text{M}$ and $43.2 \pm 30.4 \mu\text{M}$, respectively) than annual averages at station 6. Weekly averages (*Supplementary Table 2*) in the year ranged 0.29 - $13.08 \mu\text{M}$, 0.68 - $2.56 \mu\text{M}$ and 17.4 - $110.2 \mu\text{M}$, respectively, for nitrate, phosphate and silicate that primarily accounted by weekly average variability in monsoon (0.78 - $13.1 \mu\text{M}$, 0.68 - $2.56 \mu\text{M}$ and 25.3 - $110.2 \mu\text{M}$, respectively). This is also true for the respective standard deviations (annual: 0.1 - $7.5 \mu\text{M}$, 0.05 - $1.12 \mu\text{M}$ and 0.9 - $23.9 \mu\text{M}$ and monsoon: 3.1 - $7.5 \mu\text{M}$, 0.08 - $0.83 \mu\text{M}$ and 5.1 - $23.9 \mu\text{M}$) The values found here are comparable to those reported by Dehadrai (1969), DeSousa et al. (1981), DeSousa (1983, 1999), DeSousa and Sen Gupta (1986), and Sardessai and Sundar (2007) in the Mandovi-Zuari estuarine complex. Nitrate and silicate concentrations at station 6 exhibited sharp increases at the beginning of active rainfall events but gradual decreases at the end phase of the spell. Nitrate showed broad peaks with two dips occurring around the end of August and September. Nitrate reached a maximum of $14.6 \mu\text{M}$. In contrast to nitrate, nitrite showed no peaks during 2008 monsoon but in the early stages of 2009 monsoon. The average nitrite was found to be $0.34 \pm 0.4 \mu\text{M}$ in monsoon, which is much lower than the annual average ($1.89 \pm 2.35 \mu\text{M}$) at station 6 (Table 4 and *Supplementary Table 2*). Unlike nitrate and silicate, phosphate trends are not clear. Although the maximal phosphate levels were found in and at the end of monsoon (highest of $3.60 \mu\text{M}$ occurred during September rain event) its relation with rainfall is unclear. Phosphate levels seem to follow sea level changes (Fig. 2). Maximal values in phosphate were associated with the highest high tide and low values with lowest low tide. Silicate showed two broad peaks in monsoon. The first peak extended from early August to mid-August while the second extended from early to late September. The broadness of the peaks coincided with low saline and high rainfall waters. Maximal value was recorded as $125 \mu\text{M}$ and average $80 \pm 33 \mu\text{M}$. The values are comparable with the previous results in Zuari (Dehadrai, 1969; DeSousa et al., 1981; Singbal, 1981; DeSousa and Sen Gupta, 1986; Sardessai and Sundar, 2007;) and in other Indian estuaries (Sarma et al., 2009; Sarma et al., 2010; Martin, 2008; Devi et al., 1983; Pradhan et al., 2009; Upadhyay, 1988; Sen Gupta and Upadhyay, 1987; Sadharam et al., 2005) as well.

3.1.1.2 Postmonsoon

Early researchers referred this period as the recovery period of the estuary. The changes brought about by monsoon are reverted to normal seawater dominated conditions. The rainfall recorded a seasonal average value of mere $0.6 \pm 3 \text{ mm d}^{-1}$. Unusual showers at times slow the salinity recovery in the estuary in the beginning. However, by October end, salinity almost reached the levels found in

dry periods. Changes in salinity found after this period until the start of next monsoon were due to tides (Fig. 2 a and e). Average salinity recorded during postmonsoon season was found to be 28.4 ± 3.5 , which is higher than the annual average (21.5 ± 11.0). An increase in water temperature was found from 28.97°C to 30.61°C in October. Thereafter the temperature gradually decreased to 26.73°C by December end. Such a variation in temperature was also found in other estuarine waters (Sarma et al., 2009, 2010). The seasonal average temperature of $28.82 \pm 1.2^\circ\text{C}$ closely reflects annual average of $29.0 \pm 1.6^\circ\text{C}$ at this station. The concentration of dissolved oxygen was low during most of the season when compared to that in the monsoon season except in late January 2009. The minimum and maximum values were $114\ \mu\text{M}$ and $204\ \mu\text{M}$, respectively (Table 4) and are undersaturated (Fig. 2). In spite of decrease in rainfall, nitrate and nitrite showed high concentrations during postmonsoon. Nitrate showed two broad peaks; the first from late October (24-10-2008) to early November (03-11-2008) and the second from late November (23-11-2008) to early January 2009 (03-01-2009). De Sousa (1999) described a similar unnatural loading of nitrate in the Mandovi estuary, which is connected to Zuari by the Cumbarjua Canal (Fig. 1), and attributed it to release of rejects from mining industries in Goa. Although we have no direct evidence for the release of nitrate by mining rejects in Zuari estuary we are convinced of its strong possibility. Figure 1 shows that the upstream region of Zuari is surrounded by mining activities. Despite the fact that, the monsoon rainfall and the river discharge cease by the end of September (Suprit and Shankar, 2008) reduced discharge from Selaulim Dam (Shetye et al., 2007) and/or subsurface discharge through the laterite terrain (Subramaniam, 1981) into the Zuari estuary occur. Therefore, the nitrate released by mining effluents can still find its way into the estuary. The maximal concentration of nitrate ($14.4\ \mu\text{M}$) found at station 6 possibly resulted from the mining effluents. De Sousa (1999) found nitrate concentration in mining effluents to be $80\ \mu\text{M}$. The nitrate from terrain (including that from mining activity) was drained into the Zuari estuary mainly through surface and subsurface discharges in monsoon. In postmonsoon, however, the subsurface discharge might be the dominating one. This argument seems reasonable since a gradual decrease in nitrate peaks is found in this season (Fig. 2). Loading of nitrate has been observed by Edwards (1973), Kemp and Boynton (1984), Eyre (1994), Markich and Brown (1998), Moreau et al. (1998), Sarma et al. (2009) and Sarma et al. (2010) into various estuaries around the world due to anthropogenic activities. The initial nitrite peak was sharp but the subsequent one was broad. Nitrite variation in this season agreed well with changes in nitrate (Fig. 2). The highest nitrite concentration of $11.71\ \mu\text{M}$ in this study occurred in this season. The average of $2.74 \pm 3.02\ \mu\text{M}$ for postmonsoon season is higher than that in other seasons (Table 4). Devi et al., (1983) observed a similar kind of variation in nitrite in Cochin estuary during non-

monsoon months. Phosphate showed sharp peaks in the early postmonsoon season. But the phosphate peaks do not seem to have any relation with nitrate and nitrite. Phosphate varied between 0.5 and 3.2 μM with an average of $1.1 \pm 0.5 \mu\text{M}$. Silicate followed the same trend as that of phosphate. Silicate concentration decreased gradually following the September 2008 spell and discharge. Thereafter the silicate concentration was low throughout the season and varied between 13 μM and 72 μM with an average of $29 \pm 12 \mu\text{M}$.

3.1.1.3 Premonsoon

The peak in rainfall found towards the end of premonsoon was associated with 2009 premonsoon showers. Salinity variations are rhythmic and are driven by tidal circulation (Fig. 2). This period recorded the highest salinity (34.2) in the estuary with the maximal seasonal mean of 29.9 ± 3.1 in the year (Table 4). A gradual increase in temperature was found until May in which it was nearly steady. Although some wavy pattern could be seen it is unclear if it is driven only by tides. Temperature varied between 27.77 and 33.01 $^{\circ}\text{C}$ with the warmest seasonal average ($30.57 \pm 1.37^{\circ}\text{C}$) in a year. Oxygen concentration was low when compared to summer monsoon except for January-February months when oxygen concentrations were high (Fig. 2). Oxygen is undersaturated (except for August 2008 and January-February 2009 periods when station 6 experienced near saturation) throughout the year. Nutrient levels were the lowest throughout this season (Table 4) with the concentrations seem modulated by tidal circulation (Fig. 2). Nitrite showed relatively higher peaks in the first half of the season. Nitrate (8.9 μM) and nitrite (9.61 μM) peaks occurred in May 2009 following the rain events.

3.1.2 Relationship between properties

Relationships for nutrients and oxygen with salinity, temperature and rainfall are shown in Fig. 3 using the year long data from station 6. Except nitrite, all other nutrients showed negative relations with salinity and temperature. While dissolved oxygen, nitrate and silicate showed strong relations phosphate and nitrite exhibited weak relationships with salinity and temperature. Similar trends have been found by Martin et al. (2008) in Cochin estuary. The negative relations between nutrients and salinity indicate land (river) discharges load the estuary with substances that get diluted en route to sea. Except for some scatter most of the values of oxygen, nitrate and silicate seem to fall in the linear trend. The linear trend implies a near conservative behaviour of the substance despite its participation in estuarine biogeochemical processes. De Sousa et al. (1981) found near conservative behaviour for nitrate and silicate, except for phosphate, during monsoon whereas non-conservative

trends have been found for all nutrients in other seasons. The annual trends in Fig. 3, however, strongly suggest that addition or removal of oxygen, nitrate and silicate, by biogeochemical processes, in the estuarine system is of lesser significance than their control by mixing processes. Relations were poor for phosphate and nitrite since the variability was large for both these nutrients in the high salinity waters. Influence of monsoon rainfall on nutrients and oxygen concentrations has also been studied using data collected in both 2008 and 2009 summer monsoon periods. Although linear fits indicate positive trends for oxygen, nitrate, nitrite and silicate the relations were poor. However, consideration of only monsoon 2008 data (*Supplementary Figure 1*) revealed improved relations. Plots revealed that dissolved oxygen, nitrate and silicate showed strong positive relationships while phosphate showed weak negative relation. The trends exhibited by phosphate and nitrite are not clear, as these showed negative and positive relations, respectively, with both rainfall and salinity. High nutrient levels found during monsoon revealed that productivity will not be limited by nutrients during monsoon but by some other factors. Sarma et al. (2010) found high concentration of nutrients associated with the monsoon discharge in the Godavari estuary but reduced productivity due to high turbidity. Fast flushing rates in summer monsoon (Vijith et al, 2009) can also limit primary production. With the decreased discharge stability of water column increases which facilitates the occurrence of biological processes (Achrayya et al., 2012). Temperature also exhibited relations with properties similar to those with salinity (Fig. 3) suggesting significant influence of monsoon and its discharge on properties in mid-estuarine region.

As can be seen from Fig. 3 river discharge transports large quantities of weathered silicate into estuaries and oceans. If the nitrate also is exported by river discharge proportionality should be seen in silicate-nitrate relationship. Nitrate showed near equal concentrations ($\sim 14 \mu\text{M}$) during monsoon and postmonsoon seasons but silicate substantially decreased from monsoon to postmonsoon (Table 4). Occurrence of relatively higher nitrate also in postmonsoon season, when silicate decreased, suggests that nitrate might have a source other than natural discharge.

The relationships between (nitrate+nitrite) and phosphate during different seasons are shown in Fig. 4. In monsoon season though the values are much scattered concentrations of nitrate + nitrite and phosphate seem to be high. A scatter is more expected when the sources are different for two nutrients. Nitrate + Nitrite and phosphate could have different sources during monsoon season. As has been seen from Fig. 2 nitrate peaks in monsoon coincided with rain events but phosphate also peaked at times without rain. This suggests a different source for phosphate other than river discharge or low retention of nitrate+nitrite in water in proportion to the observed phosphate and

expected from the release of organic matter decomposition. This aspect of more phosphate but low (nitrate+nitrite) became more conspicuous in postmonsoon when the latter was between 2 and 6 μM while phosphate increased to 4 μM (Fig. 4). A linear relation occurred in premonsoon season.

3.1.3 Statistical Analyses

Factor Analysis and Hierarchical cluster analysis for the measured parameters were performed and the results are presented below season wise followed by annual. In view of the significant differences found in rainfall-oxygen and nutrient property relations, between monsoon of 2008 alone (*Supplementary Figure 1*) and that of 2008 and 2009 together (Fig. 3), the statistical analysis was performed for these two sets of monsoon data separately.

3.1.3.1 Monsoon 2008 (June – September)

The grouping of analyzed parameters are done by using varimax rotation factor analysis and the two factors (Fig. 5a; Table 5) are represented as factor1 (F1) and factor2 (F2) accounting for 69% of cumulative percentage. The two factors help in understanding the sources and controlling factors for nutrients and oxygen variability in the estuary during monsoon. Factor 1 accounted for 45.85% of total variance with an eigen value of 4.13. Factor 1 seems to have strong positive influence on rainfall, oxygen, nitrate and silicate but negative on salinity and temperature. The second factor accounts for 23.17% of total variance with an eigen value of 2.09. Positive loadings are found with phosphate, nitrite and sea level. Relations among parameters under Factor 1 (Table 5) suggest rainfall to be the chief controller of salinity, temperature, oxygen and nutrients (except nitrite and phosphate) levels at station 6 during monsoon. Relations found under Factor 2 suggest the influence of tides (sea level) on phosphate and nitrite. The extent of tidal incursion and the consequent seawater intrusion into the estuary will, however, depend on the magnitude/speed of river discharge (i.e. rainfall).

Hierarchical cluster analysis indicates the parameters with similarities through formation of groups or clusters. The results are presented in a two dimensional plot (dendrogram, Fig 5b). The dendrogram was based on linear pair coefficients of correlation. Two main clusters were formed from the measured variables. Nitrate, silicate, oxygen and rainfall formed the first cluster. Salinity and temperature form the second along with phosphate, nitrite and sea level. Hence, HCA results (Fig. 5b) also suggest that salinity, temperature, nitrate, silicate and dissolved oxygen abundances at station 6 are governed by rainfall while the levels phosphate and nitrite are by tidal circulation. These statistical results are in conformity with relationships found in monsoon (*Supplementary Figure 1*).

3.1.3.2 Monsoon 2008 (June – September) and Monsoon 2009 (June)

Since we missed the variability in oxygen and nutrients during the initial stages of summer monsoon rainfall in 2008 we continued our study till late June 2009. As the results in Fig. 2 that revealed concentrations of nitrate and nitrite are associated with initial rainfall 2009 event we subjected the data to check whether the statistical analyses of two sets of monsoon data (of 2008 alone and that of 2008 and 2009 together) would be different.

Results of Factor analysis of 2008 and 2009 monsoon data are shown in Fig. 6a. Distributions of the variables studied seem to have been governed by three factors (F1, F2 and F3) in difference to two factors for 2008 monsoon (Fig. 5a). The three Factors accounted for 78.63% of cumulative percentage of the variability. Factor1 accounted for 41.58% of total variance with an eigen value of 3.74. F1 indicated positive loadings on oxygen, nitrate and silicate but negative on salinity, temperature and nitrite. The second factor (F2) accounted for 20.42% of total variance with an eigen value of 1.84. F2 showed positive influence on phosphate and sea level. Factor 3 (F3) accounted for 16.63% of total variance with an eigen value of 1.5 with positive loadings on rainfall, nitrate and nitrite. These results confirm the findings in the previous section in regard to nitrate regulation by rainfall (F3) and phosphate control by tides (F2). However, combined data of 2008 and 2009 significantly highlighted the strong combined influence of rainfall and tides on nitrite. The HCA analysis (Fig. 6b) in agreement with the Factor analysis results indicated dominant control of tides on phosphate. However, the cluster analyses clearly indicated the dominant influence of rainfall (over the tide) in regulating nitrate, silicate and oxygen variability at station 6. Figures 5a and 6a are based on the results of Factor analysis in Table 5 but shown as examples here. In the remainder of this manuscript statistical results are presented in tabular form for Factor analysis and as dendrograms for Cluster analysis.

3.1.3.3. Postmonsoon

Three factors (Table 5) were found to control the variability in the estuary during postmonsoon season. These factors F1-F3 account for 61.8% of cumulative percentage of variability. Factor1(F1) account for 25.04% of total variance with an eigen value of 2.25. Factor1 indicated positive loadings on rainfall and silicate while negative on salinity. The F2 accounted for 19.57% of total variance with an eigen value of 1.76. Positive loadings are found on sea level, phosphate and temperature but negative loading on nitrite. Factor3 accounted for 17.2% of total variance with an eigen value of 1.55 with positive loadings on nitrate and negative on oxygen. The results of this

Factor analysis suggest that silicate is mainly brought in through river discharge, which is diluted by seawater (F1). Phosphate, nitrite and temperature are controlled mainly by tidal mixing (F2) whereas combined influence (F3) of rainfall and tide regulate nitrate and oxygen variability at Station 6. Cluster analysis (Fig. 7a) suggests strong influence of sea level on the variability of salinity, phosphate, nitrite, nitrate and temperature whereas rainfall regulated silicate and oxygen. While F1 suggested more influence of rainfall on salinity during this season (Table 5) Fig. 7a indicates that the latter is strongly controlled by tides. It is to be noted that nitrate at station 6 was dominantly controlled by rainfall in monsoon but by tides in post monsoon (Table 5, Figs. 6 and 7).

3.1.3.4 Premonsoon

Three factors (Table 5) were identified as controlling factors for nutrients and oxygen during the premonsoon season, which account for 74.07% of cumulative percentage. Factor 1 account for 30.19% of total variance with an eigen value of 2.72. Factor1 indicated positive loadings on salinity and sea level but negative with silicate. The F2 accounted for 25.65% of total variance with an eigen value of 2.31. Positive loadings are found with nitrate, nitrite and phosphate. Factor 3 (F3) accounted for 18.23% of total variance with an eigen value of 1.64 and has a positive loading on temperature and negative on oxygen. No Factor suggested any significant loading for rainfall implying that it is of minor significance in controlling oxygen and nutrient variabilities in this season when tidal influence is the dominant. More over, whatever the minor influence of river discharge, considered in terms of rainfall, it is likely to occur in the forms of subsurface discharge and/or leakage across the Selaulim dam. This is conformed by the Cluster analysis results in Fig. 7b, which shows that sea level and rainfall are grouped together. In both monsoon and premonsoon seasons rainfall and salinity are grouped separately and had strongly influences on identified properties as discussed above. However, in premonsoon the tidal circulation is the key factor in regulating the variability at station 6 including that of freshwater discharge.

3.1.3.5 Annual (June 2008 – June 2009)

Three factors were identified (Table 5) which account for 72.46% of cumulative percentage. Factor 1 accounted for 42.42% of total variance with an eigen value of 3.82. Factor1 indicates positive loadings on rainfall, oxygen, nitrate and silicate and negative on salinity and temperature. The second factor accounts for 15.82% of total variance with an eigen value of 1.42 and positively influence phosphate and sea level. Factor 3 (F3) accounted for 14.22% of total variance with an eigen value of 1.28 and seems to influence only nitrite. Cluster analysis (Fig. 7c) indicates rainfall to

control oxygen, silicate and nitrate whereas sea level regulates phosphate. Both these drivers exhibit influence on salinity, temperature and nitrite. In general both the Factor and Cluster analyses strongly suggest that factors controlling the variability of physical and oxygen and nutrient properties at station 6 in summer monsoon determine their variability on an annual scale too. The two major controllers are freshwater discharges (rainfall as the proxy), which continues even after monsoon in forms of subsurface and dam releases, and tides. These results (Table 5, Figs. 5-7) are in agreement with the observed strong linear relations in Fig. 3 for silicate, oxygen and nitrate with salinity and temperature (as both these physical properties are largely controlled by freshwater discharges). As nitrite and phosphate are controlled by tides the resultant relations were poor in Fig. 3.

3.2 Macro scale variations and processes in the estuary (Transect Observations)

3.2.1 Seasonal variability of physical and chemical properties along the estuary

Seasonal averages of each physical, oxygen and nutrient property in surface and bottom waters at each station along the longitudinal transect, during spring and neap tidal observations, are shown in Fig. 8. Vertical bars represent monthly variability, in terms of standard deviations, in respective season. Detailed monthly variability of each property is shown in *Supplementary Figure 2*. The variability in three different seasons have been put together in Fig. 8. Seasonal minimum, maximum and averages (with SD) of various parameters found for transect observation are listed in Table 6.

3.2.1.1 Salinity

Large variations in salinity were observed during monsoon (Fig. 8a). Freshwater dominated the upper estuary due to heavy discharge. The average salinity of the estuary was low 16.56 ± 12.29 (Table 5) during monsoon. Near zero salinity was found in surface waters at station 3 in June 2008 which was pushed further downstream (to station 5) by heavy discharge in July-August. The salinity in surface and bottom waters decreased at respective stations as the monsoon progressed (June-July to August-September; *Supplementary Figure 2*). Higher salinity than in surface waters occurred in bottom waters with a significant seaward increase. The difference in salinity between surface and bottom through the length of the estuary was more striking during neap tides than spring. Salinity stratification is prominent during monsoon, which is weaker (maximal difference occurred in mid-estuarine region) during neap tides of post- and premonsoon seasons. The stratification was highly pronounced during neap tides. The estuary seems better vertically mixed during spring tides particularly in dry periods. Influence of continuing freshwater discharge on the estuarine waters could be seen during postmonsoon when stations 1 and 2 experienced near zero salinity during neap

tides. Postmonsoon season is the recovery phase when seawater returns to dominate the estuary (Shetye et al., 2007). The extent of stratification was reduced and could only be seen during neap tides. The average salinity value increased to 21.83 ± 12.35 . Premonsoon season marks the complete recovery of the saline conditions when a maximal salinity of 36.14 recorded. Intra-seasonal differences in salinity were narrow during neap tides than spring tides and prominent during monsoon. Salinity in June 2008 was relatively less than that in June 2009.

3.2.1.2 Temperature

Temperature showed maximal variation during monsoon particularly in the lower estuary (Fig. 8a). Temperature was higher at the head that gradually decreased towards the sea but with a rise from station 9 to 10. The difference between surface and bottom waters was high in this season. Estuary exhibited two kinds of temperature variation during monsoon. In the upper half of the estuary, temperature was low in surface waters whereas in the lower estuary bottom waters showed low temperature. The trend was consistent in both spring and neap tides. The stratification found in salinity and the intrusion of high saline-low temperature seawater could be attributed to this. The minimal temperature found in the estuary during this season was 23.53°C in bottom waters of station 9 (when marine end station (10) could not be occupied due to hostile weather). The low temperatures at the head are due to cold river water discharge when air temperatures were also low. The average temperature value in monsoon did not show much variation from that of post monsoon season. The estuarine waters were warmer in June 2009 than in June 2008. The minimum and maximum temperatures recorded during postmonsoon season were 25.66 and 31.29°C , respectively. In contrast to monsoon period, lowest temperature was recorded in the bottom waters of upstream station (station 2, neap tide). Temperature was found to increase in the middle of the estuary. The trend was more pronounced during spring than in neap tide. Similar to postmonsoon, premonsoon season also recorded maximum temperature at mid estuarine locations. Maximal temperature in the estuary was recorded during premonsoon season when it ranged from 26.68 to 32.83°C with an average of $30.35 \pm 1.54^{\circ}\text{C}$. Temperature at the head of the estuary increased considerably in premonsoon when compared to the other two seasons. Premonsoon season, neap tides showed a clear difference between surface and bottom waters. *Supplementary Figure 2* suggests that the variability of temperature in the estuary followed a systematic annual cycle: by exhibiting (i) a decreasing trend from June to August, (ii) increase from August to October, (iii) decrease from October to January and (iv) increase from January to June. This trend could also be seen for station 6 in Fig.2. Longitudinal gradients in temperature in the estuary are minimal except in August. No major

differences were found in temperature between surface and bottom and between spring and neap tides in dry seasons.

3.2.1.3 Dissolved Oxygen

Dissolved oxygen variability was very significant in monsoon in this estuary (Fig. 8b). The maximal range (41 - 265 μM) in oxygen concentration occurred in this season. Surface waters recorded high values than bottom throughout the estuary during both spring and neap tides. Oxygen concentration in bottom waters decreased downstream from mid-estuarine region during both spring and neap tides. The difference between surface and bottom waters increased downstream from station 4 both during spring and neap tides. Intra-seasonal change was the highest in bottom waters at the marine end stations. Maximal concentrations of oxygen were recorded in surface waters of the estuary in August (*Supplementary Figure 2*). Postmonsoon season showed no significant difference between surface and bottom waters. The average value was found to be 169 ± 20 . Maximum value (225 μM) was recorded at the freshwater end while minimum (108 μM) in the marine end. Oxygen concentration decreased in both surface and bottom waters during neap and spring tides from head to mouth. Premonsoon dissolved oxygen values were similar in surface and bottom during spring tide. In premonsoon mid-estuarine stations recorded low oxygen than at stations 1 and 7-10 during the spring. The difference between surface and bottom water oxygen was more during neap tides.

3.2.1.4 Nitrate

The concentration of nitrate in the estuary was higher in monsoon season than in dry seasons (Fig. 8c). The average nitrate concentration in the estuary during monsoon was found to be 6.3 ± 4 μM . Nitrate decreased from upstream to mouth in both spring and neap tides. The difference between surface and bottom was larger during neap tides in monsoon. The variability in both surface and bottom waters, however, is of the same magnitude. The highest concentration (16.1 μM) during monsoon was recorded at station 2 in bottom waters (2009 observation, *Supplementary Figure 2*). Station 1 could not be sampled due to adverse conditions. Higher nitrate in bottom waters than at surface at stations 3-5 during spring tide and stations 2-3 during neap tides appears to suggest the addition of this nutrient into estuarine waters by also subsurface discharge (expected to carry nitrate from land discharges including mining remnants). In postmonsoon also nitrate was marginally higher in bottom waters at stations 2-5 because of the continuing subsurface discharge. The concentration of nitrate was lower in postmonsoon and premonsoon seasons than in monsoon. The average nitrate found in the estuary during postmonsoon was 3.2 ± 2.1 μM . Low nitrate in the estuary was recorded

during premonsoon season. Average value was recorded as $2.3 \pm 2.2 \mu\text{M}$. Spring and neap tide values did not show any particular trend but remained low in concentration. Fig. 8c indicates that the intra-seasonal variability in nitrate is more significant in the lower estuarine region in summer monsoon whereas it is in the upper estuary during the dry seasons.

3.2.1.5 Nitrite

The stratification seems to be insignificant in influencing the vertical distribution of nitrite in monsoon as its concentrations were similar in surface and bottom waters during both spring and neap tides. Nitrite was lower in the estuary in monsoon with minimal intra-seasonal variability. The variability during monsoon was between 0 and $2 \mu\text{M}$. In postmonsoon season, high nitrite was found in the mid-estuary zone. Spring and neap tidal phases showed nitrite maxima; in spring it was towards the upper mid estuary whereas in neap it was in the lower part of mid-estuary. In these regions, bottom waters in general were found to contain more nitrite than surface. The average nitrite found in postmonsoon in the estuary was $2.47 \pm 3.05 \mu\text{M}$. Nitrite concentrations in premonsoon reflected almost the same features as observed in postmonsoon. The average concentration of nitrite during premonsoon season was less ($1.56 \pm 1.69 \mu\text{M}$). The maximal intra-seasonal variability in nitrite occurred in postmonsoon, which was more during neap tides than during spring tides (Fig. 8c).

3.2.1.6 Phosphate

High variability in phosphate levels in the estuary occurred in monsoon during the spring tide when the lower mid-estuarine stations contained higher concentrations and also exhibited intra-seasonal variability (Fig. 8d). During neap tides the variability was less. The average concentration of phosphate was found to be $1.09 \pm 0.59 \mu\text{M}$. Phosphate levels do not show clear trends in concentration or intra-seasonal variability during postmonsoon. However, higher concentrations and also high variability occurred in the lower estuary during premonsoon season. Importantly, bottom waters were found to contain more phosphate than surface.

3.2.1.7 Silicate

Silicate was high at the head that was gradually diluted downstream. The variability was more during monsoon season. The maximum concentration was $128 \mu\text{M}$ during monsoon. Similar to phosphate, silicate also exhibited maximal intra-seasonal variability during spring tides in monsoon (Fig 8d). In premonsoon the variability was significant in the upper estuary during both lunar tides.

Figure 8 along with *Supplementary Figure 2* reveals that longitudinal gradients (river to sea) in salinity (low-high) and silicate (high-low) are obvious but to a lesser extent in nitrate. Mid-estuarine highs are important for nitrite, phosphate and to some extent to nitrate and temperature. Intra-seasonal variability is more significant in monsoon with measurable differences between surface and bottom; in the lower estuary particularly for salinity, temperature, dissolved oxygen and nitrate.

3.2.2. *Mid-estuarine nitrite maxima*

Figure 2 revealed peaks in nitrate and nitrite at station 6 between October end 2008 and early January 2009. Figure 8 (and *Supplementary Figure 2*) indicated that the peak in nitrite is not limited to station 6 but is a result of larger estuarine process. This is because the nitrite concentration peaked in the mid-estuary and seems associated with processes occurring longitudinally and between the head and mouth of the estuary. These peaks were not related with surface runoff since there was no rain in days preceding the peaks in nitrite and nitrate. To understand the processes that led to mid-estuarine maxima in nitrite we examined (Fig. 9) longitudinal distributions of nitrite, nitrate and oxygen saturation along with pigments (chlorophyll a and phaeophytin). These were obtained from tidal observations from October end to early January covering six tidal cycles.

October observations showed high nitrate levels in the freshwater end that decreased towards the sea. In mid-November, a mid-estuarine maximum in nitrate was found with bottom water having higher concentration than surface. Between the tidal observations on 21 November and 12 January nitrate levels in the estuary are found to decrease with a clear trough like feature in the mid-estuarine zone. Nitrite was very low on 23 October but started increasing in mid-estuary and exhibited maximal levels from 21 November to 19 December. A decrease in nitrate with simultaneous increase in nitrite suggests the possibility of denitrification. When oxygen saturation in water is over 50% denitrification is unlikely. Figure 9 indicates chlorophyll a decrease from 14 November to 19 December when phaeophytin levels in water increased gradually. Phaeophytin is a degradation product of phytoplankton. Opposite trends in chlorophyll a and phaeophytin suggest release of benthic materials, including pore fluids that are enriched in degradation products of organic materials. Pore water in sediments contain reducing conditions in which nitrate is consumed during bacterial respiration while nitrite accumulates. The release of these sedimentary materials by the tidal circulation can alter the composition of the overlying waters. High nitrite in the mid-estuarine waters thus seems to result from sedimentary release than biogeochemical processes in the water column. The observation of the influence of sedimentary releases by tidal mixing on nitrite maxima has large implications to the levels and distribution of water column properties. This draws support from the

fact that maximal levels of phosphate occurred in the lower estuarine region of the Zuari and in the entire estuary its concentration in bottom waters was higher than in surface water during post- and premonsoon periods (Fig. 8d).

3.2.3. Relations among physical and chemical properties in the estuary

Relations among various physical and chemical properties in the estuary based on transect observations are shown in Fig. 10. Table 7 lists correlation coefficients obtained for the total data (station 6 and transect observation) using the cross correlation matrix. Figure 10 and Table 7 substantiate the relations found in Fig. 3 for salinity and temperature but for the scatter resulted from large spatial variability. Dissolved oxygen, nitrate and silicate showed strong negative relationship with salinity. Large scatter in nitrate relation with salinity arises from variable dominance of physical and biogeochemical processes at different times and locations. De Sousa et al. (1981) found that nitrate and phosphate are added to estuarine waters in postmonsoon whereas these are removed during the premonsoon in the Mandovi-Zuari estuarine system. Silicate has been found to be removed from these waters both during post- and premonsoon seasons. Both nitrate and silicate, however, behaved conservatively during monsoon (De Sousa et al., 1981). Silicate deviated only negatively (Fig. 10) suggesting its removal, which is consistent with the observations of De Sousa et al. (1981). Nitrite only deviated positively due to its addition to the water column from sediments facilitated by the tidal circulation. Temperature showed negative but weak relations with all the parameters in the estuary. Dissolved oxygen showed positive relationship with silicate and negative with phosphate. Table 7 again conforms to the role of rainfall and salinity in determining the variability of of silicate, oxygen and nitrate in the whole estuary on an annual basis. Relations among dissolved oxygen and nutrients are rather poor except for silicate with oxygen and nitrate.

3.2.4 Statistical Analyses

As in the case of station 6 (because it was a fixed location) rainfall and sea level data cannot be used for transect observations. However, these two major physical drivers are reflected through salinity as a combined forcing function. Salinity is a proxy majorly for tidal influence. Therefore the total number of variables in this case are seven (Table 8) against nine in the case of station 6 (Table 5).

3.2.4.1 Monsoon 2008 (June – September)

Variability in the entire estuary during monsoon is explained by two factors (Table7) that account for 70.36% of cumulative percentage. Factor 1 accounted for 47.74% of total variance with an eigen

value of 3.34 with positive loadings on temperature, oxygen, nitrate and silicate but negative on phosphate and nitrite. The F2 accounts for 22.61% of total variance with an eigen value of 1.58. Positive loadings are found with nitrate and phosphate. Hierarchical cluster analysis (Fig. 11a) indicated three different groups / clusters. Oxygen, silicate and temperature formed the first cluster. Phosphate and nitrate formed second and salinity with nitrite formed the third group.

3.2.4.2 Monsoon 2008 (June – September) & 2009 (June)

Three factors are found to account for 80.7% of cumulative percentage. Factor 1 accounted for 39.5% of total variance with an eigen value of 2.77. Factor 1 indicated positive loadings on dissolved oxygen, nitrate and silicate but negative on salinity. The second factor accounts for 22.17% of total variance with an eigen value of 1.55. Positive loadings are found with phosphate and negative with temperature. Factor 3 (F3) accounted for 19.04% of total variance with an eigen value of 1.33 with positive loadings on nitrate and nitrite. Cluster analysis (Fig. 11b) indicated three different groups / clusters. Oxygen, nitrate and silicate formed a group while temperature and nitrite formed second. Third group consisted of salinity and phosphate. These results are consistent with the fact that salinity is negatively related to oxygen, nitrate and silicate (Fig. 10) and with that of factor (Table 5) and cluster analyses (Fig. 6) for station 6.

3.2.4.3 Postmonsoon

As in Table 5 three factors accounted for 76.87% of cumulative percentage. Factor 1 accounted for 35.2% of total variance with an eigen value of 2.46. Factor 1 indicates significant positive loadings on nitrate and silicate but negative on salinity. The F2 accounts for 22.82% of total variance with an eigen value of 1.6. Positive loadings are found with nitrite and phosphate. Factor 3 accounted for 18.85% of total variance with an eigen value of 1.32. Positive loadings occurred for temperature but negative for oxygen. The major difference in the factor analysis results of station 6 (Table 5) and entire estuary (Table 8) in postmonsoon is that nitrate was controlled by F3 at fixed location but by F1 in the estuary. Temperature was governed by F2 at station 6 but by F3 in the estuary. Cluster analysis (Fig. 11c) indicated three different groups / clusters. Nitrate, silicate and oxygen formed a cluster. Nitrite and phosphate formed the second and salinity and temperature the third.

3.2.4.4 Premonsoon

Variability in premonsoon season was controlled by three factors (Table 8) that account for 75.58% of cumulative percentage. Factor 1 accounted for 32.28% of total variance with an eigen value of

2.26. Factor1 indicated positive loadings on salinity and phosphate and negative for silicate. The second factor accounts for 21.75% of total variance with an eigen value of 1.52. Positive loadings are found with temperature but negative with oxygen. Factor 3 accounted for 21.55% of total variance with an eigen value of 1.51. Positive loadings are found with nitrate and nitrite. Results for premonsoon in Table 8 (total estuary) are in variance with those in Table 5 for station 6. At the fixed location nitrate, nitrite and phosphate are governed by F2 whereas temperature and oxygen by F3. In the entire estuary, phosphate seems to be controlled by F1, temperature and oxygen by F2 and nitrate and nitrite by F3. These differences highlight the variable dominance among physical processes (surface and subsurface freshwater discharges, tidal circulation and resuspension of sediments or release of pore fluids) themselves besides different biogeochemical processes/rates at various locations. Thus extrapolation of factors controlling variables at one location to the total in the estuary in general will lead to erroneous conclusions.

Cluster analysis (Fig. 11d) indicated three different groups / clusters. Salinity and phosphate formed the first group. Temperature formed a separate second group. Nitrate and nitrite form the third group while silicate and oxygen forming the fourth. It should be noted that the parameters strongly influenced by tidal circulation (salinity, temperature, phosphate and nitrite) formed one cluster whereas those by freshwater discharges (silicate, oxygen and nitrate) formed the other (Fig. 11).

3.2.4.5 Annual

Varimax rotation factor analysis identified two factors, which account for 56.39% of cumulative percentage. Factor 1 account for 37.52% of total variance with an eigen value of 2.63. Factor 1, seems associated with freshwater discharges and hence has, positive loadings on dissolved oxygen, nitrate and silicate and negative for salinity. The second factor, related to tides, accounts for 18.87% of total variance with an eigen value of 1.32. Positive loadings are found with nitrate, nitrite and phosphate but negative with temperature. Annual factor analysis for station 6 and the entire estuary again shows different results; three factors governed the variables at station 6 (Table 5) but two factors for the entire estuary (Table 8). Nevertheless, F1 (with rainfall) in both cases exhibit strong control on salinity, silicate, oxygen and nitrate whereas the other factors arise from tides, combined forcing of freshwater discharge and tidal circulation or other processes (resuspension, biogeochemical etc.). Cluster analysis (Fig. 11e) indicates three different groups / clusters. Nitrate, oxygen and silicate formed the first group. Salinity, nitrite and phosphate formed the second while temperature formed a separate group. As has been mentioned above variability of silicate, oxygen and nitrate are regulated by freshwater discharges whereas salinity, temperature, phosphate and

nitrite are by tidal circulation. To understand the factors governing the processes of nitrate and nitrite in the postmonsoon in the estuary we have carried out varimax rotation factor analysis for the data used in Fig. 9. Results revealed four Factors (Table 9). Factor 1 shows negative influence on salinity and positive on silicate and nitrate. The F2 regulates the positive linkages among phaeophytin, nitrite and phosphate, which seems to be driven by sedimentary releases under tidal influence. The remaining two factors perhaps are driven by combined influence of freshwater discharges, tidal circulation etc. Table 9, therefore, statistically confirms to the role of release of sedimentary materials into overlying waters and contributing to their variability in the Zuari estuary..

3.3. *Places of anthropogenic nitrate addition to the estuary*

Silicate in the estuary exhibited excellent inverse relation with salinity (Fig. 10), which is the strongest among the variables studied (Tables 6 and 7). Thus silicate, with its sole source being the freshwater discharge whether of surface or subsurface discharge, would serve as an indicator of natural inputs. On the other hand, nitrate has both natural and anthropogenic sources in the Mandovi-Zuari estuarine complex, as has been discussed above. A plot between silicate and nitrate+nitrite (in which the points are identified with stations; Fig. 12) would help identify the locations of possible anthropogenic inputs of nitrogen nutrients. In monsoon highest nitrate+nitrite occurred at stations 2-4 (B-D in Fig. 12) where silicate was not maximal. Silicate exhibited highest concentrations further downstream (stations 4-7; D-G in Fig. 12) revealing significant inputs of silicate through subsurface discharges at these locations where there are no distributaries. It appears that in monsoon nitrate+nitrite are added to the estuary by surface runoff (station 1 could not be approached due to unfavourable conditions for sampling) while silicate was also added by subsurface discharges. Fig. 12 also suggests that the influence of transport of materials from Mandovi estuary through the Cumbarjua canal is meager. In postmonsoon also silicate was added at the head of the estuary when nitrate+nitrite were added downstream indicating the dominant surface (river) runoff influence on silicate (stations 1-3) but both (surface and subsurface, stations 2-7) discharges on nitrate+nitrite. On the other hand, subsurface discharges drain significant quantities of silicate and nitrate+nitrite at stations 1-6 in premonsoon. Higher concentration in bottom waters than at surface at these stations indicate the dominance of subsurface than surface (leaky discharges from the Selaulim dam) supplies. Therefore, higher nitrate+nitrite were added at the head of the estuary by surface discharge in monsoon and by subsurface discharge in premonsoon. But in the postmonsoon the addition occurred in the mid-estuarine zone (stations 3-7) through subsurface discharge. Mining effluent

releases thus add nitrate+nitrite to the upper and mid-estuarine regions because these regions are either proximate to areas of mining activity or subsurface transport through porous laterite terrain.

3.4. Evaluation of significance of Physical and biogeochemical forcings

The detailed statistical analysis of the variability and relationships among the properties studied at the fixed location and the entire estuary help us in evaluating the significance of physical and biogeochemical forcings on the observed variability. The Factor analysis indicated three Factors to account for controlling the variability of the properties, both seasonally and annually, at station 6 (Table 5). These three Factors accounted for 79% the variability in monsoon (2008-09 data), 62% in postmonsoon, 74% in premonsoon and 73% in a year. Among the three Factors two factors are associated with rainfall and sea level, the two major physical drivers of circulation in the Zuari estuary. The third accountable Factor is presumably associated with another forcing associated with physics (such as sedimentary releases wither by resuspension or upward diffusion). The unaccountable Factors (=100 – total of accountable Factors in %) contributions are 21% in monsoon, 38% in postmonsoon, 26% in premonsoon and 27% in a year at station 6. Since the Factors associated with physical drivers are accounted in Table 5 the unaccountable and unknown factors could be that of biogeochemical processes or their rates. In the absence of detailed biogeochemical measurements clear identification of biogeochemical Factors is outside the scope of this work. Moreover, identification of the accountable biogeochemical Factors might prove daunting since each of the oxygen and nutrient variables may be regulated by different biogeochemical reactions, rates and processes even at a specific location. The physical forcings thus seem to control 60-80% variability of dissolved oxygen and nutrients at station 6 leaving biogeochemical factors to account for 20-40%.

Analysis of transect results suggest again three Factors to control the variability in studied properties in the estuary on a seasonal basis (Table 8) with the accountability ranging from 76% to 81%. In this case, however, rainfall and tide height can not be included in statistical analysis for the estuary and therefore we have to rely on their indirect indicators. Salinity is of prime significance since it reflects the effects of freshwater discharges and tides. Next important indicator is temperature, which can be influenced by these two and their combined forcing besides by air temperature. Therefore, unlike in the case of a fixed location where Factor and control forcing associations (rainfall and sea level) are reasonably discernible identification of associations is difficult for the whole estuary. Nevertheless, Table 8 suggests one Factor in each season is clearly associated with salinity while another possibly with temperature. The third Factor is difficult to identify as it may be associated with unknown

forcing perhaps associated with salinity and temperature variations. Despite these limitations of linking Factors and real control forcings the variability of oxygen and nutrients in the entire Zuari estuary is governed by physical forcings in different seasons. The biogeochemical Factors appear to account for about 20-25%. Physical (Factors) forcings, therefore, are mainly accountable for seasonal variability in dissolved oxygen and nutrients both at a fixed location and in the entire Zuari estuary leaving the biogeochemical Factors secondary. The annual analysis for the entire estuary yielded a different result wherein only two Factors (Table 8) accounted for 56% of the variability. The biogeochemical (Factors) forcings have to account for the 44%. This different result might have been a consequence of variable biogeochemical processes and rates in time and space in the estuary. Thus one needs to exercise caution in extrapolating the understanding of factors controlling the variability of a biogeochemical property at a fixed location to the estuary, particularly on an annual basis.

3.5. *The resilient Zuari estuary*

As can be seen from the foregoing sections silicate and nitrate are being added to the estuary by freshwater discharges predominantly during monsoon. Nitrate addition assumes special significance in view of its anthropogenic origin. Therefore, it is important to know whether the added nutrients are retained in the estuary or not. The historical information (Table 10) on various parameters in the Zuari estuary reveals that nitrate concentrations over the years have not changed and our observed value of 16.1 μM is the highest reported so far. There could have been a possibility of missing the times and locations of higher concentrations occurrence by earlier studies since their sampling strategies have been limited in time and space in the estuary. Nevertheless, near similar nitrate concentrations over the last four decades indicate that nitrate does not accumulate in the estuarine system. In spite of its addition to the estuarine water Fig. 10 clearly reveals the occurrence of very low levels of nitrate at the mouth region suggesting its dilution or removal in the estuary. Additionally flushing of the estuary is very rapid in monsoon (Shetye et al., 2007) that may limit the available time for its biogeochemical removal, which is in agreement with its conservative behaviour in this season (De Sousa et al., 1981). The fact that the estuary is flushed completely year after year in monsoon makes this estuary resilient to human interference as in the case of nitrate shown here.

Carpenter and Brock (2006) have discussed different measures available to check the resilience or stability of a population in ecosystems of which variance is one. Ives (1995) proposed the 'variance' tool and stated that 'if populations perturbed far from mean densities tend to move rapidly back towards mean densities, then the system will have greater stochastic resilience, since this will reduce

the variability in population density'. Assuming that the estimated standard deviations in Table 4 and *Supplementary Table 2* serve as approximate indicators of variance we adopt Ives (1995) approach for the results at station 6 for the annual and seasonal averages of nitrate. Nitrate averages \pm SD are found to be 7.5 ± 4.1 , 3.6 ± 3.1 , 1.7 ± 1.6 and 4.4 ± 4.1 μM respectively for summer monsoon, postmonsoon and premonsoon seasons and a year. In terms of mean \pm SD postmonsoon nitrate nearly reflects that of annual. Monsoon showed maximal variability with the highest mean whereas premonsoon the lowest. These trends suggest that the system (at station 6) positively deviates from annual average in monsoon (when the nitrate variability in the entire estuary is also largest as shown in Fig. 8) and negatively in premonsoon. This evaluation for nitrate also holds good for silicate trends. The Zuari estuarine system thus stabilizes back to normal conditions, including that for anthropogenically added nitrate, in postmonsoon confirming its resilient nature annually with respect to nutrients.

4. Conclusions

Peninsular rivers in India are strongly influenced by monsoon rainfall. Zuari is one of the minor rivers in Goa flowing westward into the Arabian Sea and is strongly influenced by rainfall and freshwater discharge associated with the southwest monsoon. Several studies have been carried out in the last few decades to find the levels and distributions of dissolved oxygen and nutrients in the Zuari estuary but none have been aimed to understand the factors controlling their distribution. In this attempt we studied micro to macro scale variability of dissolved oxygen and nutrients in time and space in the estuary. Our extensive data strongly suggest that oxygen and nutrient distributions are governed by hydrological, physical and biogeochemical processes, in that order. Intra-seasonal variability in salinity, nitrate and silicate at the fixed location in monsoon was associated with fluctuations in rainfall. While nitrate and nitrite exhibited notable intra-seasonal variability in postmonsoon minimal variability was observed in premonsoon. Dissolved oxygen was undersaturated throughout the year perhaps due to its utilization in microbial oxidation of mangrove and land derived organic materials. Transect studies revealed stratification during neap tides in all seasons which is stronger in monsoon. Nitrate and silicate are being added in upstream regions in monsoon whereas nitrite exhibited peaks in mid-estuarine zone in dry seasons. Linear relations, although weak, suggested biological influence on dissolved oxygen and nutrient levels. Results of statistical analyses (Correlation, Factor and Cluster Analyses) indicated that on annual basis salinity, temperature, nitrate, silicate and oxygen variability at the fixed location in the estuary was governed by rainfall while sea level controlled that of phosphate, and both these forcings regulated nitrite. On

the other hand, in the entire estuary annual salinity variability accounted for variability of oxygen, nitrate and silicate whereas temperature variability accounted for that of nitrite and phosphate. Our statistical results suggest that rainfall (a proxy of freshwater discharge) and tides govern the variability of physical, dissolved oxygen and nutrient parameters in the Zuari estuary to a large extent. These observations imply that the biogeochemical processes are of significance at only local or short term scales. A comparison of the presently observed nitrate concentration with those reported in literature suggests their unchanged levels in the estuary over the years. This observation together with our statistical results suggests that the regular monsoonal flushing of the estuary every year makes the system resilient to human interference (pollution through mining rejects etc.), in general, which seems to return to normalcy by postmonsoon.

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Figure Captions

Fig. 1. - The Zuari estuary is shown with the locations of Selaulim dam at the river end and mining activity. Transect stations from upstream (station 1) to mouth (station 10) are about 43 km apart and covered longitudinal salinity gradients in all seasons. Daily or alternate day sampling was carried out at station 6 marked with a star symbol. Tidal measurements were carried out at T (Verem), a location in the adjoining Mandovi estuary, which is about 10 km from the transect station 10. Solar intensity was measured at the top of our Institute's building located at S. This map was plotted by using Generic Mapping Tool (GMT).

Fig. 2. – Variability of (a) rainfall and salinity, (b) dissolved oxygen and its saturation (in %), (c) nitrate and temperature, (d) nitrite and solar radiation intensity, (e) phosphate and sea level (tide height) and (f) silicate at station 6 of the Zuari estuary. Measurements were made from 01 August 2008 to 24 June 2009 in surface water on a daily and alternate day basis during summer monsoon and non-monsoon seasons, respectively. Prior to 1 August 2008 nutrients were measured only during transect studies. Closed squares in (c) to (f) show nutrient concentrations measured during transect studies. Rainfall, Salinity, Temperature, solar intensity and sea level data were collected from 23 May 2008 to 24 June 2009. Dashed vertical lines separate wet summer monsoon and dry post- and premonsoon seasons.

Fig. 3. – Relations for nutrients and dissolved oxygen with salinity (left panels) and temperature (middle panels) are depicted on an annual basis at station 6. Relations with rainfall are shown in the right panels for summer monsoon periods covered in 2008 and 2009. The lines shown are linear regression lines. Correlation coefficients (r) and slopes (s) are listed.

Fig. 4. – Relations between (nitrate + nitrite) and phosphate at station 6 in different seasons.

Fig. 5 – Diagrammatic representation of results obtained by (a) Factor analysis (R-mode) with two main factors F1 and F2, and (b) Hierarchical Cluster Analysis (shown as Dendrogram) that show controls of and relationships among various parameters at station 6 during the monsoon period studied in 2008.

Fig. 6 –Diagrammatic representation of results obtained by (a) Factor analysis (R-mode) with three main factors F1, F2 and F3, and (b) Hierarchical Cluster Analysis (Dendrogram) that show controls of and relationships among various parameters at station 6 after combining the observations in monsoon periods of 2008 and 2009.

Fig. 7. Results of Hierarchical Cluster Analysis (shown as Dendrogram) for the variables studied at station 6 for (a) postmonsoon, (b) premonsoon and (c) all seasons.

Fig. 8. Seasonal changes in averages of various parameters at each station in surface and bottom waters in the Zuari estuary based on transect observations during spring and neap tides every month. The vertical lines at each station show the variability in terms of standard deviation of monthly results obtained in each season. Here monsoon observations of both 2008 and 2009 are combined. Parameters shown are: (a) Salinity and temperature, (b) dissolved oxygen, (c) nitrate and nitrite and (d) phosphate and silicate. Due to space limitations monthly changes in all these parameters during spring and neap tides are shown as *Supplementary Figure 2*.

Fig. 9. Trends in oxygen saturation, pigments (chlorophyll and phaeophytin), nitrite and nitrate in surface and bottom waters of the Zuari estuary between 23 October 2008 and 12 January 2009.

Fig. 10. Annual relations for nutrients and dissolved oxygen with salinity (left panels) and temperature (middle panels), for phosphate and silicate with oxygen (top two panels on the right), and for phosphate, silicate and oxygen with nitrate+nitrite (lower three panels on the right). Shown are linear regression lines with slope and correlation coefficients.

Fig. 11. Results of Hierarchical Cluster Analysis (shown as Dendrogram) for the transect (entire estuarine zone) observations for (a) monsoon covered in 2008, (b) monsoon covered both in 2008 and 2009, (c) postmonsoon, (d) premonsoon and (e) all seasons.

Fig. 12. – Plot depicts levels of silicate and (nitrate+nitrite) at stations 1-10 in different seasons to find places of their possible additions in Zuari estuarine waters.

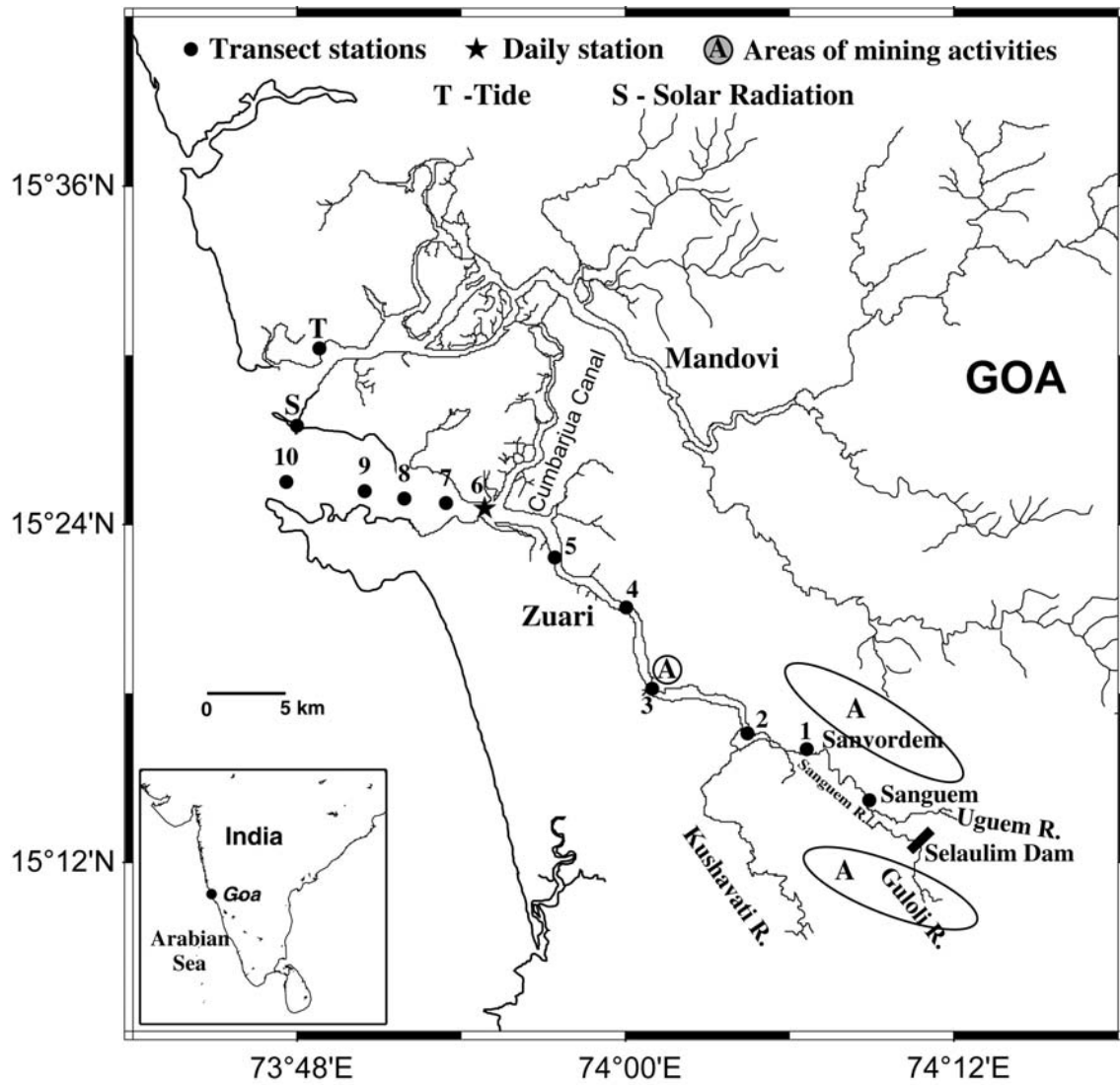


Fig. 1.

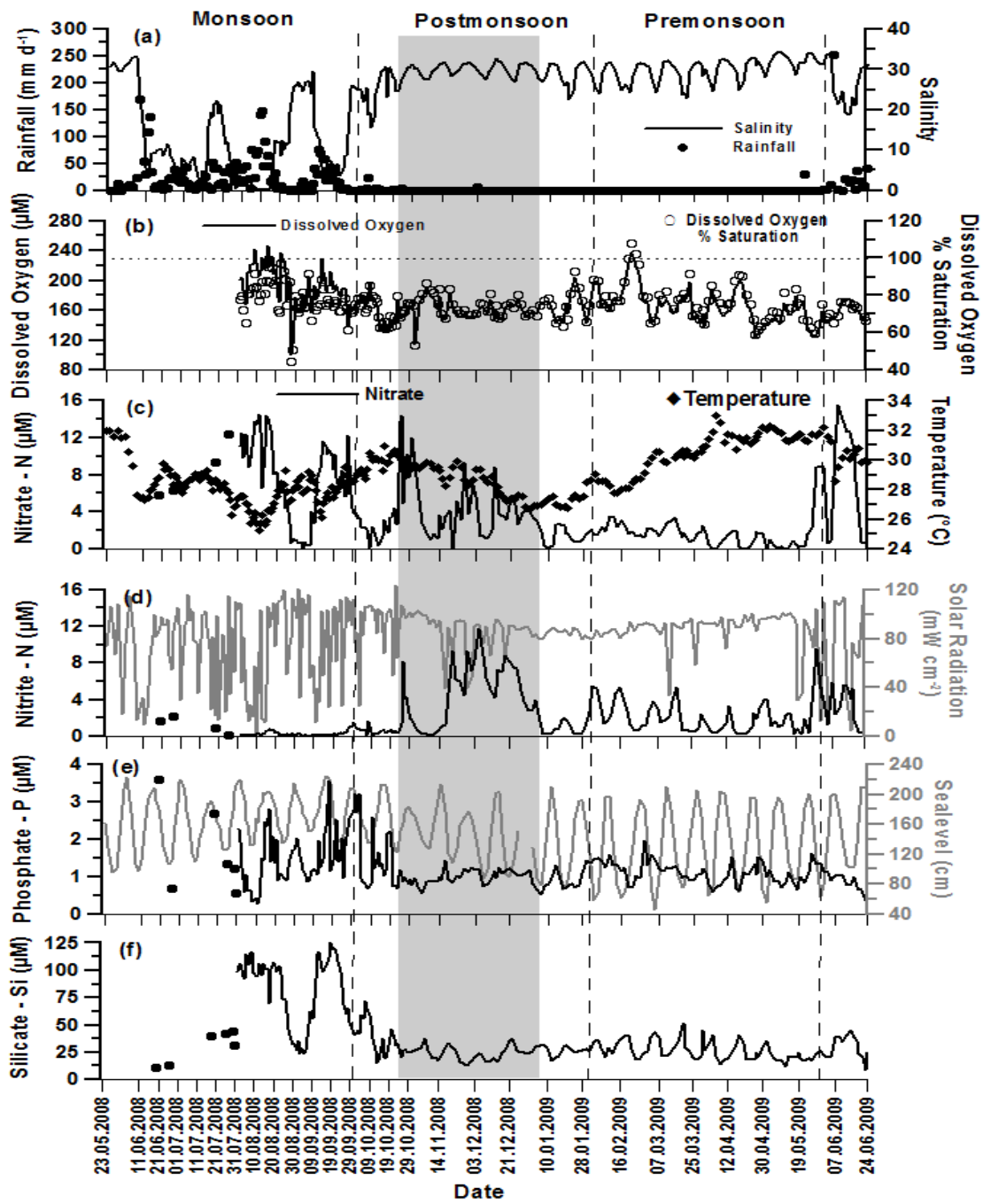


Fig. 2

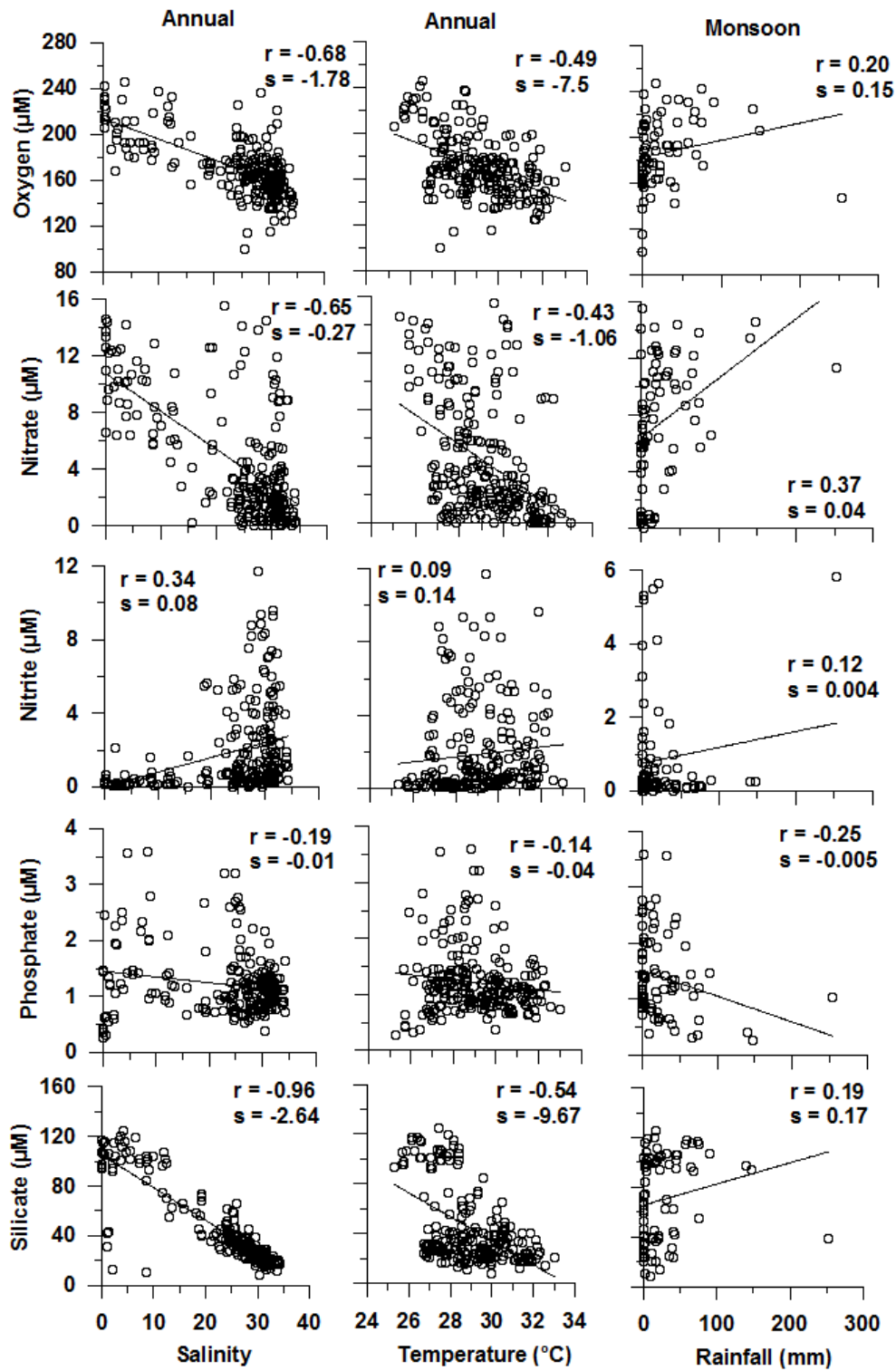


Fig. 3

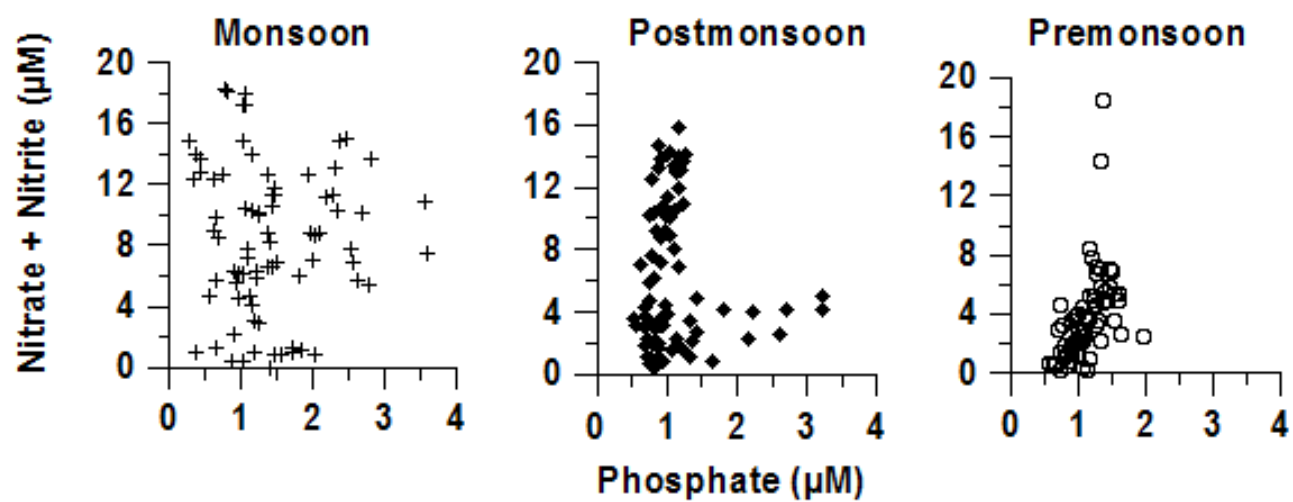
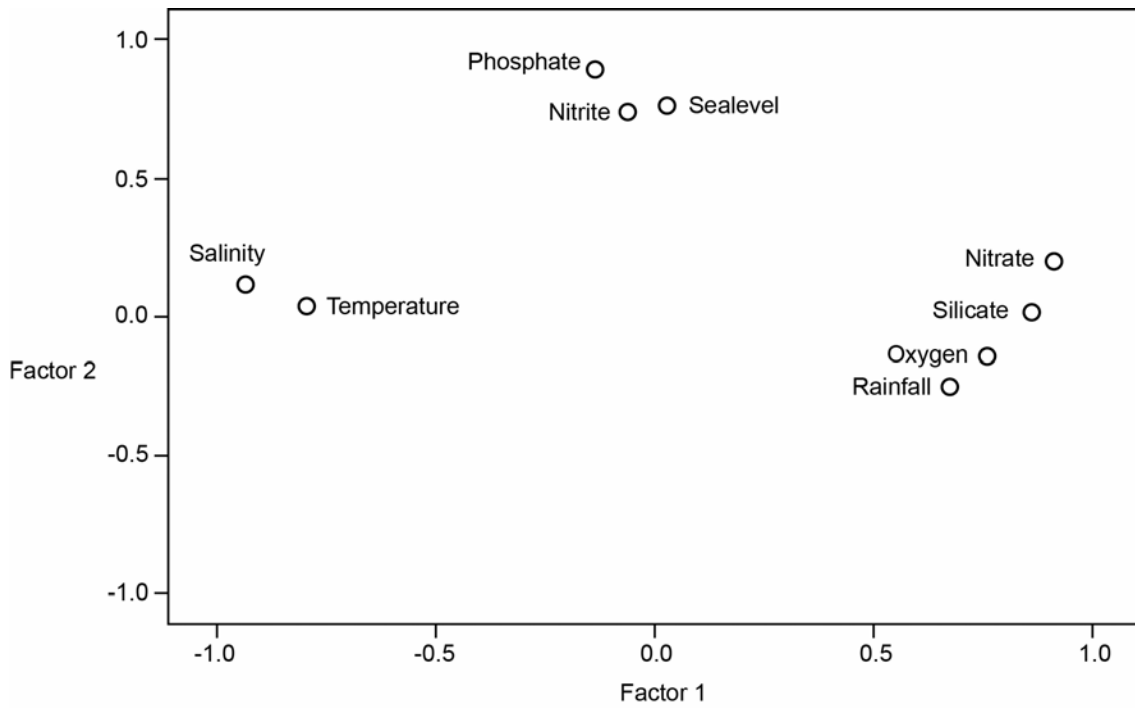
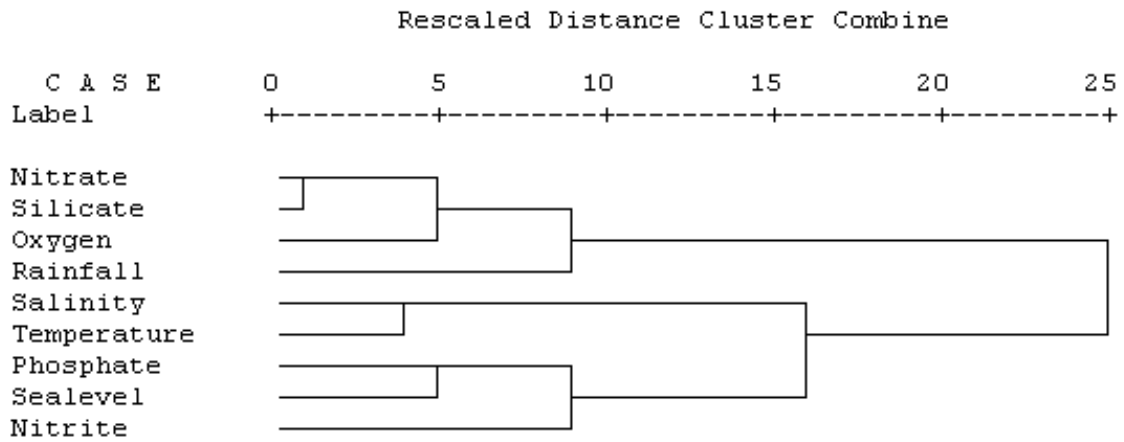


Fig. 4



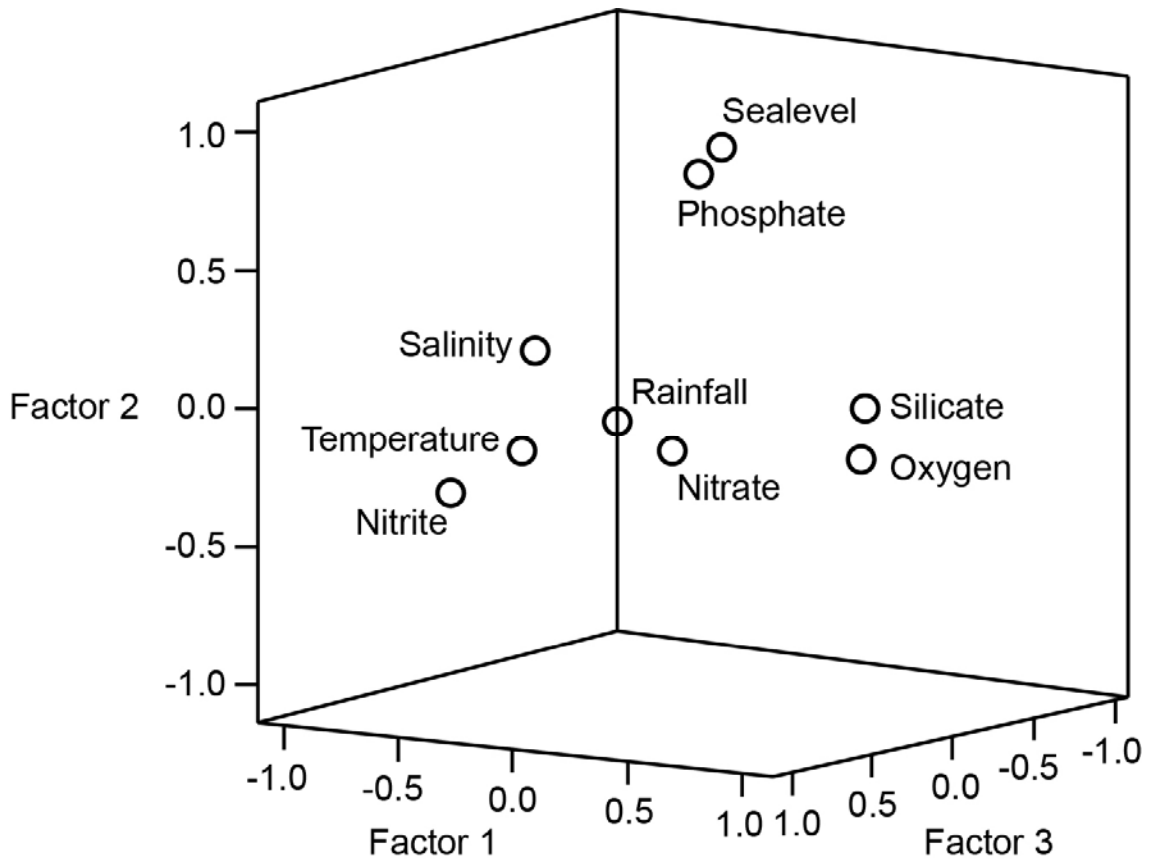
(a)

Dendrogram using Average Linkage (Between Groups)



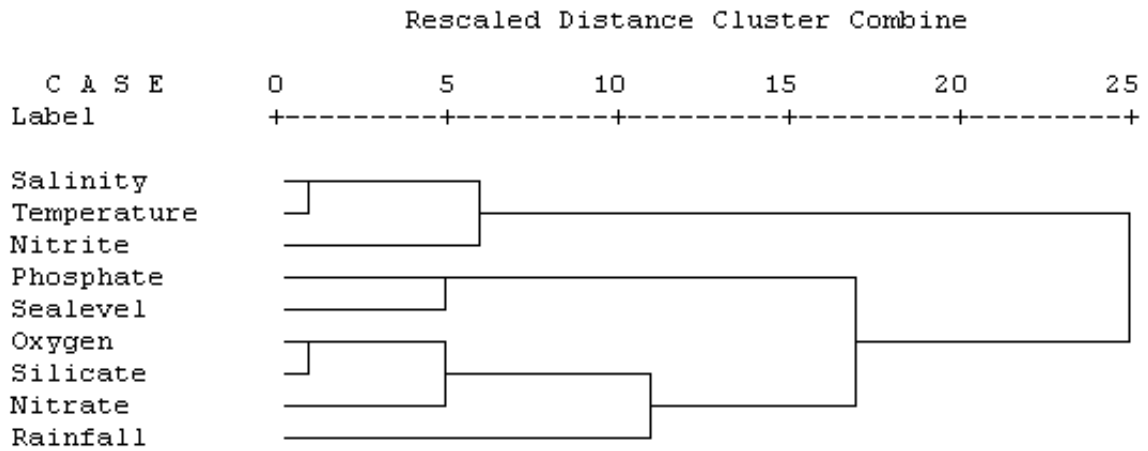
(b)

Fig. 5



(a)

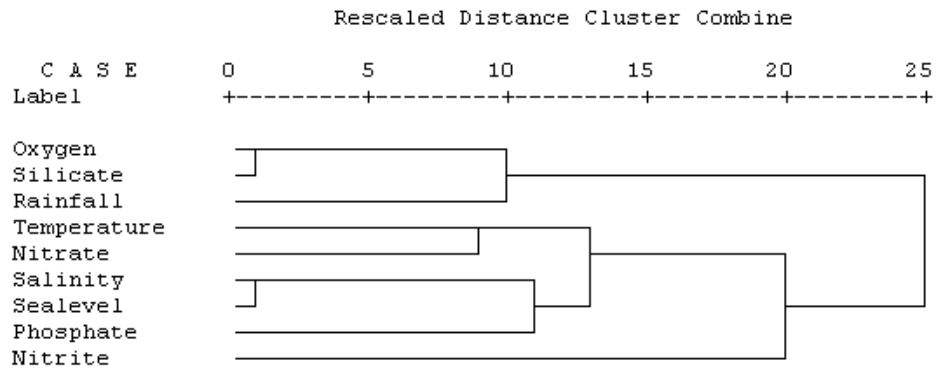
Dendrogram using Average Linkage (Between Groups)



(b)

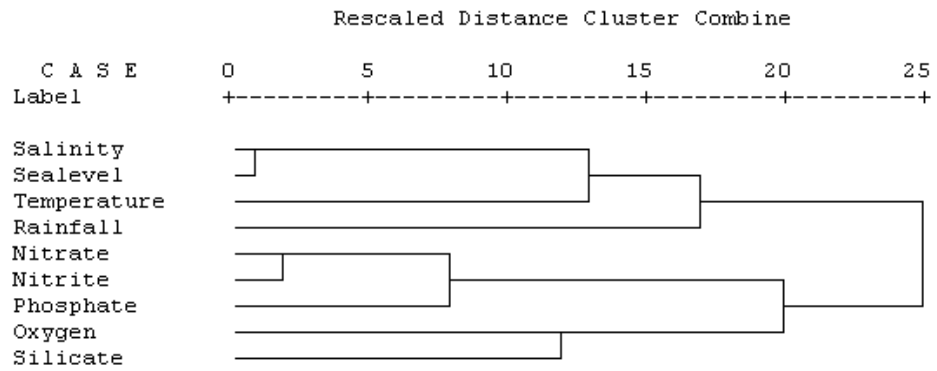
Fig. 6

Dendrogram using Average Linkage (Between Groups)



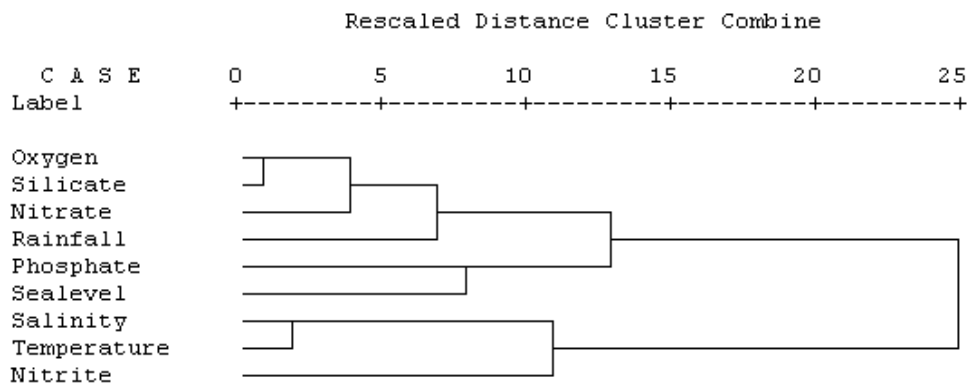
(a)

Dendrogram using Average Linkage (Between Groups)



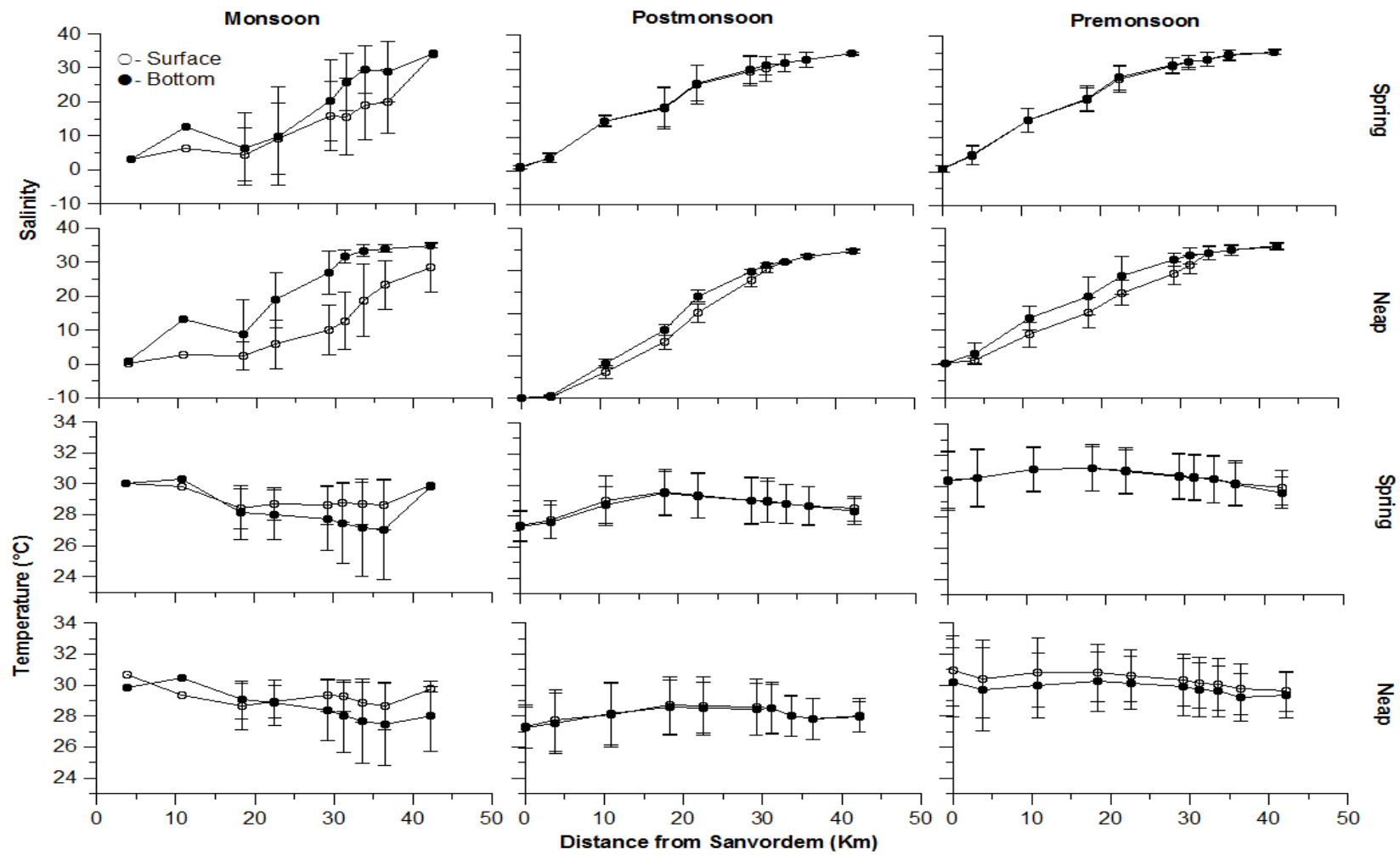
(b)

Dendrogram using Average Linkage (Between Groups)

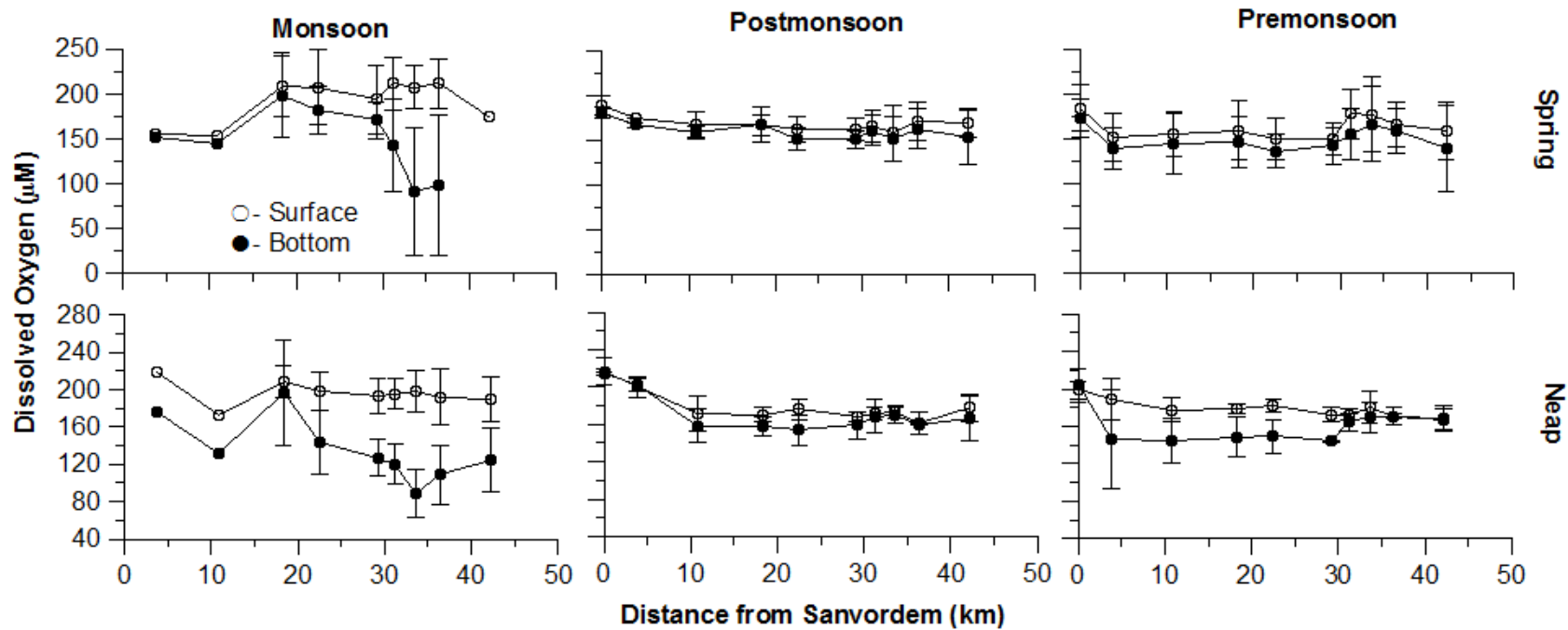


(c)

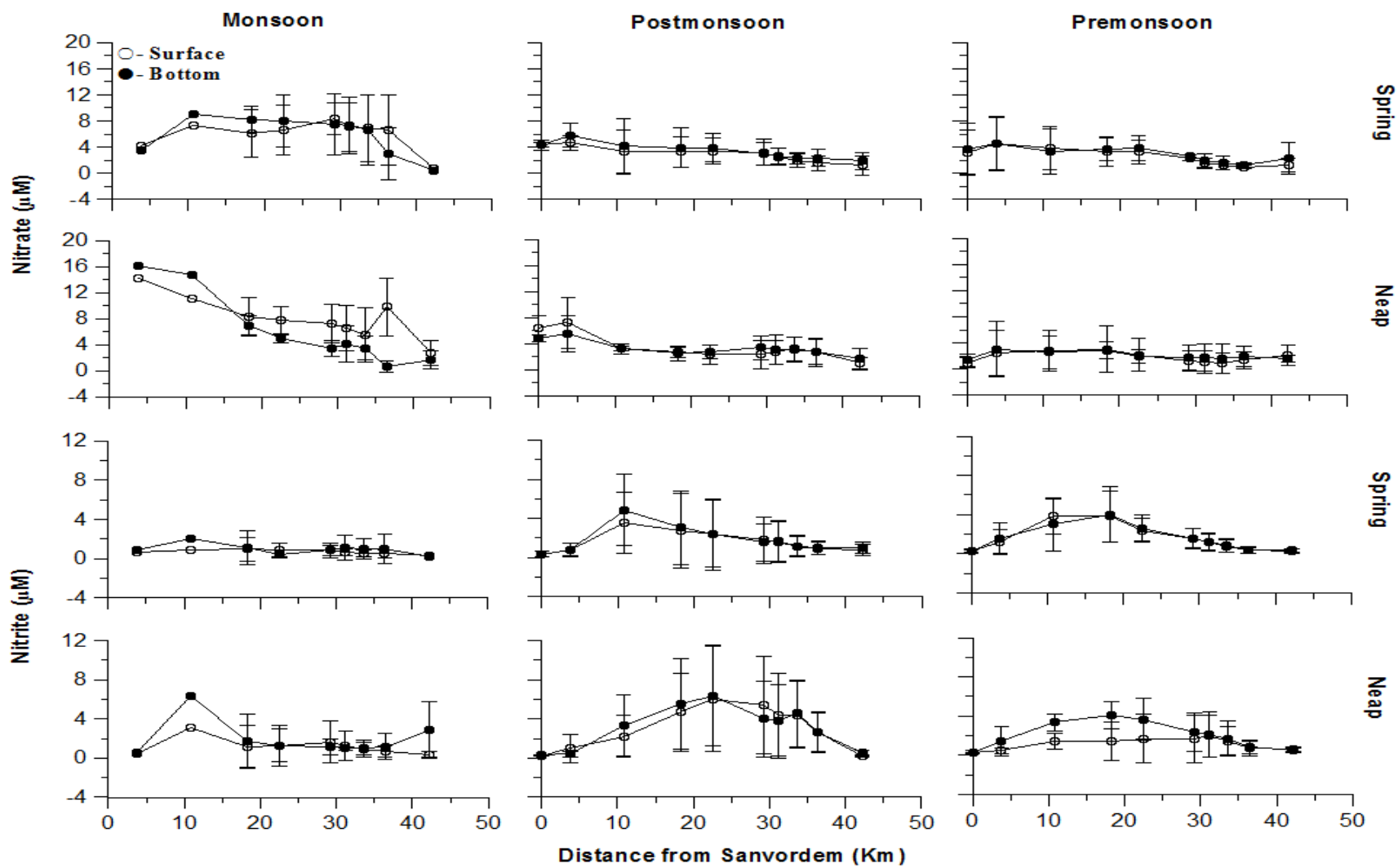
Fig. 7



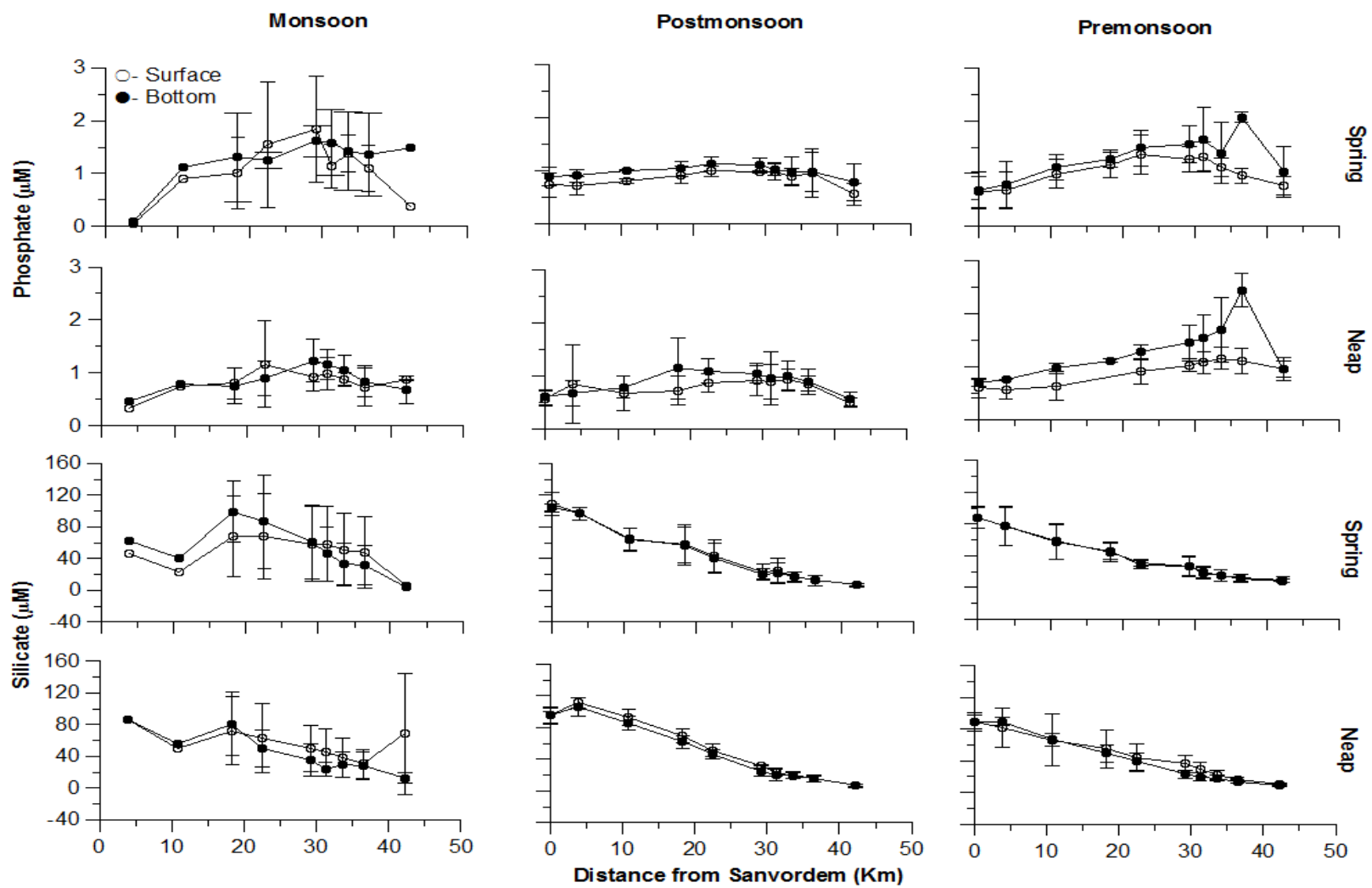
(a)



(b)



(c)



(d)

Fig. 8

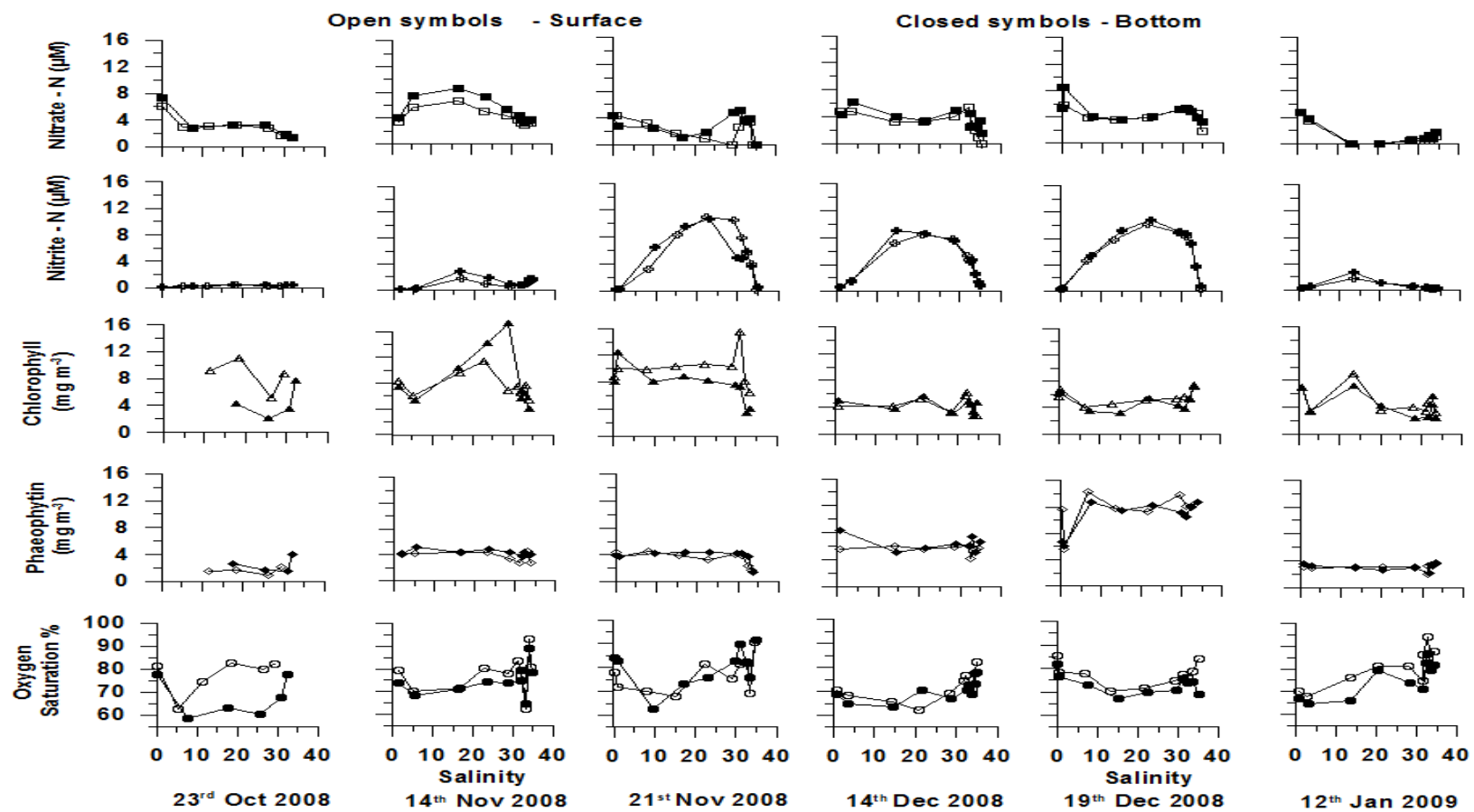


Fig. 9

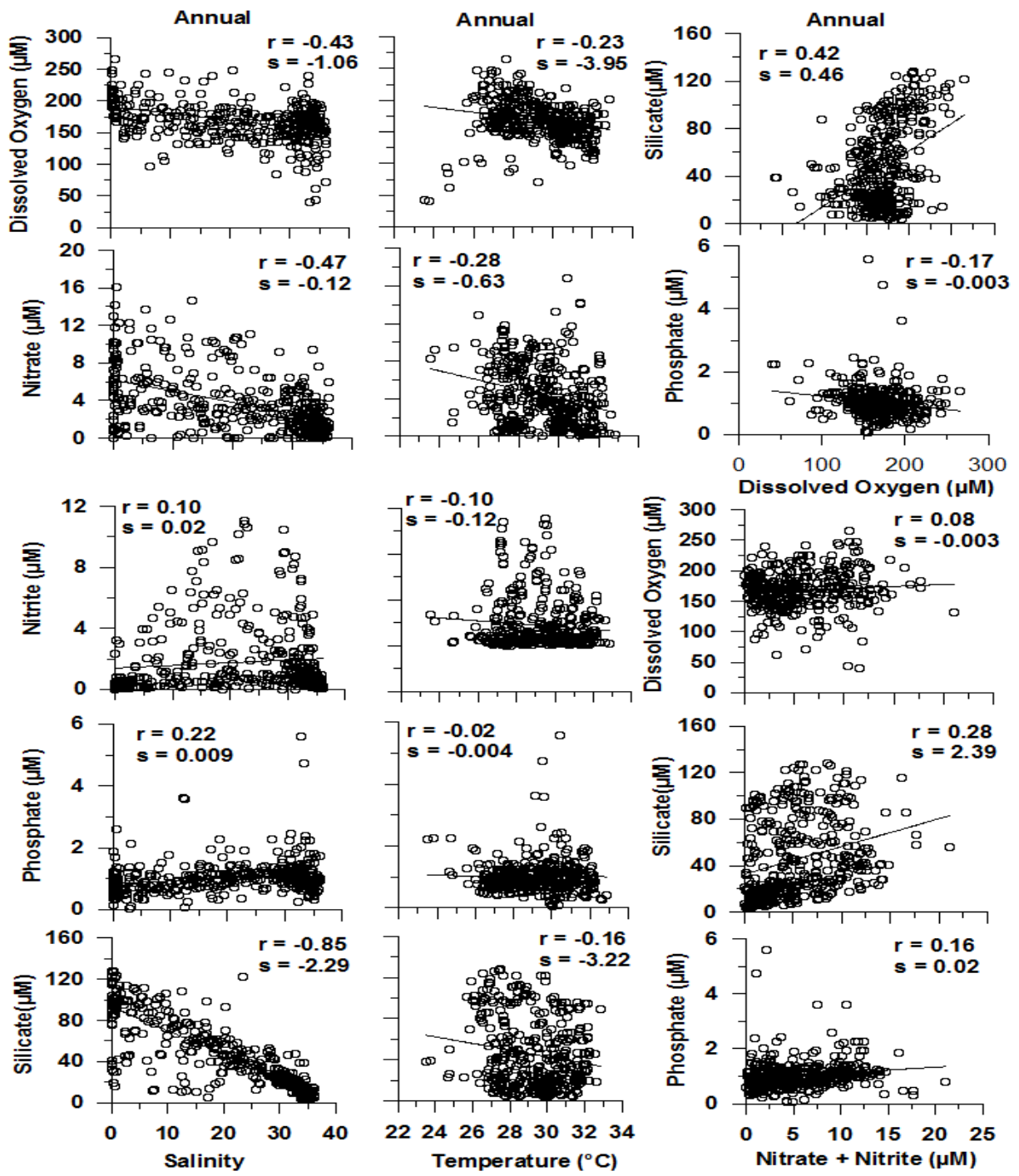
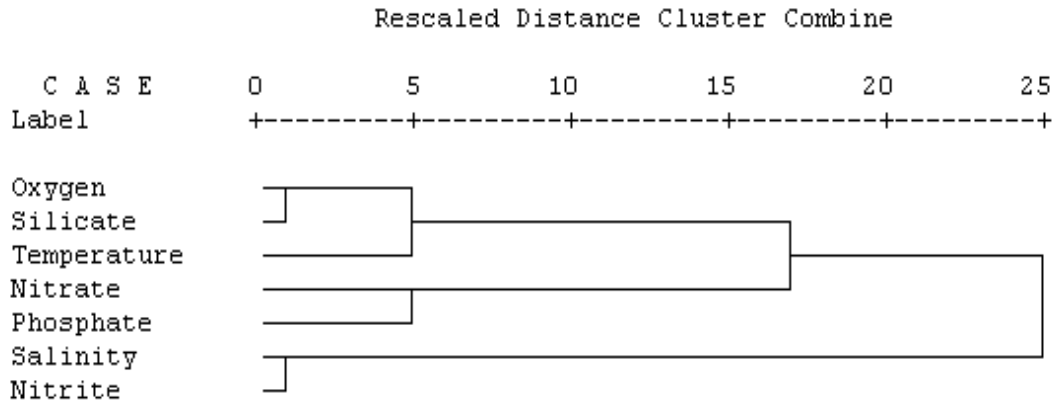


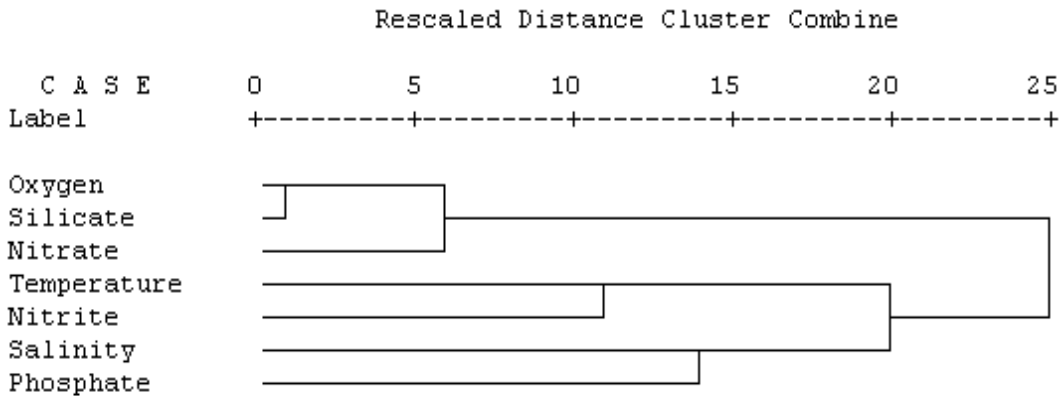
Fig. 10

Dendrogram using Average Linkage (Between Groups)



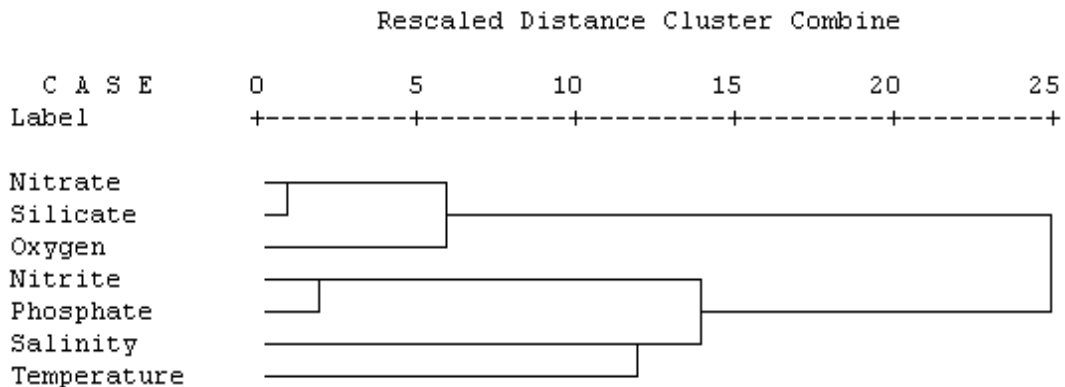
(a)

Dendrogram using Average Linkage (Between Groups)



(b)

Dendrogram using Average Linkage (Between Groups)



(c)

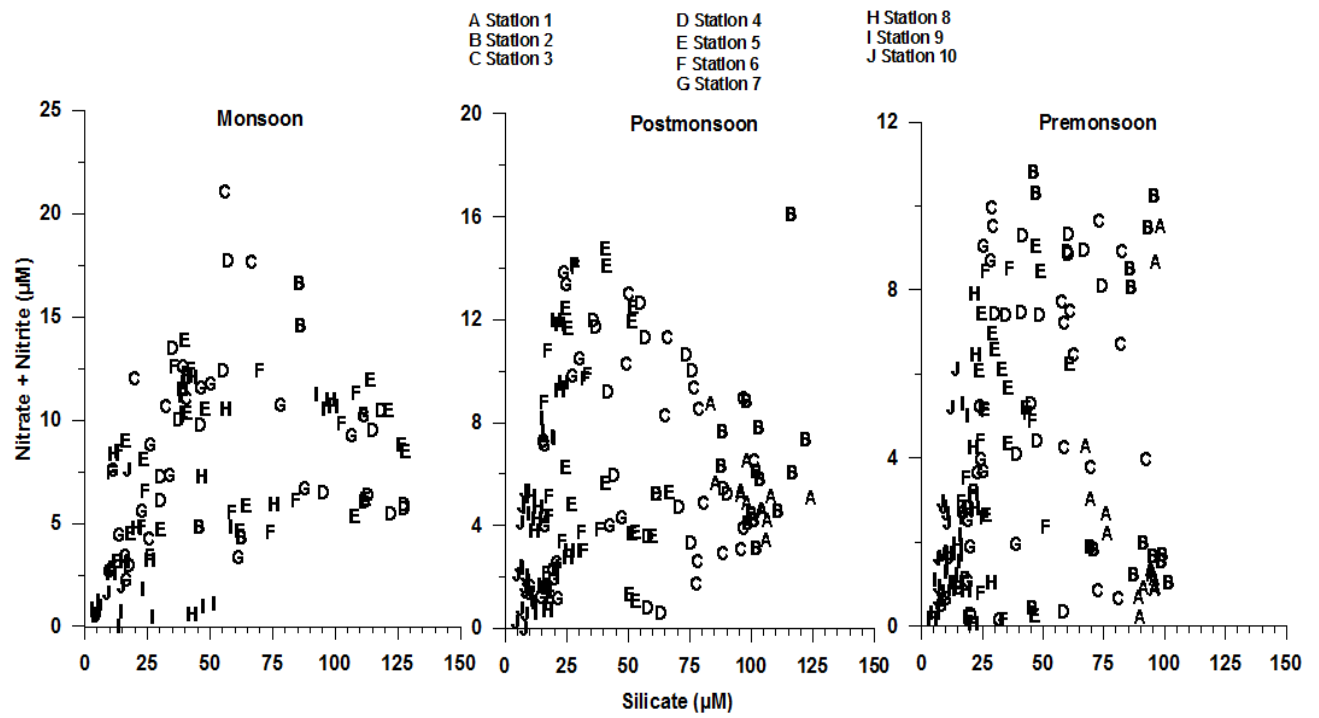


Fig. 12

Table Captions

Table 1. Number, name and depth of sampling stations in the Zuari estuary (see Fig. 1 for locations).

Table 2. Details of spring and neap tidal phase observations along the longitudinal transect in the Zuari estuary in different seasons.

Table 3. Results of KMO-A and Bartlett's tests.

Table 4. Ranges and averages (\pm SD) of hydrological, physical and nutrient parameters observed at station 6 in different seasons (SD = standard deviation).

Table 5. Results of Factor analysis of various parameters studied at station 6 in different seasons. Monsoon results of 2008 and 2009 are considered separately since those of 2008 missed the effects of early summer monsoon rainfall.

Table 6. Ranges and averages (\pm SD) of hydrological, physical and nutrient parameters observed in the Zuari estuary during transect observations in different seasons.

Table 7. Coefficients of correlation among various parameters studied in the Zuari estuary. Both daily and transect data were used in this statistical analysis. P-values listed in the table were calculated using online p-value calculator from <http://graphpad.com/quickcalcs/PValue1.cfm>.

Table 8. Same as in Table 4 but for entire Zuari estuary (based on transect observations).

Table 9. Factor analysis to understand the factors controlling variables studied in Figure 9.

Table 10. Available information on physical, dissolved oxygen and nutrients in the Zuari estuary.

Table 1. Number, name and depth of sampling stations in the Zuari estuary (see Fig. 1 for locations).

Station Number	Station Name	Depth (m)
1	Sanvordem	4.9
2	Kushawathy	9.9
3	Shiroda	9.1
4	Borim	12.9
5	Loutalim	10.5
6	Cortalim	9.6
7	Sancoale	7.1
8	Island	5.0
9	Chicalim	5.0
10	Mormugao	16.0

Table 2. Details of spring and neap tidal phase observations along the longitudinal transect in the Zuari estuary in different seasons.

S. No	Season	Month of Observation	Spring Phase	Stations Sampled	Neap Phase	Stations Sampled
1	Monsoon	June 2008	20.06.2008	3-9	27.06.2008	3-9
2		July 2008	19.07.2008	4-9	26.07.2008	4-9
3		August 2008	18.08.2008	4-9	25.08.2008	4-9
4		September 2008	18.09.2008	4-9	25.09.2008	4-10
5		June 2009	24.06.2009	2-10	18.06.2009	2-10
6	Postmonsoon	October 2008	16.10.2008	4-10	23.10.2008	2-7
7		November 2008	14.11.2008	1-10	21.11.2008	1-10
8		December 2008	14.12.2008	1-10	19.12.2008	1-10
9		January 2009	12.01.2009	1-10	19.01.2009	1-10
10		February 2009	09.02.2009	1-10	16.02.2009	1-10
11	Premonsoon	March 2009	30.03.2009	1-10	20.03.2009	1-10
12		April 2009	27.04.2009	1-10	20.04.2009	1-10
13		May 2009	26.05.2009	1-10	19.05.2009	1-10

Table 3. Results of KMO-A and Bartlett's tests.

S.No	Season	KMO-A	Bartlett's (significance)
Zuari regular			
1	monsoon 2008	0.743	0.000
2	monsoon 2008-2009	0.670	0.000
3	postmonsoon	0.575	0.000
4	premonsoon	0.628	0.000
5	annual	0.737	0.000
Zuari Transect			
6	monsoon 2008	0.716	0.000
7	monsoon 2008-2009	0.556	0.000
8	postmonsoon	0.593	0.000
9	premonsoon	0.442	0.000
10	annual	0.597	0.000

To be qualified for factor analysis KMO-A value of a data set should be greater than 0.5 and Bartlett's test should have significance lower than 0.05

Table 4. Ranges and averages (\pm SD) of hydrological, physical and nutrient parameters observed at station 6 in different seasons (SD = standard deviation).

	Monsoon			Postmonsoon			Premonsoon		
	Min	Max	Mean \pm SD	Min	Max	Mean \pm SD	Min	Max	Mean \pm SD
Rainfall (mm d ⁻¹)*	0	169	25 \pm 32	0	24	0.6 \pm 3	0	30	0.5 \pm 4
Salinity	0.04	33.06	11 \pm 9.2	15.68	32.6	28.4 \pm 3.5	22.78	34.2	29.9 \pm 3.1
Temperature (°C)	25.29	31.56	28 \pm 1.07	26.73	30.96	28.82 \pm 1.2	27.77	33.01	30.57 \pm 1.37
Dissolved Oxygen (μ M)	100	246	191 \pm 15	114	204	161 \pm 15	124	236	165 \pm 24
Nitrate (μ M)	ND	14.6	7.5 \pm 4.1	0.2	14.4	3.6 \pm 3.1	ND	8.9	1.7 \pm 1.6
Nitrite (μ M)	ND	2.14	0.34 \pm 0.4	0.16	11.71	2.74 \pm 3.02	0.23	9.61	2.1 \pm 1.79
Phosphate (μ M)	0.3	3.6	1.5 \pm 0.8	0.5	3.2	1.1 \pm 0.5	0.6	2	1.1 \pm 0.3
Silicate (μ M)	23	125	80 \pm 33	13	72	29 \pm 12	12	52	27 \pm 9

Monsoon – June to September; Postmonsoon – October to January; Premonsoon – February to May

* - Total amount of rainfall received during monsoon is 2976 mm, postmonsoon is 50 mm and premonsoon is 30 mm in 2008-2009

ND - Non Detectable

Table 5. Results of Factor analysis of various parameters studied at station 6 in different seasons. Monsoon results of 2008 and 2009 are considered separately since those of 2008 missed the effects of early summer monsoon rainfall.

Parameter	Monsoon 2008		Monsoon 2008-09			Postmonsoon			Premonsoon			Annual		
	F1	F2	F1	F2	F3	F1	F2	F3	F1	F2	F3	F1	F2	F3
Rainfall	0.6	0.2	0.1	0.0	0.7	0.5	0.0	0.1	0.1	0.2	0.0	0.6	0.0	0.0
	73	53	65	29	41	74	18	76	58	34	37	46	25	34
Salinity	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	0.9	0.1	0.9	0.0	0.3	0.8	0.0	0.2	0.8	0.0	0.3	0.9	0.0	0.2
	35	16	07	10	19	9	09	95	86	47	55	17	77	45
Temperature	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	0.7	0.0	0.8	0.3	0.1	0.3	0.5	0.3	0.0	0.3	0.9	0.7	0.1	0.0
	94	4	27	03	35	73	6	46	72	18	07	14	38	37
Oxygen	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	0.7	0.1	0.8	0.1	0.1	0.2	0.1	0.6	0.2	0.3	0.7	0.7	0.2	0.3
	58	42	29	33	69	65	92	17	84	77	93	19	24	65
Nitrate	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	0.9	0.1	0.4	0.0	0.7	0.0	0.0	0.8	0.0	0.8	0.0	0.7	0.2	0.2
	1	99	35	62	62	39	17	23	19	43	17	70	64	48
Nitrite	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	0.0	0.7	0.6	0.3	0.5	0.2	0.6	0.3	0.4	0.7	0.0	0.1	0.1	0.9
	62	44	62	48	59	32	2	7	09	89	69	10	92	25
Phosphate	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	0.1	0.8	0.0	0.8	0.0	0.0	0.6	0.0	0.1	0.7	0.1	0.0	0.8	0.0
	37	96	07	10	43	17	18	53	28	95	17	96	17	44
Silicate	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	0.8	0.0	0.8	0.0	0.2	0.8	0.0	0.2	0.8	0.1		0.8	0.1	0.2
	61	15	95	79	07	77	91	85	84	28	-0.2	74	41	63
Sealevel	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	0.0	0.7	0.1	0.9	0.0	0.3	0.7	0.1	0.9	0.1	0.0	0.0	0.7	0.3
	29	67	15	08	10	12	97	74	24	62	54	88	61	36

Table 6. Ranges and averages (\pm SD) of hydrological, physical and nutrient parameters observed in the Zuari estuary during transect observations in different seasons.

	Monsoon			Postmonsoon			Premonsoon		
	Min	Max	Mean \pm SD	Min	Max	Mean \pm SD	Min	Max	Mean \pm SD
Rainfall (mm d ⁻¹)*	0	169	25 \pm 32	0	24	0.6 \pm 3	0	30	0.5 \pm 4
Salinity	0.07 (3s)	35.23 (10b)	16.56 \pm 12.29	0.04 (1s,b)	35.09 (10s,b)	21.83 \pm 12.35	0.04 (1s,b)	36.14 (10b)	22.58 \pm 12.58
Temperature (°C)	23.53 (9b)	31.11 (4s)	28.63 \pm 1.59	25.66 (2b)	31.29 (5s)	28.43 \pm 1.41	26.68 (2b)	32.83 (1s)	30.35 \pm 1.54
Dissolved Oxygen (μ M)	40.83 (8b)	265.41 (5s)	175.16 \pm 46.46	107.95 (10b)	225.08 (1s)	169.27 \pm 20.03	71.46 (10b)	238.86 (8s)	163.39 \pm 26.87
Nitrate (μ M)	ND (9s,b)	16.1 (2b)	6.27 \pm 3.98	ND (6,10s)	12.93 (2s)	3.21 \pm 2.08	ND (6,7,8,9s)	9.68 (2b)	2.31 \pm 2.22
Nitrite (μ M)	ND (4,9b)	6.39 (3b)	1.08 \pm 1.31	0.06 (1s)	11.06 (5s)	2.47 \pm 3.05	0.04 (8s)	6.47 (4b)	1.56 \pm 1.69
Phosphate (μ M)	0.05 (2s)	3.63 (5s)	1.09 \pm 0.59	0.15 (2s)	1.96 (4b)	0.88 \pm 0.29	ND (4s,9b)	2.44 (7b)	1.04 \pm 0.42
Silicate (μ M)	3.16 (9s)	128.18 (5s)	51.51 \pm 37.68	4.28 (10s)	123.99 (1s)	46.37 \pm 35.24	4.47 (8s)	101.46 (2s)	40.55 \pm 29.53

Monsoon – June to September; Postmonsoon – October to January; Premonsoon – February to May

* - Total amount of rainfall received during monsoon is 2976 mm, postmonsoon is 50 mm and premonsoon is 30 mm in 2008-2009

ND - Non Detectable

1,2,3,4,5,6,7,8,9,10- The numbers given in brackets represent the station number and alphabets (s,b) represent surface and bottom waters

Table 7. Coefficients of correlation among various parameters studied in the Zuari estuary. Both daily and transect data were used in this statistical analysis. P-values listed in the table were calculated using online p-value calculator from <http://graphpad.com/quickcalcs/PValue1.cfm>

	Rainfall	Salinity	Temperature	Dissolved Oxygen	Nitrate + Nitrite	Nitrite	Nitrate	Phosphate	Silicate
Rainfall (n=224)	1	-0.61 ^e	-0.41 ^e	0.40 ^e	0.34 ^e	-0.19 ^v	0.50 ^e	-0.06 ⁿ	0.51 ^e
Salinity (n=631)		1	0.22 ^e	-0.49 ^e	-0.33 ^e	0.17 ^e	-0.50 ^e	0.09 ^s	-0.86 ^e
Temperature (n=631)			1	-0.31 ^e	-0.30 ^e	-0.03 ⁿ	-0.34 ^e	-0.09 ^s	-0.28 ^e
Dissolved Oxygen (n=609)				1	0.11 ^v	-0.20 ^e	0.26 ^e	-0.11 ^v	0.48 ^e
Nitrate + Nitrite (n=632)					1	0.55 ^e	0.84 ^e	0.19 ^e	0.30 ^e
Nitrite (n=632)						1	0.02 ⁿ	0.04 ⁿ	-0.17 ^e
Nitrate (n=632)							1	0.21 ^e	0.47 ^e
Phosphate (n=631)								1	-0.02 ⁿ
Silicate (n=632)									1

Levels of significance (p-value)

e= Extremely significant (p < 0.0001)

v= Very significant (p < 0.01)

s = Significant (p < 0.1)

n= Not significant (p > 0.1)

Table 8. Same as in Table 4 but for entire Zuari estuary (based on transect observations).

Parameter	Monsoon 2008		Monsoon 2008-09			Postmonsoon			Premonsoon			Annual	
	F1	F2	F1	F2	F3	F1	F2	F3	F1	F2	F3	F1	F2
Salinity	-0.895	-0.197	-0.932	0.096	0.046	-0.922	0.17	0.169	0.958	0.017	-0.168	-0.909	0.12
Temperature	0.622	-0.36	-0.036	-0.829	0.276	0.014	-0.069	0.922	-0.111	0.851	-0.384	-0.329	-0.508
Oxygen	0.899	0.067	0.757	-0.243	-0.343	0.435	-0.305	-0.593	-0.24	-0.877	-0.246	0.644	-0.153
Nitrate	0.35	0.849	0.748	0.321	0.478	0.751	0.274	0.05	-0.156	0.056	0.785	0.615	0.513
Nitrite	-0.743	0.166	-0.211	-0.114	0.915	-0.053	0.834	-0.143	0.03	-0.106	0.716	-0.157	0.564
Phosphate	-0.282	0.813	-0.049	0.816	0.149	0.003	0.823	0.234	0.63	0.122	0.314	-0.257	0.665
Silicate	0.77	0.03	0.846	0.12	-0.221	0.926	-0.152	-0.106	-0.922	-0.023	0.21	0.9	-0.048

Table 9. Factor analysis to understand relations and controlling parameters for variables studied in Figure 9.

Parameter	F1	F2	F3	F4
Salinity	-0.905	0.260	0.089	0.207
Temperature	-0.218	-0.068	0.893	-0.082
Nitrate	0.643	0.363	0.027	0.261
Nitrite	-0.096	0.831	-0.016	-0.211
Phosphate	-0.197	0.735	0.047	-0.077
Silicate	0.877	-0.271	-0.008	-0.247
Chlorophyll	0.370	0.106	0.773	0.276
Phaeophytin	0.251	0.658	-0.556	0.193
Oxygen Saturation	-0.194	-0.223	0.036	0.873

Table 10. Available information as reported on physical, dissolved oxygen and nutrients in the Zuari estuary.

Year	Month	Salinity	Temperature (°C)	Oxygen (ml L ⁻¹)	Nitrate (µM)	Nitrite (µM)	Phosphate (µM)	Silicate (µM)	Reference
1968, 1969	Aug, Feb	12.3-32.4	24.5-28	2.8-4.7			0.3-1.75		Dehadrai, P.V., 1969
1971, 1972	Aug 1971 Feb, Apr 1972	4.31-36.42	26.2-31.4	3.01-5.71	0.64-2.86		0.32-2.37	3.85-69.83	Singbal, S.Y.S., 1973
1974-1975	June 1974 – Sep 1975	9.0-34.0	23.5-32	2.8-6.0	0-8.5		0.4-2.1		De Sousa, 1977
1975	Feb, Apr, Jun, Aug, Oct, Dec	4-34	25.5-31.5	3.2 – 5.5	0.2- 5.8		0.3-1.7	5-90	Singbal, 1985
1977-1978	Oct 1977 – Sep 1978				0.5-13		0.5-3	10-160	DeSousa et al., 1981
1977-1978	Oct 1977- Sept 1978	2-35	24.5-31.5	3-5.5	0.5-13.5		0.5 - 2.5	5-210	Qasim and Sen Gupta, 1981
1977-1978	Oct.1977 – Sep 1978			6.2-8.2	0.06-0.26 (mg L ⁻¹)				Sen Gupta & Singbal, 1985
1980	Feb 1980 – Oct 1981	0-32		1.2 – 6					De Sousa & Sen Gupta, 1986
2002, 2003	Apr, May, Sept 2002, Mar 2003				0.2 – 5.9		ND - 1.25		Sardessai and Sundar, 2007
2003, 2004	Sep 2003- Apr 2004	22.2-34.9		1.5-7.5 (mg L ⁻¹)	0-6.3	0.1-3.0	0.1-13.8	0.5-714	Shirodkar et al., 2012
2008-2009	June 2008- June 2009	0.04-36.14	23.53-33.01	40.83-265.41(µM)	ND-16.1	ND-11.71	ND-3.63	3.2-128.2	This Study

SUPPLEMENTARY INFORMATION

Supplementary Table 1. Results of correlation analyses between various parameters carried out through Spearman's (not-normally distributed data) and Pearson's (normally distributed data) tests.

Supplementary Table 2. Daily, weekly and seasonal averages (\pm SD) of various properties studied at station 6 in the Zuari estuary.

Supplementary Figure 1. Relations for nutrients and dissolved oxygen with rainfall at for summer monsoon period of 2008 only. The lines shown are linear regression lines. Correlation coefficients (r) and slopes (s) are listed.

Supplementary Figure 2. Longitudinal distributions of physical, oxygen and nutrient properties in surface and bottom waters of the Zuari estuary during Spring and Neap tides each month. Parameters shown are: (a) Salinity, (b) temperature, (c) dissolved oxygen, (d) nitrate, (e) nitrite, (f) phosphate and (g) silicate. Averages along with SD, computed based on the monthly variability at each station in surface and bottom waters during spring and neap tides are shown in Figure 8 to depict the mean seasonal trends.

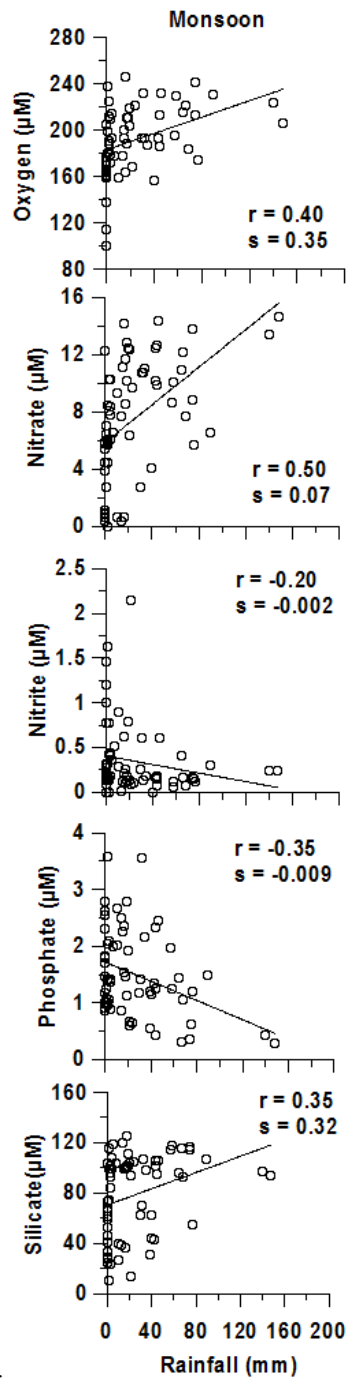
Supplementary Table 1. Results of correlation analyses between various parameters carried out through Spearman's (not-normally distributed data) and Pearson's (normally distributed data) tests.

S.No	Parameter	Spearman's (r)	Significant at $\alpha=0.05$	Pearson's (r)	Significant at $\alpha=0.05$
Regular Station					
1	Salinity Vs DO	-0.615	Y	-0.678	Y
2	Salinity Vs Nitrate	-0.514	Y	-0.653	Y
3	Salinity Vs Nitrite	0.457	Y	0.342	Y
4	Salinity Vs Phosphate	-0.089	N	-0.184	Y
5	Salinity Vs Silicate	-0.858	Y	-0.886	Y
6	Temperature Vs DO	-0.445	Y	-0.485	Y
7	Temperature Vs Nitrate	-0.440	Y	-0.428	Y
8	Temperature Vs Nitrite	0.262	Y	0.095	N
9	Temperature Vs Phosphate	-0.116	N	-0.129	N
10	Temperature Vs Silicate	-0.448	Y	-0.529	Y
11	Rainfall Vs DO	0.436	Y	0.204	N
12	Rainfall Vs Nitrate	0.494	Y	0.374	Y
13	Rainfall Vs Nitrite	-0.179	N	0.118	N
14	Rainfall Vs phosphate	-0.243	Y	-0.251	Y
15	Rainfall Vs silicate	0.347	Y	0.188	N
Transect					
16	Salinity Vs DO	-0.403	Y	-0.429	Y
17	Salinity Vs Nitrate	-0.476	Y	-0.471	Y
18	Salinity Vs Nitrite	0.101	Y	0.097	N
19	Salinity Vs Phosphate	0.224	Y	0.218	Y
20	Salinity Vs Silicate	-0.864	Y	-0.849	Y
21	Temperature Vs DO	-0.360	Y	-0.227	Y
22	Temperature Vs Nitrate	-0.305	Y	-0.227	Y
23	Temperature Vs Nitrite	-0.037	N	-0.095	N
24	Temperature Vs Phosphate	0.010	N	-0.019	N
25	Temperature Vs Silicate	-0.127	Y	-0.165	Y
26	DO Vs Phosphate	-0.203	Y	-0.189	Y
27	DO Vs Silicate	0.347	Y	0.418	Y

Supplementary Table 2. Daily, weekly and seasonal averages (\pm SD) of various properties studied at station 6 in the Zuari estuary. Average is indicated as Avg.

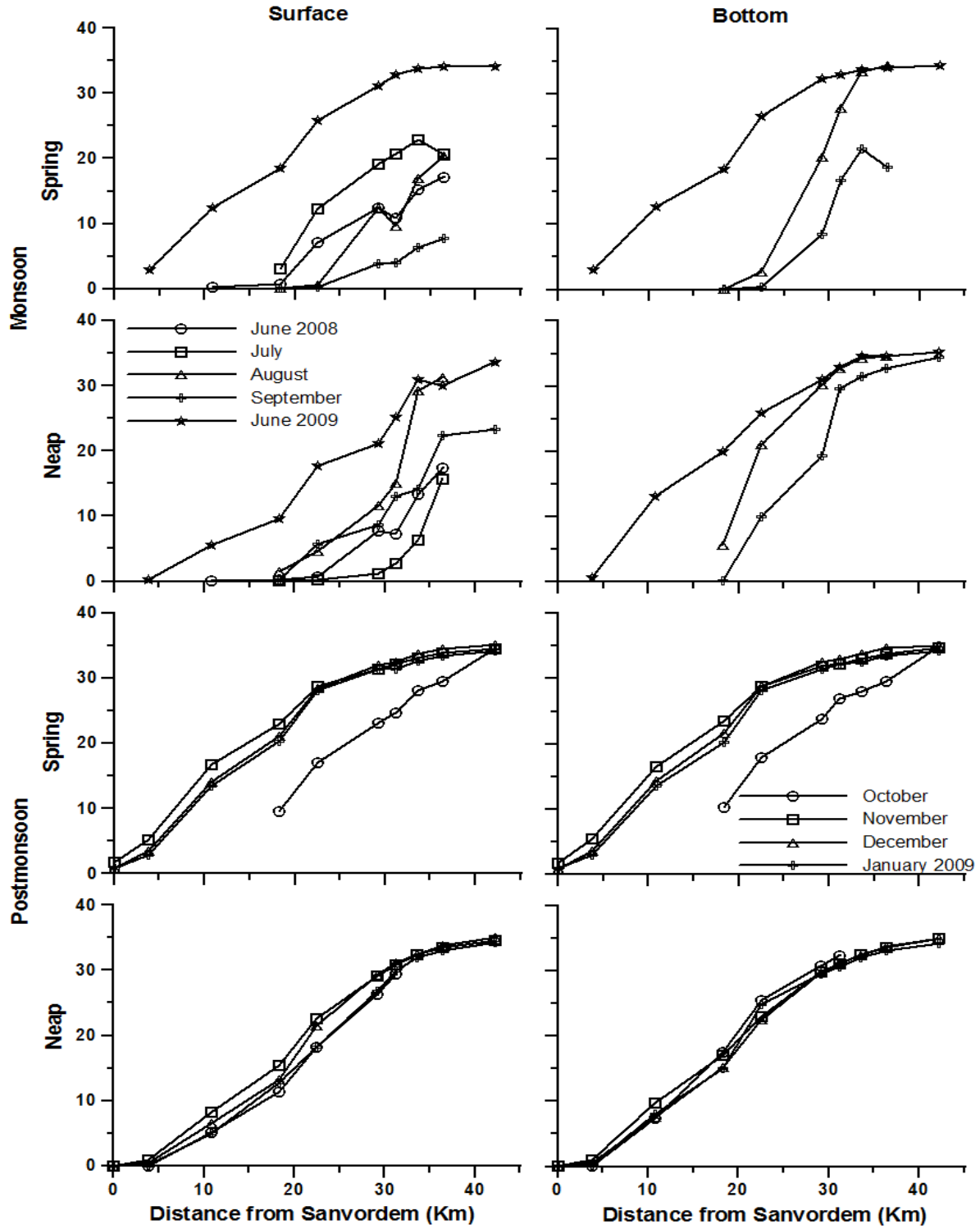
	Rainfall (mm)	Salinity	Temperature ($^{\circ}$ C)	Oxygen (μ M)	Nitrate (μ M)	Nitrite (μ M)	Phosphate (μ M)	Silicate (μ M)
Daily Avg	12.4 \pm 28.2	21.5 \pm 11.0	29.0 \pm 1.6	171 \pm 26	4.4 \pm 4.1	1.89 \pm 2.35	1.21 \pm 0.57	43.2 \pm 30.4
Week 1	28.8 \pm 23.7	1.6 \pm 0.9	27.0 \pm 0.7	201 \pm 18	10.6 \pm 1.4	0.13 \pm 0.04	1.19 \pm 0.67	102.2 \pm 7.7
2	89.6 \pm 39.6	0.1 \pm 0.2	25.9 \pm 0.4	222 \pm 12	12.0 \pm 2.7	0.24 \pm 0.09	0.68 \pm 0.54	103.1 \pm 10.0
3 (S)	17.9 \pm 15.8	8.3 \pm 4.7	26.9 \pm 0.7	219 \pm 22	10.7 \pm 3.2	0.62 \pm 0.13	2.07 \pm 0.53	98.8 \pm 13.0
4 (N)	1.3 \pm 1.4	16.4 \pm 6.6	28.1 \pm 0.7	188 \pm 46	4.6 \pm 2.3	0.17 \pm 0.05	1.08 \pm 0.21	79.1 \pm 21.5
5	4.2 \pm 6.6	26.1 \pm 0.9	28.2 \pm 0.4	160 \pm 22	0.7 \pm 0.4	0.18 \pm 0.09	1.62 \pm 0.28	31.8 \pm 5.8
6	32.5 \pm 30.9	18.9 \pm 7.9	28.2 \pm 0.7	179 \pm 17	3.0 \pm 2.9	0.08 \pm 0.09	1.05 \pm 0.15	51.8 \pm 23.9
7 (S)	37.3 \pm 16.6	4.9 \pm 1.9	27.2 \pm 0.7	203 \pm 15	10.4 \pm 0.9	0.14 \pm 0.04	1.98 \pm 0.83	107.5 \pm 7.2
8 (N)	6.4 \pm 6.5	6.0 \pm 2.1	28.3 \pm 0.7	188 \pm 6	7.8 \pm 1.5	0.28 \pm 0.14	1.63 \pm 0.55	110.2 \pm 14.3
9	0.1 \pm 0.3	24.4 \pm 2.3	28.8 \pm 0.3	162 \pm 12	5.6 \pm 3.1	0.99 \pm 0.37	2.56 \pm 0.43	53.5 \pm 11.4
10	3.9 \pm 8.9	20.3 \pm 3.3	29.5 \pm 0.6	175 \pm 11	2.1 \pm 1.0	0.71 \pm 0.47	1.14 \pm 0.92	56.8 \pm 10.5
11 (S)	1.3 \pm 1.7	27.3 \pm 3.1	30.1 \pm 0.5	155 \pm 17	1.5 \pm 1.0	0.38 \pm 0.20	1.49 \pm 0.53	30.0 \pm 12.5
12 (N)	0.5 \pm 0.8	27.5 \pm 2.4	30.3 \pm 0.3	146 \pm 14	2.9 \pm 0.9	0.5 \pm 0.16	1.36 \pm 0.69	32.1 \pm 9.5
13	0.5 \pm 1.2	29.9 \pm 1.3	29.8 \pm 0.3	157 \pm 6	10.4 \pm 3.3	3.29 \pm 2.58	0.96 \pm 0.12	25.9 \pm 3.9
14	0.0 \pm 0.0	28.8 \pm 1.3	29.7 \pm 0.2	163 \pm 29	5.9 \pm 3.8	0.83 \pm 0.68	0.78 \pm 0.15	29.2 \pm 4.6
15 (S)	0.0 \pm 0.0	30.7 \pm 0.9	29.5 \pm 0.2	174 \pm 8	1.9 \pm 1.2	0.41 \pm 0.25	0.90 \pm 0.05	21.1 \pm 4.3
16 (N)	0.0 \pm 0.0	30.0 \pm 1.6	28.9 \pm 0.5	161 \pm 16	2.5 \pm 1.8	4.09 \pm 3.89	1.02 \pm 0.27	27.7 \pm 6.0
17	0.0 \pm 0.0	30.9 \pm 0.8	29.4 \pm 0.7	154 \pm 2	5.9 \pm 3.2	5.55 \pm 0.99	1.07 \pm 0.13	19.3 \pm 6.9
18	1.6 \pm 3.2	30.2 \pm 1.3	28.9 \pm 0.5	155 \pm 7	4.4 \pm 2.4	9.12 \pm 1.95	1.19 \pm 0.05	18.4 \pm 4.3
19	0.0 \pm 0.0	30.2 \pm 2.1	28.6 \pm 0.3	161 \pm 12	3.4 \pm 3.7	6.1 \pm 2.01	0.90 \pm 0.18	18.8 \pm 2.9
20 (S,N)	0.0 \pm 0.0	31.0 \pm 1.4	27.7 \pm 0.4	156 \pm 8	4.0 \pm 1.0	7.12 \pm 1.40	1.12 \pm 0.12	21.4 \pm 5.3
21	0.0 \pm 0.0	29.3 \pm 2.4	27.5 \pm 0.2	169 \pm 5	4.5 \pm 1.4	7.01 \pm 1.42	1.09 \pm 0.08	31.4 \pm 6.1
22	0.0 \pm 0.0	30.8 \pm 1.0	26.8 \pm 0.1	155 \pm 4	3.8 \pm 0.5	3.23 \pm 0.56	1.03 \pm 0.19	24.7 \pm 0.9
23	0.0 \pm 0.0	28.6 \pm 2.1	27.1 \pm 0.2	166 \pm 8	1.4 \pm 1.4	1.57 \pm 1.75	0.68 \pm 0.12	30.6 \pm 1.1
24 (S)	0.0 \pm 0.0	30.0 \pm 2.0	27.2 \pm 0.4	152 \pm 10	1.9 \pm 1.3	0.70 \pm 0.25	1.06 \pm 0.22	19.9 \pm 2.6
25 (N)	0.0 \pm 0.0	26.1 \pm 2.8	27.1 \pm 0.4	171 \pm 24	1.5 \pm 0.7	1.43 \pm 0.72	0.72 \pm 0.05	28.9 \pm 2.8
26	0.0 \pm 0.0	31.3 \pm 0.7	27.8 \pm 0.6	165 \pm 21	1.2 \pm 0.4	0.56 \pm 0.41	1.09 \pm 0.33	27.1 \pm 1.2
27	0.0 \pm 0.0	26.8 \pm 2.5	28.7 \pm 0.2	181 \pm 19	1.9 \pm 0.4	4.13 \pm 1.46	1.42 \pm 0.06	31.4 \pm 5.0
28 (S)	0.0 \pm 0.0	31.1 \pm 0.7	28.2 \pm 0.4	168 \pm 9	2.9 \pm 0.9	1.85 \pm 0.54	1.39 \pm 0.18	24.4 \pm 4.5
29 (N)	0.0 \pm 0.0	26.2 \pm 1.7	28.1 \pm 0.3	201 \pm 29	2.3 \pm 0.5	3.71 \pm 1.65	1.04 \pm 0.29	35.6 \pm 4.9
30	0.0 \pm 0.0	31.4 \pm 0.1	28.9 \pm 0.2	201 \pm 25	1.4 \pm 0.1	0.85 \pm 0.25	1.32 \pm 0.55	20.5 \pm 2.9

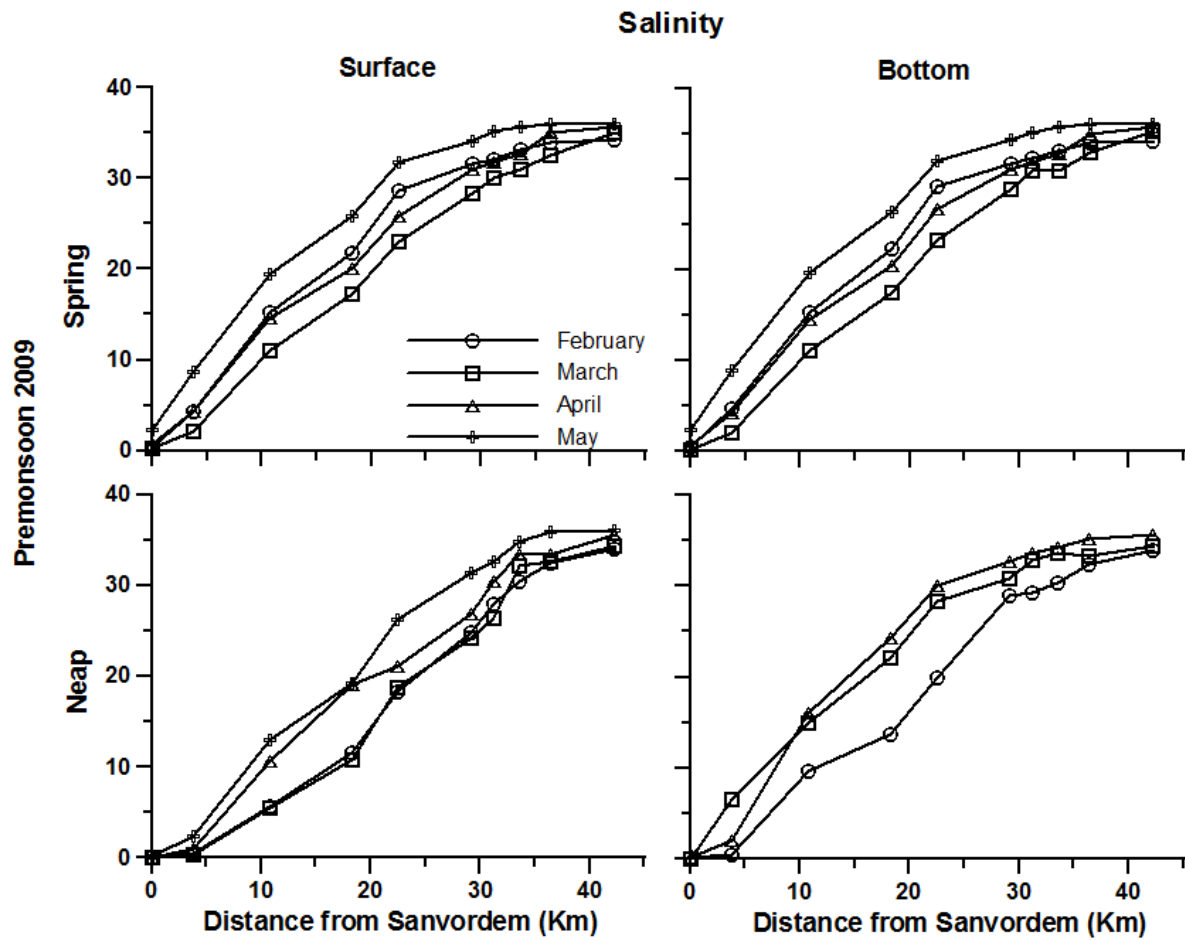
31	0.0 ± 0.0	27.4 ± 2.7	30.2 ± 0.4	158 ± 16	1.9 ± 0.3	2.71 ± 1.06	1.39 ± 0.16	36.6 ± 7.7
32	0.0 ± 0.0	31.5 ± 0.9	30.0 ± 0.2	165 ± 9	2.8 ± 0.5	2.34 ± 1.02	1.22 ± 0.06	24.0 ± 3.4
33 (N)	0.0 ± 0.0	25.8 ± 3.0	30.4 ± 0.2	179 ± 11	1.5 ± 0.7	1.98 ± 2.07	1.01 ± 0.11	37.9 ± 11.9
34 (S)	0.0 ± 0.0	30.6 ± 1.6	30.5 ± 0.3	150 ± 7	1.7 ± 0.6	1.11 ± 0.86	1.05 ± 0.13	26.4 ± 12.8
35	0.0 ± 0.0	28.2 ± 2.6	31.8 ± 0.9	165 ± 20	0.6 ± 0.9	1.05 ± 0.74	0.81 ± 0.23	30.4 ± 8.2
36	0.0 ± 0.0	32.4 ± 0.2	31.8 ± 0.7	157 ± 3	1.1 ± 0.4	0.92 ± 0.48	0.91 ± 0.12	17.4 ± 3.0
37 (N)	0.0 ± 0.0	28.1 ± 2.8	31.3 ± 0.4	186 ± 18	1.1 ± 1.1	1.23 ± 1.45	0.99 ± 0.43	32.6 ± 6.6
38 (S)	0.0 ± 0.0	32.1 ± 1.0	31.4 ± 1.0	148 ± 20	0.9 ± 0.8	1.06 ± 1.00	1.14 ± 0.13	19.8 ± 3.1
39	0.0 ± 0.0	30.5 ± 1.8	32.1 ± 1.8	137 ± 6	1.1 ± 0.8	3.28 ± 1.02	1.28 ± 0.24	27.7 ± 6.0
40	0.0 ± 0.0	34.0 ± 0.3	32.0 ± 0.3	146 ± 4	0.3 ± 0.1	1.28 ± 0.29	0.83 ± 0.1	18.1 ± 1.0
41	0.0 ± 0.0	31.5 ± 2.2	31.4 ± 2.2	165 ± 12	0.4 ± 0.4	1.60 ± 1.09	0.87 ± 0.19	18.6 ± 4.6
42 (N)	7.6 ± 15.2	32.3 ± 1.2	31.5 ± 1.2	159 ± 14	0.6 ± 0.7	0.89 ± 0.72	0.95 ± 0.14	20.2 ± 2.9
43 (S)	0.3 ± 0.5	32.4 ± 1.3	31.9 ± 1.3	138 ± 15	7.2 ± 3.3	5.16 ± 3.79	1.37 ± 0.20	22.6 ± 3.8
44	66.0 ± 124.7	28.4 ± 6.4	30.2 ± 6.4	148 ± 6	7.1 ± 7.5	3.35 ± 1.99	1.02 ± 0.08	29.9 ± 10.7
45	11.6 ± 10.5	20.9 ± 3.3	30.3 ± 3.3	173 ± 3	13.1 ± 0.8	4.75 ± 1.42	0.87 ± 0.15	40.2 ± 5.1
46(N,S)	20.2 ± 15.2	27.0 ± 4.3	30.3 ± 4.3	156 ± 11	4.8 ± 3.9	2.19 ± 2.04	0.80 ± 0.34	25.3 ± 11.0
Range of weekly Avg (in a year)	0.0 - 89.6	0.12 - 34.02	25.9 - 31.88	137 - 221	0.29 - 13.08	0.08 - 9.12	0.68 - 2.56	17.4 - 110.2
Std Dev range of weekly Avg (in a year)	0.0 - 124.7	0.2 - 7.9	0.1 - 6.4	20 - 46	0.1 - 7.5	0.04 - 3.89	0.05 - 1.12	0.9 - 23.9
Range of weekly Avg (monsoon)	0.1 - 89.6	0.1 - 28.4	25.9 - 30.3	148 - 221	0.78 - 13.1	0.08 - 4.75	0.68 - 2.56	25.3 - 110.2
Std Dev range of weekly Avg (monsoon)	0.3 - 124.7	0.2 - 7.9	0.3 - 6.4	3 - 46	3.1 - 7.5	0.04 - 2.04	0.08 - 0.83	5.1 - 23.9
Monsoon Avg	25.0 ± 32.0	11.0 ± 9.2	28.0 ± 1.1	191 ± 15	7.5 ± 4.1	0.34 ± 0.40	1.50 ± 0.80	80.0 ± 33.0
Postmonsoon Avg	0.6 ± 3.0	28.4 ± 3.5	28.8 ± 1.2	161 ± 15	3.6 ± 3.1	2.74 ± 3.02	1.10 ± 0.50	29.0 ± 12.0
Premonsoon Avg	0.5 ± 4.0	29.9 ± 3.1	30.6 ± 1.4	165 ± 24	1.7 ± 1.6	2.10 ± 1.79	1.10 ± 0.30	27.0 ± 9.0



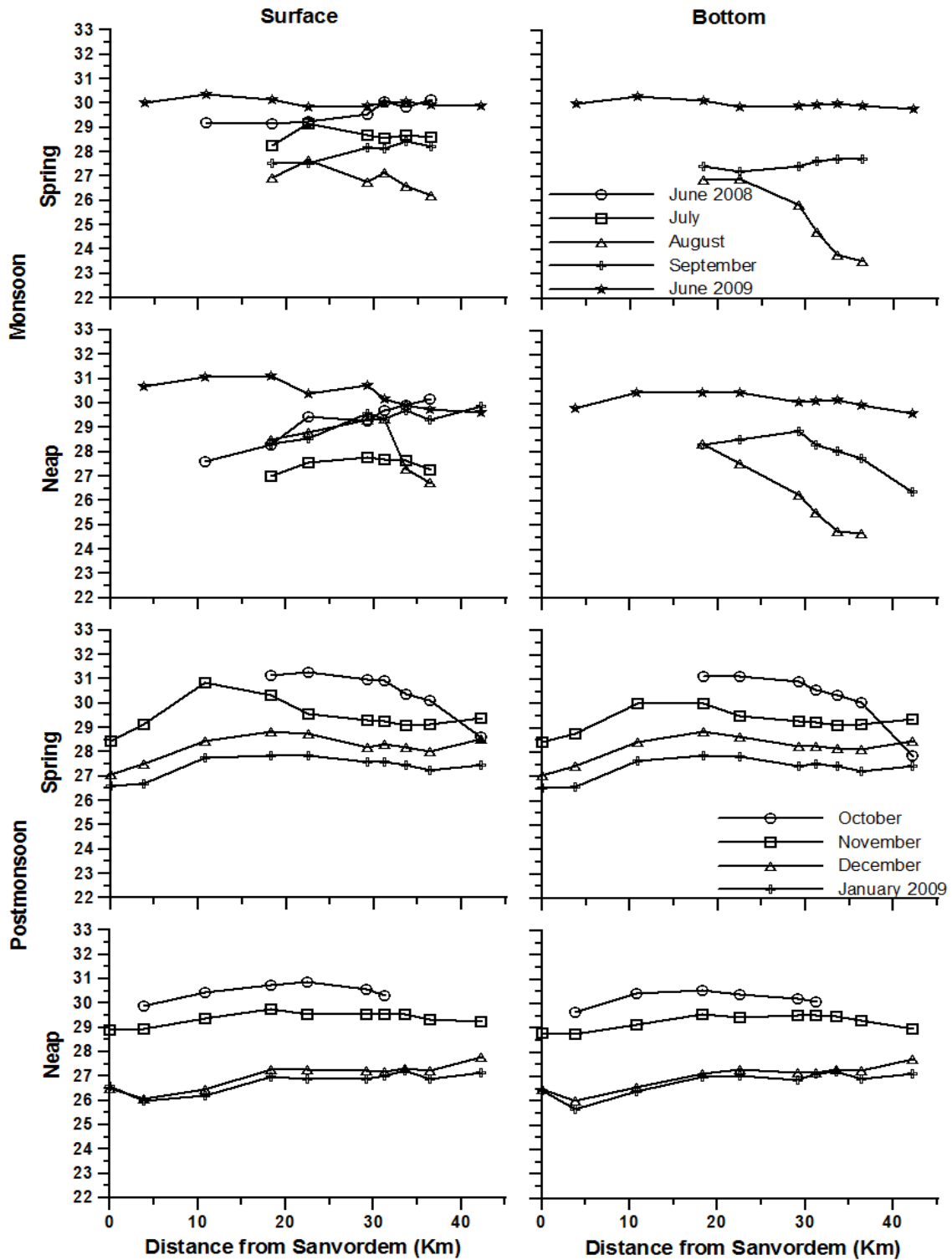
Supplementary Figure. 1

(a) Salinity

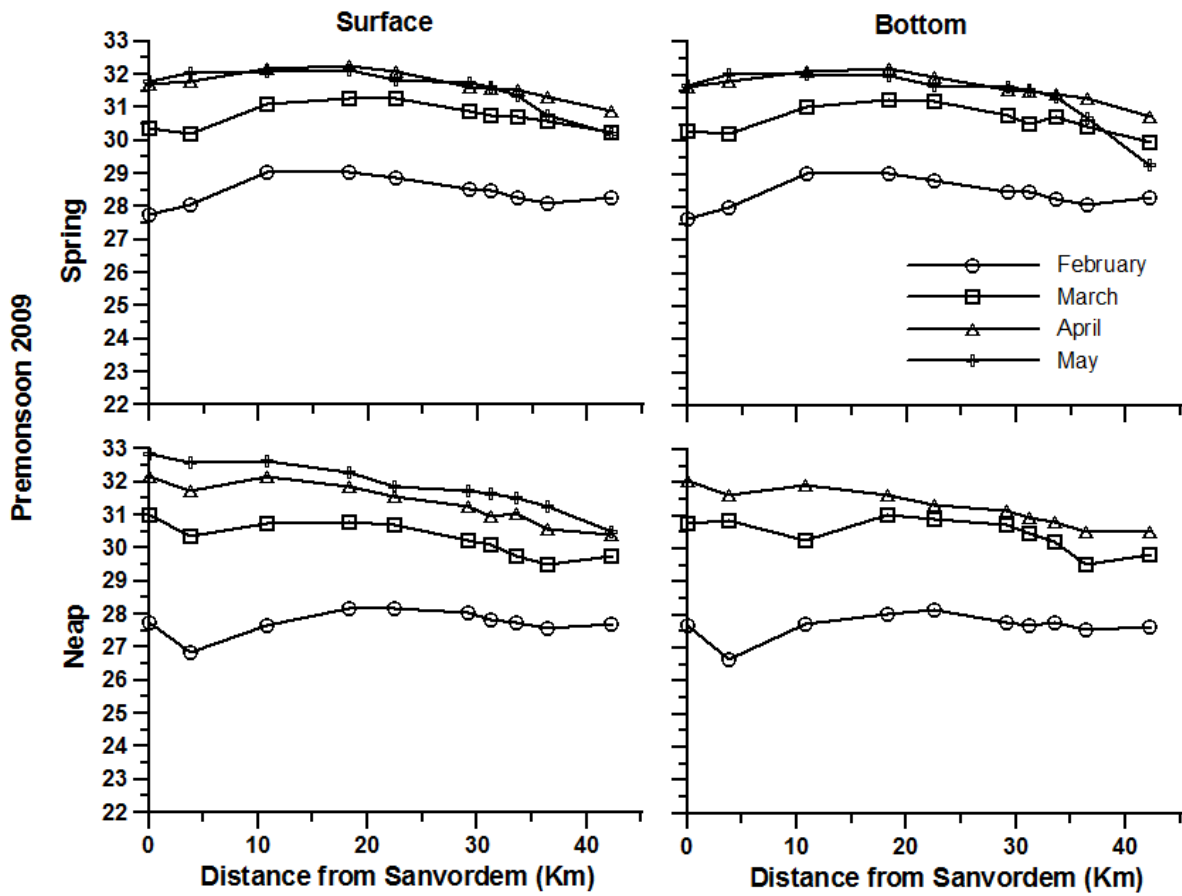




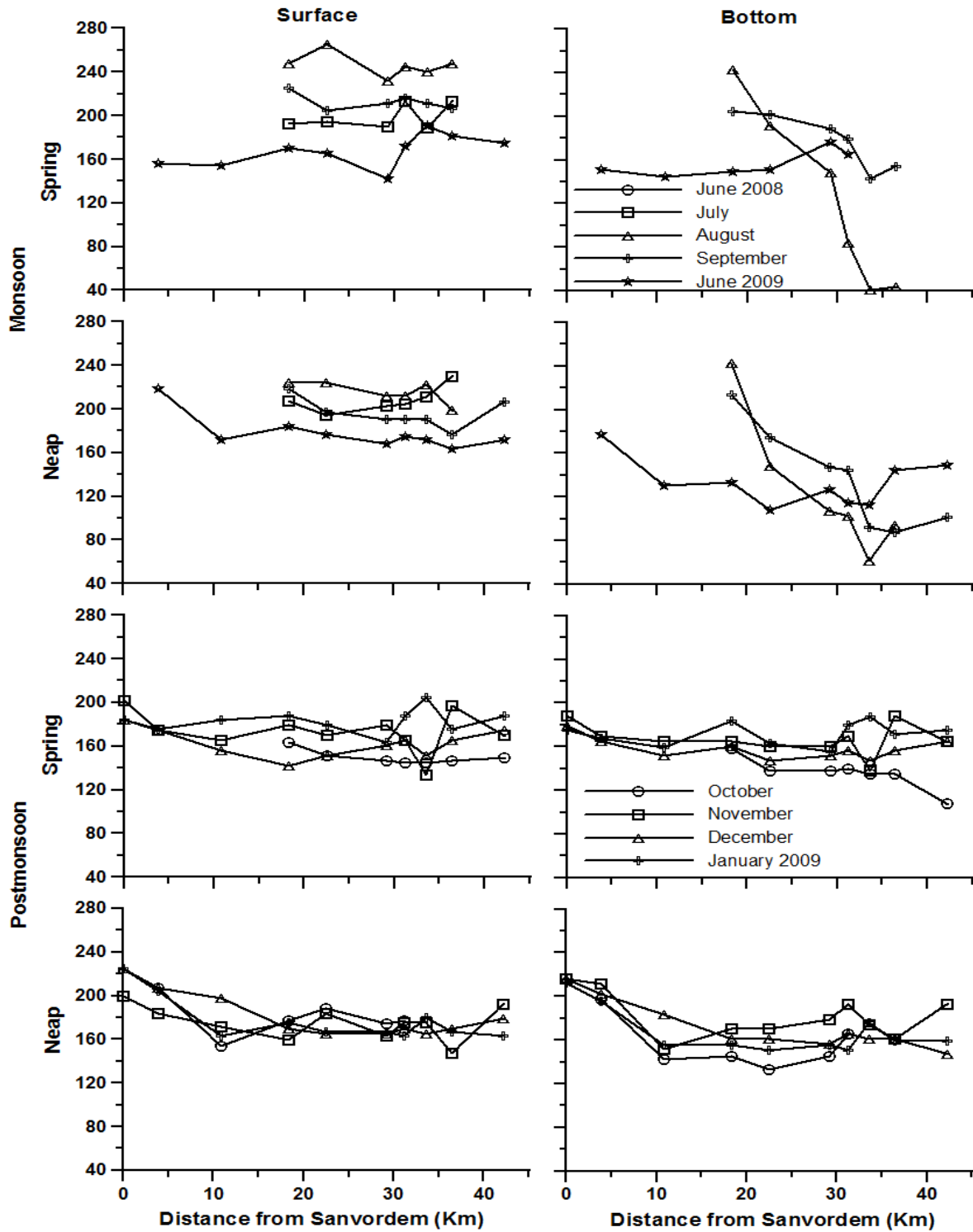
(b) Temperature (°C)



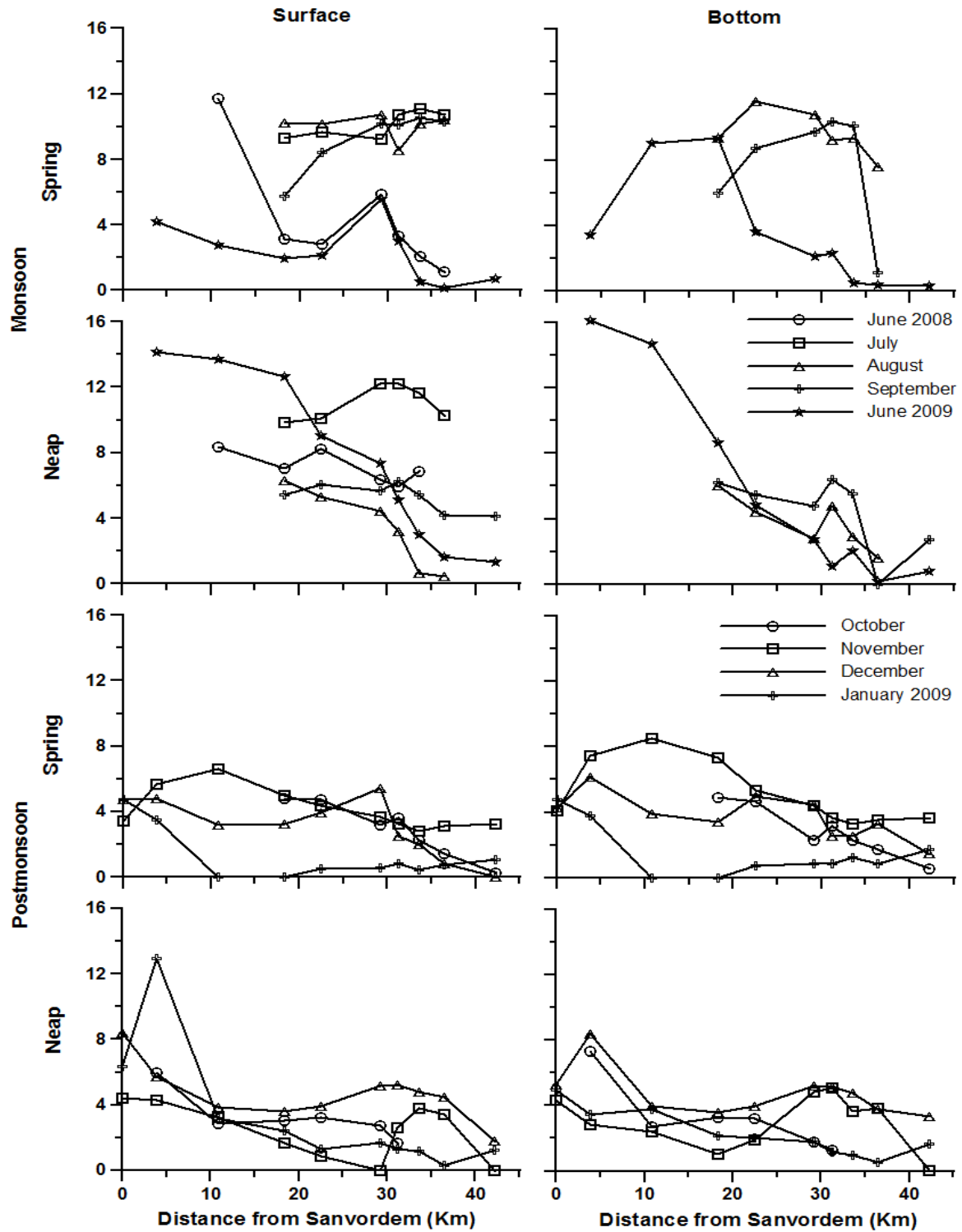
Temperature (°C)



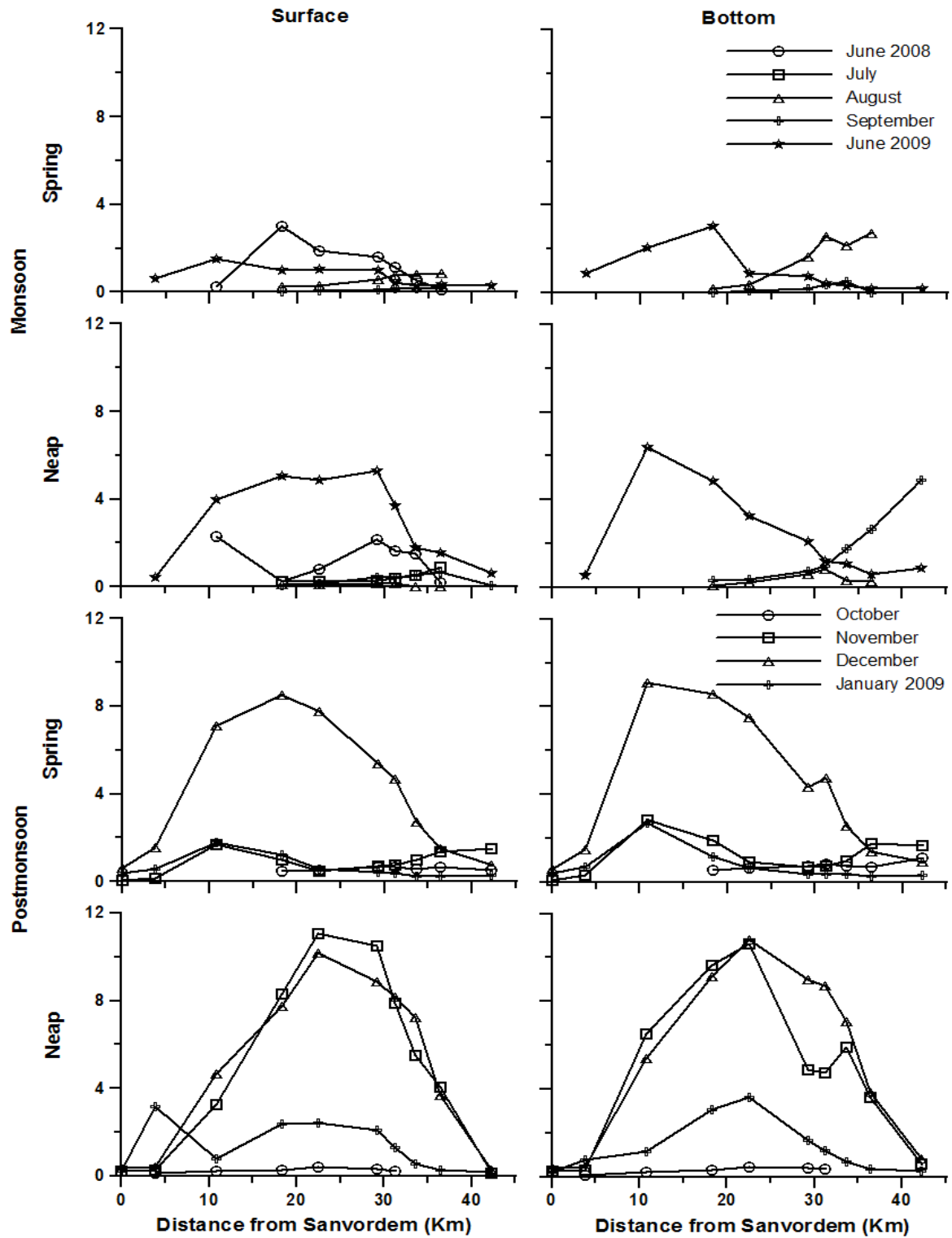
(c) Oxygen (μM)



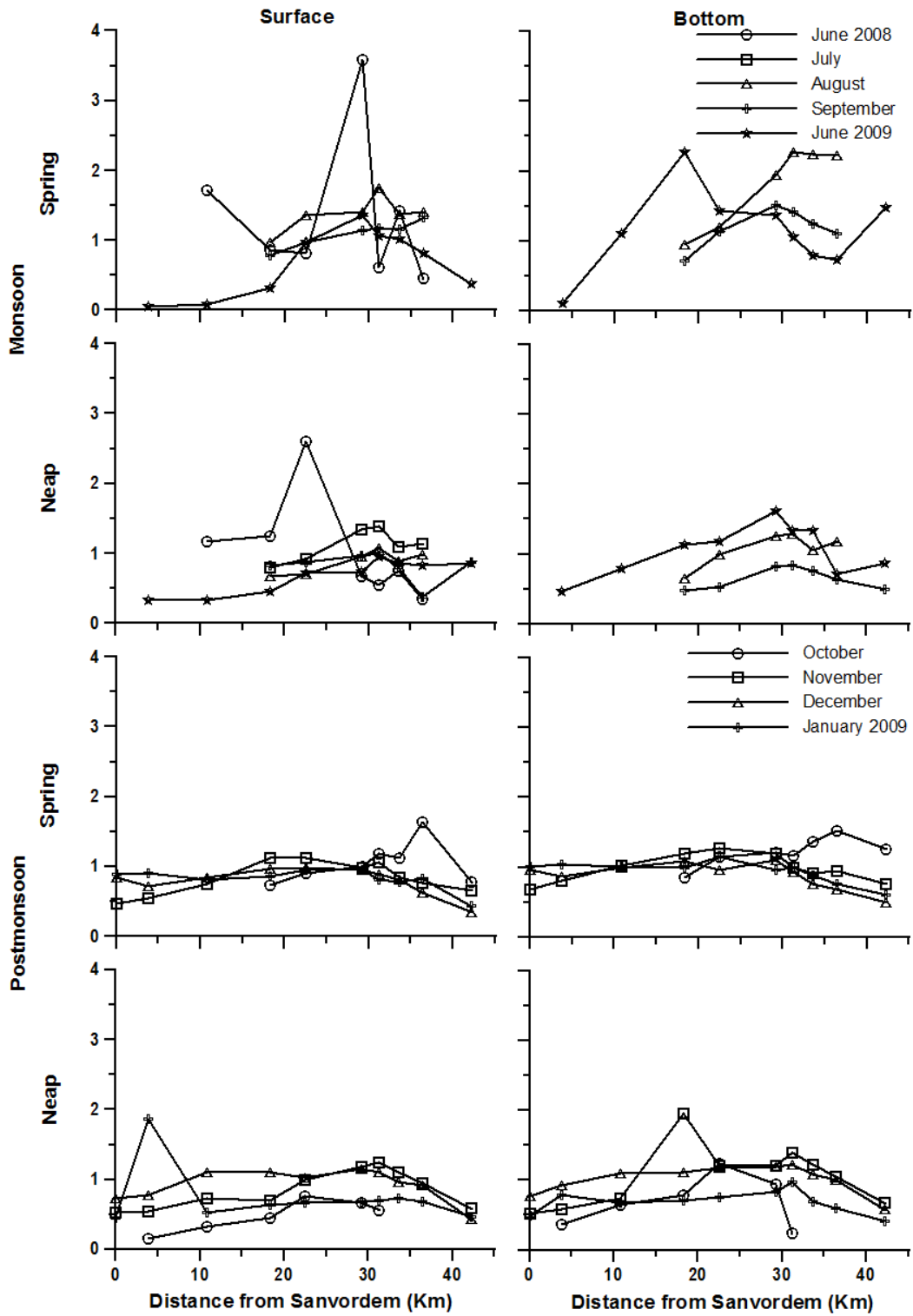
(d) Nitrate (μM)



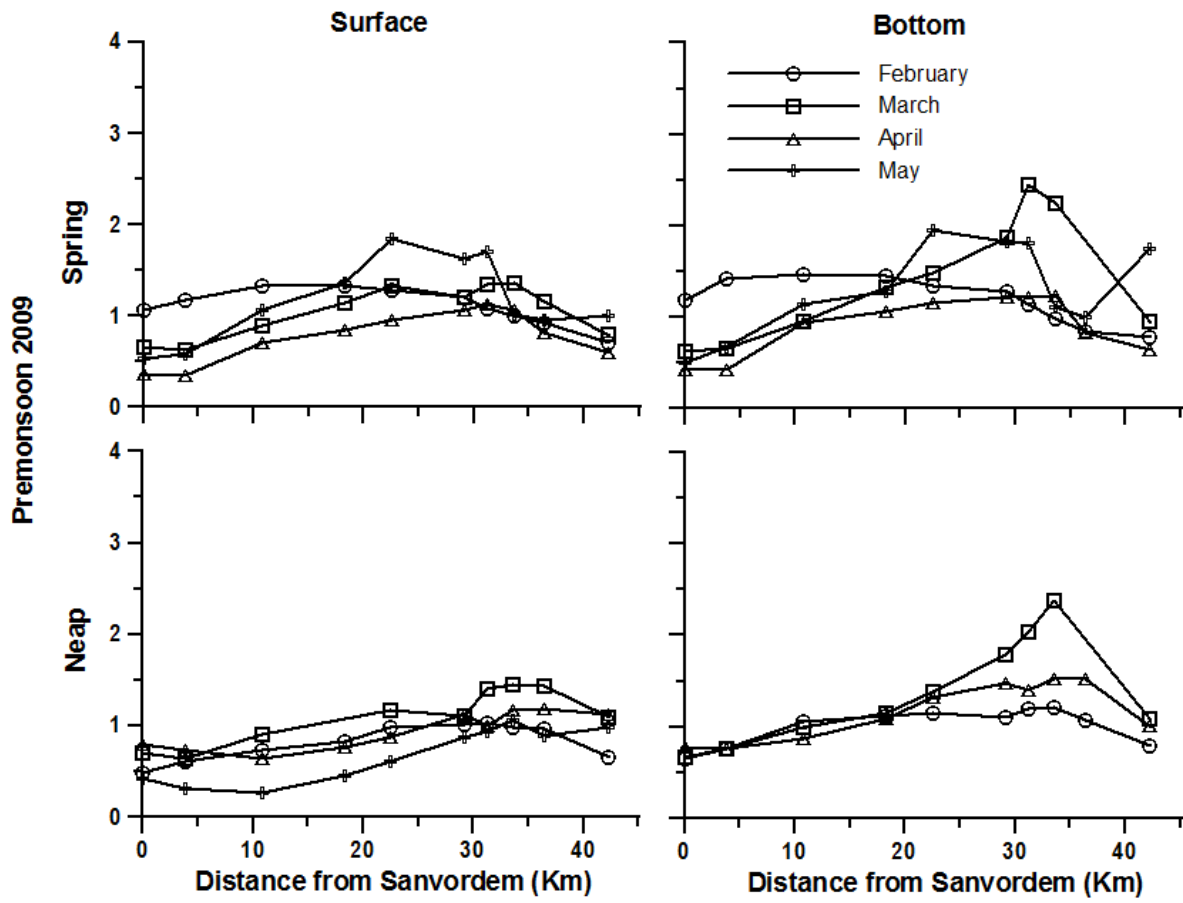
(e) Nitrite (μM)



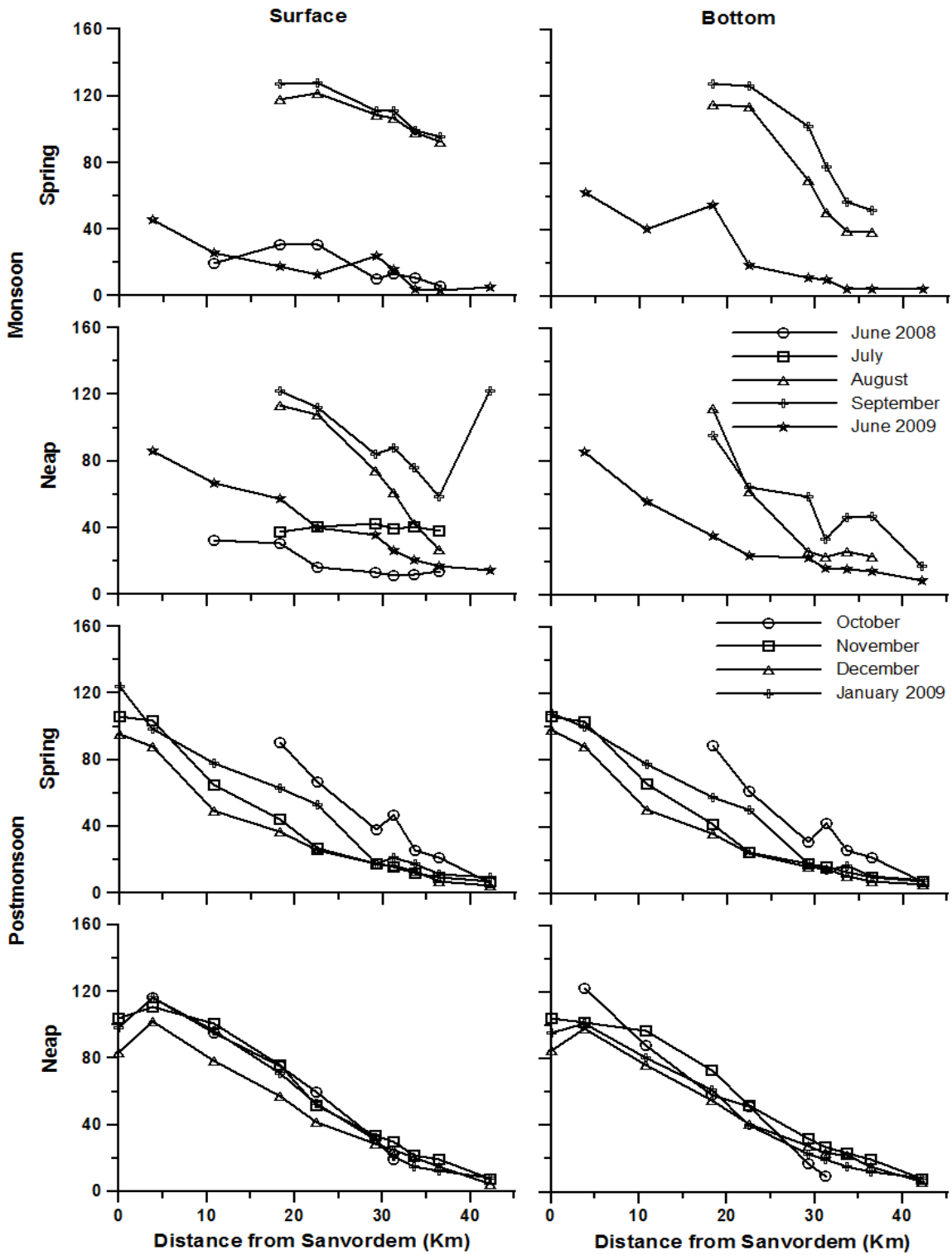
(f) Phosphate (μM)

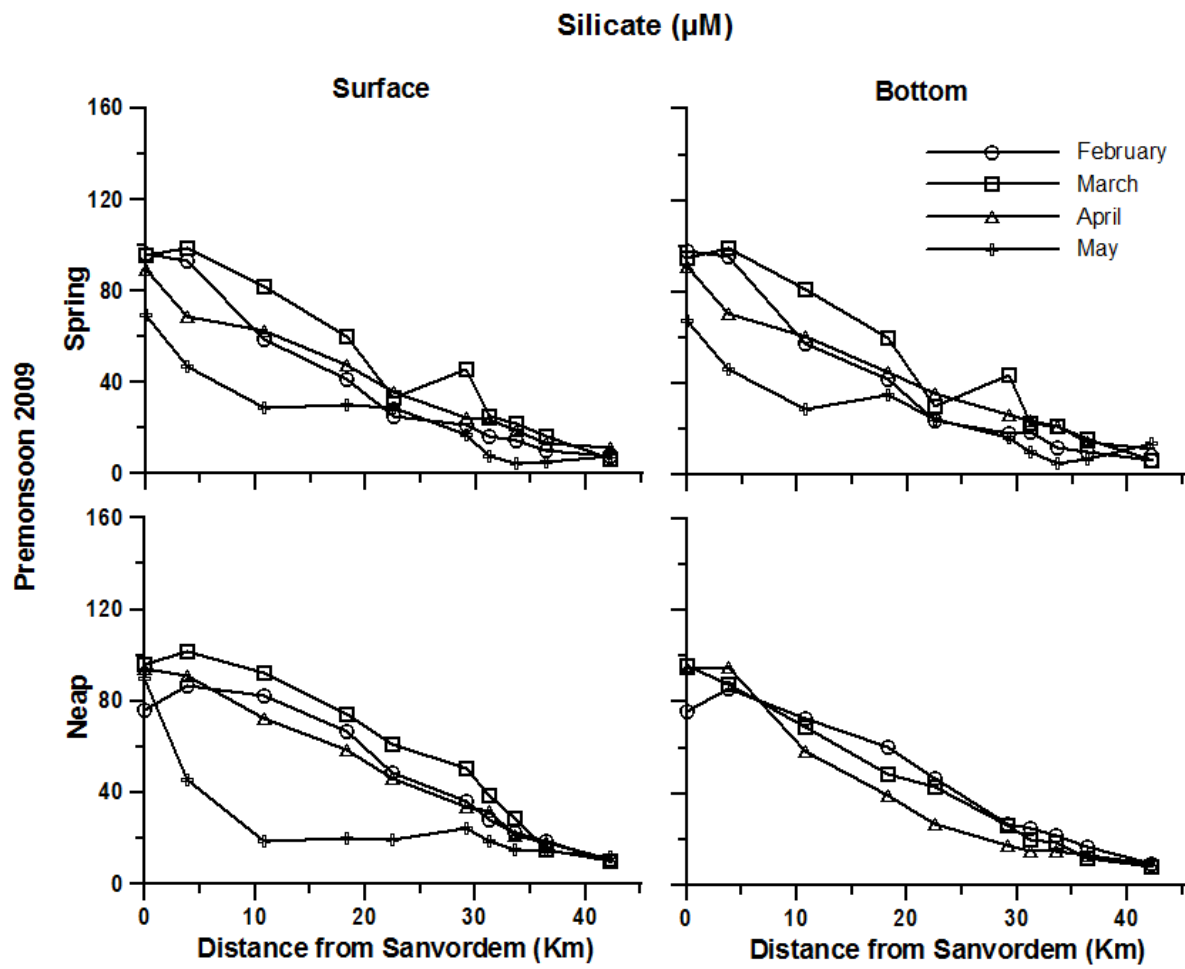


Phosphate (μM)



(g) Silicate (μM)





Supplementary Figure. 2