

Intra-annual variability in nutrients in the Godavari Estuary, India

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Abstract

Daily variations in nutrients were monitored for 15 months (September 2007 to November 2008) in the Godavari estuary, Andhra Pradesh, India, at two fixed locations. River discharge has significant influence on nutrients loading to the estuary, which peaks during June to August (peak discharge period; monsoon) whereas exchanges at the sediment-water interface, groundwater and rainwater contribute significantly during other period. Despite significant amount of nutrients brought by discharge to the study region, phytoplankton biomass, in terms of chlorophyll-a (Chl *a*), did not increase significantly due to high suspended load and shallow photic depth. Nutrients showed downward gradient towards downstream of the estuary from upstream due to dilution by nutrient poor seawater and biological uptake. The N:P ratios were higher than Redfield ratio in both upstream and downstream of the estuary during no discharge period suggesting PO₄ to be a limiting nutrient for phytoplankton production, at levels <0.10 μmol L⁻¹. On the other hand, Si:N ratios were always more than unity during entire study period at both the stations indicating that Si(OH)₄ is not a limiting nutrient. Our results suggest that suspended matter limits phytoplankton biomass during peak discharge period whereas PO₄ during no discharge period.

1. Introduction

Estuaries are prominent zones regulating material fluxes from land to sea (Crossland et al. 2005). Capacity of the estuaries in reducing river nutrient loads to shelf seas has been appreciated as one of the most valuable functions of these ecosystems (Costanza et al. 1997). Estuaries receive considerable amounts of freshwater, nutrients, dissolved and particulate organic matter, suspended matter, and contaminants from land and exchange materials and energy with the open ocean. Estuaries also receive nutrients and organic matter loads from wetlands such as marshes (Meybeck 1982; Kemp 1984, Howarth et al. 1996) and mangroves (Odum and Heald 1972; 1975; Twilley 1988; Robertson et al. 1992).

Nitrogen (N), phosphorus (P) and silica ($\text{Si}(\text{OH})_4$) are the key nutrient substances that generally limit phytoplankton growth in natural waters. Increasing evidence (Lewis 1996; Talling and Lemoalle, 1998) shows that N-limitation is a wide spread phenomenon in tropical lakes and rivers., e.g., Mandovi-Zuari (Ram et al., 2003), Cochin estuary (Gupta et al., 2009) and Hoogly estuary (Mukhopadhyay et al., 2006). However, seasonal P limitation has been found in several estuaries (eg. Gle et al. 2008; Xu et al. 2008). Higher rates of nutrient inputs (Nixon et al. 1986) lead to higher organic carbon production (Kelly and Levin 1986) in estuarine ecosystems where the active biological pump transfers significant amounts of organic carbon to the sediments (Wollast 1998; Smith and Hollibaugh 1993). Particulate organic carbon (POC) in the estuary may not be available for metabolic breakdown (Ittekkot and Laane 1991). Nevertheless, the fate of the organic carbon in a coastal ecosystem depends on its origin, composition, and stability of the water column.

Studies have been made in Mandovi-Zuary estuarine system (Ram et al. 2003), Godavari estuary (Bouillon et al. 2003), Hoogly estuary (Mukhopadhyay et al. 2006), Cochin estuaries (Martin et al. 2008) of India to understand seasonal changes in nutrients and organic carbon cycles. The nutrients concentrations were 2 to 3 times higher during peak monsoon (high discharge) period compared to the non-monsoon (no discharge) period in the Mandovi-Zuari estuarine system, however primary production was lower during former than latter period due to high suspended load (Ram et al., 2003). Similar observations were found in the Cochin back waters where river discharge controls the nutrients flux to the estuary during peak discharge period whereas anthropogenic activities (industries) and sediment re-suspension alters the nutrient stoichiometry during non-discharge periods (Martin et al., 2008).

Mukhopadhyay et al. (2006) noticed that out of the total transport of nutrients, 71% of the dissolved inorganic nitrogen (DIN) and 79% of dissolved reactive phosphate and silicate were transported during peak monsoon period in the Hoogly estuary. However, the conventional seasonal observation scheme, involving one or two-time sampling in a season, will not yield adequate information to evaluate controlling factors of nutrient cycles in an estuary due to complexity of processes that significantly vary in time; from daily to intraseasonal time scale and also during the transitions of seasons. It is very important to examine short-term changes in nutrients for sufficiently longer periods, e.g. about a year, at a specific location to understand the sources and cycling of nutrients particularly in tropical monsoon driven estuaries. Therefore, our present attempt aims to understand the processes controlling nutrient abundances in a tropical monsoon estuary in relation to plankton productivity through daily observations over a 15-month period at two locations in Godavari estuarine system in the central east coast of India.

2. Material and methods

2.1. Study area

The Godavari estuarine system is located around 16° 15' N and 82° 5' E covering an area of 330 km². The Godavari is one of the major rivers in India with a basin of 3.1 x 10⁵ km² and 25 tributaries and an annual discharge of 105 km³ (Rao, 1975). This river ranks 34th and 32nd in terms of catchment area and water discharge, respectively, amongst the 60 largest rivers of the world (Ludwig et al. 1996; Gaillardet et al. 1999). The basin climate is generally dry with an average annual rainfall of 1512 mm y⁻¹ of which more than 75% of the annual mean is received during the summer monsoon (June – September; CPCB 1995). The river originates at about 1600 m above the mean sea level near Nasik in the Western Ghats (a continuous mountain chain along the west coast of the peninsular India) and traverses about 1480 km before draining into the Bay of Bengal (Fig. 1). Godavari river serves needs for local agricultural activities and domestic use. Near the town Rajahmundry the river flow is regulated by a century old dam at Dowaleiswaram. After the dam the river is divided into two major distributaries – one flowing towards the east forming the Gautami-Godavari estuary and the other towards the south known as Vasista-Godavari estuary.

The present study was conducted in the Gautami-Godavari estuary, which is the major one between the two estuaries. Poor access facility prevented us from the high intensity sampling study in the Vasista-Godavari estuary. The time-series observations along the Gautami distributary were carried out every

day at two locations, one (Yanam) representing downstream and the other (Kotipalli) the upstream (**Fig. 1**). Kotipalli station is about 15 km upstream of Yanam and mostly freshwater dominates throughout the year whereas salinity at Yanam varies from near freshwater to brackish water (~30) during no discharge period. These two stations were selected to examine the variability in nutrients in two different environments. Sampling at both the locations was carried out at a fixed time (1100 hrs) to minimize uncertainties arising from diurnal changes mainly of solar radiation/photosynthesis and tides. This approach allows us to make a meaningful comparison between observations of any two days of the present study over a year long period. At both locations the water depth across the channel varied from 1 to 10 m and the mean water depth was 7 ± 2 m. The catchment area is subjected to large-scale erosion and deforestation resulting in high source of organic carbon to the estuary than other (Balakrishna and Probst 2005).

2.2. Sampling and analyses

Solar radiation is measured using a sensor (Li Cor, USA) mounted on automated weather station installed on the tower close to our sampling station (Yanam) and measurements were logged at one minute interval. Photic depth was measured using secchi disc. Temperature and salinity profiles were measured using a portable Conductivity-Temperature-Depth profiler (CTD; SBE-19 plus, Sea-Bird Electronics, USA) at estuarine location, Yanam. Surface water samples were collected using a 5 litre Niskin bottle for chlorophyll-*a* (Chl *a*), nutrients and suspended solid matter (SSM). Nutrients analyses were carried on filtered water samples following the standard spectrophotometric procedures (Grasshoff et al. 1983). The precisions of nitrate+nitrite (NO_3+NO_2), ammonium, phosphate, and silicate were ± 0.02 , 0.02, 0.01, and 0.02 μmol , respectively. About 150 ml of a water sample was filtered, through preweighed 0.22 μm polycarbonate filters (Millipore), dried at 40° C and reweighed to quantify SSM (g L^{-1}). Another 150 ml of the water sample was filtered through glass fiber filter (GF/F; Whatman) and Chl *a* retained on the filter was extracted with N,N, Dimethyl formamide, at 4°C in dark for 24 h, and spectrofluorometrically measured (Suzuki and Ishimaru, 1990). The analytical precision for Chl *a* analysis was $\pm 4\%$. All these analyses were completed within 12 hours of sampling at the shore-based laboratory set up at Yanam, on the bank of the river. Net community production and community respiration were measured using dissolved oxygen incubation experiment and complete description of the method can be found in Sarma et al. (2009). Benthic fluxes were measured using benthic chamber made by acrylic material of 5L capacity. Benthic chamber was made on the surface sediment and

samples were collected at one hour interval for 12 hours. Based on the slope of change in nutrient concentrations with time, benthic fluxes were calculated. Sediment cores of 5-10 cm long were collected using acrylic tubes and were sectioned at one centimetre interval in the inert atmosphere in the glove box to avoid oxidation of redox compounds. Sediment samples were transferred to 50 ml polypropylene tubes and were sealed in the glove box. Pore waters were extracted in the sediment samples by centrifuging the tubes at 1200 rpm for 10 minutes. Ground water samples were collected at 100-200 m away from the bank of the river from the wells. Benthic flux experiment, pore water and ground water analysis were carried out two times, i.e., 2nd February 2008 and 15th June 2008 and the mean values were considered. The daily mean river discharge data were obtained from the Irrigation Department, Dowaleswaram.

3. Results

3.1. Atmospheric and Hydrographic features.

The daily-integrated solar radiation, measured at a height of 15 m above the mean sea level on the bank of Godavari River (**Fig. 2a**), showed the classical seasonal evolution of a temperate region with the lowest in November - February (winter) and the highest in June to September (summer). The Dowaleswaram dam controlled summer monsoon freshwater discharge, into the Godavari estuary through Low Dam, reached its maximal in August (with a monthly average of $4140 \text{ m}^3 \text{ s}^{-1}$). There was virtually no discharge between January and May due to drying of the river in the upstream (Fig. 2b). The inter-annual variability in the October – November discharge was due to changes in the precipitation pattern in the upstream. The study region received rainfall more in summer (917 mm; June to August) than in winter (47 mm; November to February) (Dr. R.G.P. Desai, personal communication 2009). Based on the discharge, the study period was divided into three; 1) peak discharge period (discharge $> 2000 \text{ m}^3 \text{ s}^{-1}$; June to September), 2) moderate discharge period (>0 to $<2000 \text{ m}^3 \text{ s}^{-1}$; October to December) and 3) no discharge period (January to May).

Surface water temperature during the study period followed the classical seasonal evolution characterized by minimal values in winter (November to February, average of $24.0 \pm 1.4^\circ \text{ C}$; mean \pm SD) and maximal values in summer (July to September, average of $31.2 \pm 1.2^\circ \text{ C}$; Figure 2c). During the discharge period the salinity was minimal in the Godavari, both at upstream and downstream, but higher when discharge does not occur (Fig. 2d). During peak discharge period, the entire water column of the

estuary was filled with the freshwater. The saline water slowly intruded into the estuary as the river discharge gradually decreases from moderate to no discharge period. When the river discharge virtually stopped by the end of December, the entire estuary was filled with saline water of 30 ± 1.5 (Fig. 2d). The maximal salinity gradient at Yanam between the peak and no discharge periods was 31 ± 1 . During 2007-2008, the average salinity at Yanam amounted to 12.2 ± 10 .

The SSM was high during the discharge periods (Fig. 2e), with an annual average at downstream of $0.09 \pm 0.1 \text{ g L}^{-1}$. As a result, the photic depth during peak discharge period decreased to $< 0.1 \text{ m}$ and increased to $\sim 3 \text{ m}$ when no discharge occurred (Sarma et al. 2009). The temporal variations in SSM concentrations at both upstream and downstream were almost similar (Fig. 2e).

3.2. Variability in nutrients and chlorophyll *a*.

The variability in nutrients and Chl *a* was largely controlled by the river discharge (Fig. 3 a-e). The Chl *a* concentrations were lower during the discharge period (Fig. 3 a) when higher nutrients were found in the estuary along with high SSM (Fig. 3 b-e). Peaks in Chl *a* ($\geq 16 \text{ mg m}^{-3}$) were observed during October-November that coincided with decreases in discharge and SSM. The monthly mean $\text{NO}_3 + \text{NO}_2$ concentrations in the downstream ranged between 2.45 ± 1.4 and $35.7 \pm 2.9 \text{ } \mu\text{mol L}^{-1}$ (Table 1). The mean $\text{NO}_3 + \text{NO}_2$ abundance during the peak discharge period was $30.5 \pm 8 \text{ } \mu\text{mol L}^{-1}$ that decreased to $11.7 \pm 7 \text{ } \mu\text{mol L}^{-1}$ for the moderate discharge period and to $3.6 \pm 2 \text{ } \mu\text{mol L}^{-1}$ during no discharge period (Table 2). Like $\text{NO}_3 + \text{NO}_2$, PO_4 and Si(OH)_4 also showed similar peaks in association with runoff whereas ammonium did not display such gradients (Fig. 3 b-e, Table 1,2). Nevertheless, the PO_4 peak was sharp and more closely related to river discharge than $\text{NO}_3 + \text{NO}_2$ peak, which was broader and not necessarily regulated by discharges from the dam alone. Increasing trends in $\text{NO}_3 + \text{NO}_2$ levels, both at upstream and downstream, have begun well before the discharge from dam peaked but the decreasing trend coincided with that of freshwater. Nutrients distributions during no discharge period exhibited episodic increases and when Chl *a* abundances also enhanced (Fig. 3 a-e).

The $\text{NO}_3 + \text{NO}_2$ concentrations (Table 1 and 2) in the upstream varied between 2.8 ± 2.5 and $50.8 \pm 24 \text{ } \mu\text{mol L}^{-1}$ with higher mean concentration during peak discharge period ($36.1 \pm 22 \text{ } \mu\text{mol L}^{-1}$) than in moderate ($11.3 \pm 18 \text{ } \mu\text{mol L}^{-1}$) and no discharge periods ($5.3 \pm 2 \text{ } \mu\text{mol L}^{-1}$). Similar patterns were observed for PO_4 and Si(OH)_4 whereas ammonium showed significant monthly variability (1.6 ± 0.9 to 10.1 ± 11

$\mu\text{mol L}^{-1}$). However, NO_3+NO_2 and ammonium mean concentrations in dry periods (**Table 2**) were almost similar (5.3 and $5.8 \mu\text{mol L}^{-1}$ respectively).

The ammonium concentrations were ~ 2 to $4 \mu\text{mol L}^{-1}$ at downstream in September but increased to ~ 7 to $9 \mu\text{mol L}^{-1}$ during November, January, April, July and August at both downstream and upstream (Table 1; Fig. 3 c). Most of the time these changes were found to be similar, with reference to time and magnitude in upstream and downstream. Interestingly, some of these events were found to be associated with local rainfall events. The annual mean ammonium concentrations ($4.9\pm 4 \mu\text{mol L}^{-1}$) suggests that it accounts to $\sim 36\%$ of DIN (dissolved inorganic nitrogen = nitrate + nitrite + ammonium) in the Godavari river. The monthly mean PO_4 concentrations were mostly $< 2 \mu\text{mol L}^{-1}$ during entire study period except in July and August when ~ 2 to $7 \mu\text{mol L}^{-1}$ levels were observed (Table 1; Fig. 3e). The PO_4 concentrations were higher during the peak discharge period (4.78 ± 6 and $4.23\pm 5 \mu\text{mol L}^{-1}$ at downstream and upstream, respectively with the highest concentration up to $21 \mu\text{mol L}^{-1}$) followed by moderate (1.0 ± 1.4 and $1.0\pm 1.3 \mu\text{mol L}^{-1}$) and dry periods (0.27 ± 0.2 and $0.66\pm 0.6 \mu\text{mol L}^{-1}$). The Si(OH)_4 concentrations were mostly higher than $20 \mu\text{mol L}^{-1}$ at both upstream and downstream (Table 1). Maximal values in Si(OH)_4 (Table 2 and Fig. 3d) occurred during peak discharge period (121.8 ± 72 and $92.2\pm 40 \mu\text{mol L}^{-1}$ in the upstream and downstream, respectively) and minimum in no discharge period (48.5 ± 31 and $18.9\pm 24 \mu\text{mol L}^{-1}$, respectively) (Table 2). The most prominent feature in this study (Table 2; Fig. 3b,d) was the occurrence of significant decrease in average NO_3+NO_2 concentrations from moderate discharge period ($11.3\pm 18 \mu\text{mol}$ and $11.7\pm 7 \mu\text{mol L}^{-1}$ in the upstream and downstream, respectively) to no discharge period (5.3 ± 2 and $3.6\pm 2 \mu\text{mol L}^{-1}$, respectively) whereas no significant change in SiO_4 occurred in upstream (43.1 ± 43 and $48.1\pm 31 \mu\text{mol L}^{-1}$ during moderate and no discharge periods, respectively). However, Si(OH)_4 decreased by a half in the downstream (41.9 ± 28 to $18.9\pm 24 \mu\text{mol L}^{-1}$ from moderate to no discharge period respectively) due to dilution with seawater as Si(OH)_4 concentration are typically lower ($< 2 \mu\text{mol L}^{-1}$) in seawater.

The phytoplankton blooms, in terms of Chl *a* concentrations, in the upstream and downstream coincided during October-November with similarity in magnitude. However, smaller Chl *a* peaks during dry period did not occur simultaneously at both the locations (Fig. 3a) suggesting different controlling mechanisms. The NO_3+NO_2 and PO_4 concentrations in the surface waters of Godavari estuary were relatively high during peak discharge periods with a decreasing trend from upstream to the downstream.

From September to November, NO_3+NO_2 concentrations decreased by an order of magnitude at both the locations (down to $<4 \mu\text{mol L}^{-1}$; Table 1). Again, NO_3+NO_2 concentrations increased to $\sim 5 \mu\text{mol L}^{-1}$ in the middle of November and then decreased to reach their lowest values of $\sim 3 \mu\text{mol L}^{-1}$ by January (Table 1 and Fig. 3b). Similar increase in NO_3+NO_2 was observed by the end of January and the middle of April to $\sim 3-8 \mu\text{mol L}^{-1}$ at the two stations where the peak levels remained for one week to 10 days before it decreased, back to the lowest levels in May (Table 1; Fig. 3b).

3.3. Nutrient ratios

In order to better define potential nutrient control on biological productivity, we compared nutrient ratios, between dissolved inorganic nitrogen (nitrate + nitrite + ammonium = N), $\text{Si}(\text{OH})_4$ and PO_4 measured during different periods, according to Redfield ratios ($\text{Si:N:P} = 16:16:1$). The N:P ratios ranged between 16.3 ± 15 and 47.6 ± 22 in the downstream whereas it was from 10.8 ± 8 to 46.0 ± 17 in the upstream region (Table 1). The mean N:P ratios were higher than Redfield ratio ($\text{N:P}=16$) in both upstream and downstream with a large difference (20.6 to 39.7; Table 2). On the other hand, Si:N ratios varied between 0.6 ± 0.3 and 15.5 ± 5 in the upstream whereas from 0.9 ± 0.6 to 6.9 ± 4.5 in the downstream and were largely higher than unity (Table 1 and 2).

4. Discussion

4.1. Nutrient variability in relation to freshwater inputs

During the study period average nutrient concentrations ($18.4 \pm 14 \mu\text{mol L}^{-1}$ for DIN (NO_3+NO_2 + ammonium), $42.6 \pm 36 \mu\text{mol L}^{-1}$ for $\text{Si}(\text{OH})_4$, and $1.5 \pm 3.8 \mu\text{mol L}^{-1}$ for PO_4) in Godavari were well below those of the San Francisco Bay (Cloern 1996), Chesapeake Bay (Ward and Twilley 1986), Pearl River estuary (Yin et al. 2001) and the Guadiana estuary (Domingues et al. 2005). Among the three nutrients PO_4 concentrations were low (Fig. 3e). Qasim (2001) noted that inorganic PO_4 in the Godavari estuary is the lowest compared to that in the other Indian estuaries. The maximal DIN concentrations in the downstream and upstream occurred in the summer monsoon (Fig 3b). The PO_4 and DIN levels seem to be stable in the Godavari estuary as the concentrations during 2007 and 2008 were comparable to those found in 1988 and 2001 (Qasim 2001; Tripathy et al. 2005).

In shallow coastal ecosystems, the major sources of nutrients are from rivers, ground water, atmosphere and sediments (Nowicki and Nixon 1985; Malone et al. 1988; Paerl 1997; Conley 2000). In the Godavari estuary, despite high concentration of nutrients in ground water, ($79.2 \pm 42 \mu\text{mol L}^{-1}$ of $\text{NO}_3 + \text{NO}_2$, $6.6 \pm 3 \mu\text{mol L}^{-1}$ of PO_4 and $44.4 \pm 9 \mu\text{mol L}^{-1}$ of $\text{Si}(\text{OH})_4$), the contribution to the estuary is relatively moderate as major nutrient inputs are associated with river discharge during June to September. Significant correlations ($p < 0.001$) for $\text{NO}_3 + \text{NO}_2$ ($r_s = 0.69$), PO_4 ($r_s = 0.66$) and SiO_4 ($r_s = 0.57$) concentrations with discharge in to the downstream (**Table 3**) and r_s of 0.32, 0.32 and 0.60 respectively in the upstream (**Table 4**) confirm the influence of river discharge on nutrient levels. The nutrient loads from river runoff are intense depending on the precipitation in the basin. All nutrient peaks synchronized with each other, except ammonium, between upstream and downstream, reflecting the pulsed nature of hydrological events in this area. These rapid nutrient inputs are of considerable importance since they can modify the phytoplankton community structure. Sarma et al. (2009) observed that the increase in primary production is due to shallowed photic depth associated with changes in SSM and also flushing time in the Godavari estuary and not related to nutrient peaks. The average SSM concentration was $0.11 \pm 0.15 \text{ g L}^{-1}$ during study period that went up to 1 g L^{-1} during the peak discharge (Fig 2f; Sarma et al. 2009). All nutrients showed positive correlations with SSM whereas Chl *a* displayed the negative (Table 3). Therefore primary production in the Godavari system is mainly controlled by light availability in the water column than nutrients, particularly during the peak discharge period. In addition to this, high flushing time during peak discharge period (less than a day; Sridevi et al., manuscript in preparation) also contributes significant decrease in primary production during this period.

Most of the data fall below the simple mixing line between upstream and downstream in the salinity to nutrients relationship suggesting biological uptake of nutrients (**Fig. 4**). For instance, the mean drawn down of DIN from the mixing line was $\sim 14 \mu\text{mol L}^{-1}$ and using Redfield ratio of 16 for C/N, it is equivalent to $92.4 \mu\text{mol L}^{-1}$ of organic carbon production. Based on the mean residence time of estuary (~ 10 days), the removal of nutrients through primary production is $\sim 28 \text{ mmolC m}^{-2} \text{ d}^{-1}$ and it is close to that of mean measured gross primary production of $33.5 \text{ mmolC m}^{-2} \text{ d}^{-1}$ (Sarma et al., 2009). The difference between measured and estimated production is mainly resulted from the decrease in nutrients due to seawater dilution by tides and injection of nutrients through ground water and benthic exchanges.

Ammonium levels, on the other hand, suggested periodic inputs that did not coincide with the trends of $\text{NO}_3 + \text{NO}_2$, PO_4 and $\text{Si}(\text{OH})_4$. The peaks in ammonium were not associated only with peak in discharge.

However, ammonium peaks during moderate and no discharge periods were synchronized with other nutrients (Fig. 3). Inputs of ammonium can come from water-sediment interface, *in situ* ammonium production or ground water discharges. Our benthic exchange experiments revealed that average pore water ammonium concentration were $\sim 42 \pm 8 \mu\text{mol L}^{-1}$ that contributes to $\sim 60\text{-}70\%$ of DIN in the pore water. The mean rate of exchange of ammonium at the sediment-water interface at downstream was $3.1 \pm 0.6 \text{ mmol m}^{-2} \text{ h}^{-1}$ during March and June 2009. On the other hand, mean ground water ammonium concentrations were $24 \pm 4 \mu\text{mol}$, with likely contribution of 30-80% of DIN. Groundwater ammonium concentrations along the Godavari bank showed large spatial variability with relatively higher levels in the upstream region ($>20 \mu\text{mol L}^{-1}$) than in the downstream ($<15 \mu\text{mol L}^{-1}$). Consequently, the contributions of ground water in upstream and downstream to that of ammonium in the downstream are expected to be different. These observations suggest that sedimentary and groundwater inputs contribute significantly to the ammonium inventories in the downstream and upstream waters. Interestingly no notable decrease in concentrations was found from upstream to downstream suggesting the importance of local ammonium sources than river inputs (Table 3).

The PO_4 concentrations during discharge period averaged to $\sim 4.4 \pm 6 \mu\text{mol L}^{-1}$ at both the locations with a maximum of $\sim 21 \mu\text{mol L}^{-1}$ (Fig. 3e). Unlike DIN, PO_4 concentrations rapidly decreased (to $\sim 1 \pm 1.4 \mu\text{mol L}^{-1}$) with a drop in the discharge. Generally PO_4 is bound to calcium and iron in estuaries (Stal et al. 1996; De Wit et al. 2001). About 60% of PO_4 inputs to estuarine water occur from sediment-water exchange. In benthic exchange experiments, it was found that the mean exchange rate of PO_4 from sediments to be $0.18 \pm 0.08 \text{ mmol m}^{-2} \text{ h}^{-1}$ at downstream during March and June 2008. The PO_4 concentrations showed a slight increase from January to May in Godavari estuary, although plant biomass could be a sink for PO_4 (De Wit et al. 2001) indicating the importance of remineralization. However, PO_4 dynamics in shallow waters are not well deciphered in view of its rapid biological (Admiraal and Werner 1983) and geochemical (Pomeroy et al. 1965) processes. The PO_4 is highly reactive with suspended matter and sediments (Deborde et al. 2007).

Both ammonium and PO_4 showed periodic inputs into the both upstream and downstream. Except at some occasions, mostly the episodic increase in ammonium and PO_4 events are almost similar in upstream and downstream during no discharge period. What would be the possible source of ammonium and PO_4 into the Godavari? It was observed that local precipitation (15 to 32 mm) occurred at the study

site from 25-28th November 2007, 15-22nd January 2008, 31st April to 15th May 2008 and again on 28th June 2008 (57 mm). Following the local precipitation events, PO₄ concentrations on average increased by about 0.1 to 0.15 μmol L⁻¹ in both the locations, which is ~30% of the ambient concentrations (see stippled vertical bars on Fig. 3). The potential reason could be overflowing of waters from the agriculture field along the bank of the river, where ammonium phosphate is normally used as a fertilizer. Therefore, this study suggests that local rainfall has significant impact on the short-term nutrient variations in the Godavari estuary.

Godavari river discharge has significant impact on the estuarine nutrient concentrations. The inter-annual variability in nutrients during peak discharge period was related to amount of discharge, which is dependant on the precipitation in the catchment area. The river discharge during September 2007 was higher (2385 m³ s⁻¹) than in September 2008 (1517 m³ s⁻¹; Fig 2b). Although we have begun our study in September 2007, well after the peak discharge period, the influence of difference in discharge was reflected by the amount of nutrients in the estuary. For instance, DIN, PO₄ and Si(OH)₄ concentrations were 50.8±24, 1.56±1, 184.3±34 μmol, respectively, in September 2007 whereas these were 29.1±6, 1.2±1 and 71.0±51 μmol, respectively, in September 2008 at the upstream station (Table 1). The Si(OH)₄ loading into the estuary through discharge reflects the weathering patterns in the catchment area and thus is highly dependent on climatic variability (Turner et al. 2003). With a mean Si:N ratios of ~2, the river waters are under the influence of DIN waste. This ratio is still above the critical ratio of 1, reported for eutrophic rivers such as the Bay of Brest, the Morlaix river and the Mississippi River (Wafar et al. 1983; Del Amo et al. 1997; Turner et al. 2003) suggesting Godavari river is not highly polluted.

Sarma et al. (2009) observed the highest primary production rates during the moderate discharge period (i.e., October to mid of December) in the Godavari. During this period, phytoplankton community was largely dominated by diatoms (mainly *Thalassiosira sp.*, and *Chaetoceros sp* ; our unpublished data). The phytoplankton bloom developed as the freshwater input decreased and the transparency increased due to reduction in suspended solids (<0.2 g L⁻¹). The lowered nutrients, especially DIN and Si(OH)₄, in October - November resulted from reduced discharge and development of phytoplankton blooms and also dilution by seawater. Moreover, Si:N ratios during this bloom development period were higher than mean (3.6±3 and 7.6±7 at downstream and upstream, respectively) indicating Si(OH)₄ may not be a limiting nutrient during entire study period (Table 2). The relationship between DIN and DIP shows that

DIN is generally above the N:P Redfield ratio during entire study period (**Fig. 5a-c**). Despite such higher N:P ratios, the concentrations of DIP were $>0.2 \mu\text{mol L}^{-1}$ during moderate and high discharge periods whereas they decreased to $<0.2 \mu\text{mol L}^{-1}$ during no discharge period (Fig. 5a) clearly indicating that DIP is limiting nutrient for the phytoplankton production. The temporal distribution of DIN and DIP (Figure 3) suggests that DIP decreased rapidly soon after decrease in discharge whereas DIN decrease was rather slow, resulting in higher N:P ratios.

Following these diatom blooms in October to December, phytoplankton populations are potentially controlled by PO_4 availability during no discharge period, especially at the downstream, when high N:P ratios (32.0 ± 20 , 20.0 ± 17 in downstream and upstream respectively; Table 2) and PO_4 concentrations were mostly $<0.1 \mu\text{mol L}^{-1}$ were observed. During this period, the PO_4 deficiency in the Godavari waters was linked to a pronounced decrease in freshwater inputs and autotroph's consumption. Si(OH)_4 was never found as a deficient nutrient as Si:N ratios were always greater than one in both the regions. As a result, diatoms were mostly present in the downstream water during study period (manuscript under preparation). It is consistent with Sarma et al. (2009) who reported that the $\sim 80\%$ of the total Chl *a* was contributed by $<10 \mu\text{m}$ sized phytoplankton during moderate discharge period, whereas $\sim 70\%$ of total Chl *a* contributed by $>10 \mu\text{m}$ sized phytoplankton during other period. This suggests that Si(OH)_4 is never a limiting nutrient in the Godavari estuary.

These higher Si(OH)_4 levels during moderate and no discharge period compared to DIN concentrations (41.9 ± 28 , $18.9 \pm 24 \mu\text{mol L}^{-1}$ in the downstream and 43.1 ± 43 , $48.5 \pm 25 \mu\text{mol L}^{-1}$ in the upstream during moderate and no discharge periods, respectively; Table 2) are paradoxical since (1) diatoms are present all through the year and marine diatoms Si:N uptake ratio is ~ 1 and (2) N recycling is faster than that of Si(OH)_4 (Harrison 1993). In addition to this, PO_4 deficiency during moderate and no discharge period is mainly caused due to sequestration of PO_4 into the sediment as most of PO_4 is bound to calcium and iron and removed to sediment (Stal et al. 1996; De Wit et al. 2001).

In order to examine the potential controlling nutrient during no discharge period, we have carried *in vitro* nutrient enrichment experiment at downstream (Yanam) during April 2008. Surface water samples were collected in four 20 L transparent plastic bottles (Nalgene). The initial concentrations of nutrients and Chl *a* in the incubated sample were given in Table 5. In order to understand influence of individual nutrients on phytoplankton biomass, each bottle was enriched with NO_3 , ammonium, PO_4 and Si(OH)_4

up to 10, 10, 5, and 30 $\mu\text{mol L}^{-1}$ respectively and incubated under sunlight by overflowing the surface waters in the incubation chamber for 36 hours. The samples were periodically stirred to avoid settling of the phytoplankton. In addition to this, sample was also incubated as control where no nutrients were added. Sampling was carried out at every 6 hours over 36 hours. It was observed that Chl *a* increased significantly in PO_4 added bottle by >4 times within 24h after incubation, whereas in other nutrients added bottles it was increased by $\sim 1 \text{ mg m}^{-3}$ (**Fig. 4 and Table 5**). On the other hand, minimal changes in Chl *a* ($\sim 0.51 \text{ mg m}^{-3}$) were observed both in control as well as Si(OH)_4 added bottle. The experimental results further confirm that PO_4 seems to be the major limiting nutrient during no discharge period.

4.2. Nutrient cycling in the Godavari estuary

From our study of nutrient variability, a conceptual scheme of possible functioning, representing the main sources and sinks of nutrients in Godavari estuary has been presented for peak discharge period, moderate discharge and no discharge periods (**Fig. 7a**). During the peak discharge period the main source of nutrients to the Godavari estuary is through discharge from upstream river. Along with the nutrients and dissolved organic carbon (DOC), SSM is also brought into the estuary that results in decreases in light penetration, and high flushing time lead to subsequent decrease in production (Sarma et al. 2009). Nutrients are also supplied through rain; as their concentrations are higher in the rain water ($12.2 \mu\text{mol L}^{-1}$ of DIN and $0.8 \mu\text{mol L}^{-1}$ PO_4) and mean rainfall during this period was 594 mm (Dr. R.G.P. Desai personal communication). Moreover, nutrients inputs from sediment-water exchange were also expected to be high as heavy discharge erodes upper few centimeters of the sediment. The nutrients levels in the pore water of the upper 2 cm were quite high ($80.5 \mu\text{mol L}^{-1}$ of DIN and $8.9 \mu\text{mol L}^{-1}$ of PO_4). The heterotrophic respiration was less during the peak discharge period ($-8.5 \pm 18.2 \text{ mmol C m}^{-2} \text{ d}^{-1}$) than other periods ($\sim 30 \pm 29 \text{ mmol C m}^{-2} \text{ d}^{-1}$; Sarma et al. 2009). The primary production, measured using dissolved oxygen incubation, during peak discharge period was net heterotrophic ($-0.97 \pm 9.5 \text{ mmol C m}^{-2} \text{ d}^{-1}$) and >90% was supported by terrestrial organic supplies (Sarma et al., 2009). The mean N:P ratios during peak discharge period (20.6 ± 21 and 39.7 ± 22) and Si:N ratios (2.2 ± 2 and 11.0 ± 7) are higher than the Redfield ratio of 16 and 1 respectively in the downstream and upstream of Godavari. Due to low production and higher respiration rates, the biogenic deposits to the sediments may be relatively low. During the discharge period, nutrients concentrations were relatively higher (Table 2) but SSM is the main factor to control phytoplankton production (Sarma et al. 2009).

During moderate discharge period (Fig. 5b), discharge was relatively low ($<2000 \text{ m}^3 \text{ s}^{-1}$) and less nutrients are brought into the estuary when SSM levels also decrease significantly ($<0.5 \text{ g L}^{-1}$) from that of peak discharge period. Nutrients inputs from the atmosphere also decrease at this time since the rainfall was less (average of 196 mm over moderate discharge period) than peak discharge period (594 mm). Significant amounts of nutrients supply may occur through ground water exchange, as the concentrations of nutrients are higher in the ground water than estuary. The nutrient inputs from sediments are expected to be significant due to increase in residence time of water in the estuary (Fig. 2c) facilitated by decrease in river discharge. As a result of nutrient availability and less SSM, primary production was found to be the highest (gross primary production of $44.7 \pm 39.6 \text{ mmolC m}^{-2} \text{ d}^{-1}$) when net community production showed net autotrophy ($15.7 \pm 30.8 \text{ mmolC m}^{-2} \text{ d}^{-1}$; Sarma et al. 2009). The mean N:P ratios during this period were 26.0 ± 19 and 23.1 ± 19 whereas Si:N ratio is greater than 1 (3.6 ± 3 and 7.7 ± 7) in the downstream and upstream respectively. Nevertheless, due to high primary production, biodeposit to the sediment may be higher than peak discharge period.

During no discharge period (Fig. 5c), the nutrients input from the upstream river completely stops. Due to no precipitation, the atmospheric deposition is also negligible. The major source of nutrients during this period is through ground water and pore water exchange. The community respiration is the highest ($-30.7 \text{ mmolC m}^{-2} \text{ d}^{-1}$) compared to other periods that might result in enhanced regenerated nutrients concentrations. Nevertheless, primary production decreases from that of bloom period and net community production was net autotrophic ($26.7 \text{ mmolC m}^{-2} \text{ d}^{-1}$) in the photic zone. The mean N:P ratios during this period were 32.0 ± 20 , 20.0 ± 17 and Si:N ratios were 2.1 ± 2 , 13.9 ± 18 respectively. However the PO_4 concentrations during no discharge period were relatively low 0.27 ± 0.2 and $0.66 \pm 0.6 \mu\text{mol}$ and *in vitro* experiments suggested that PO_4 seems to be a limiting nutrient during this period.

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Legend to figures:

Figure 1: Location of the time-series stations, at Yanam and Kotipalli in Godavari estuary, India.

Figure 2: Daily variability in (a) Solar radiation, (b) River discharge, (c) Temperature, (d) Salinity and (e) SSM in the Godavari estuarine location. SSM in the surface waters of estuarine (closed circles) and upstream (open circles). The solid vertical bars represents the periods of peak discharge.

Figure 3: Comparison of daily variations in surface (a) Chl *a*, (b) NO_3+NO_2 , (c) ammonium, (d) $\text{Si}(\text{OH})_4$, and (e) PO_4 in the estuarine (closed diamonds) and upstream (open circles) stations. River discharge during study period was shown as thick line. The solid vertical bar represents the periods of peak discharge and dotted bars when significant rainfall was observed.

Figure 4: Relationship between salinity with a) DIN, b) DIP and c) $\text{Si}(\text{OH})_4$ on log scale. The bold line represents mixing line between upstream and downstream waters.

Figure 5: Relationship of DIN to DIP during a) no discharge, b) moderate discharge and c) peak discharge period and DIN to $\text{Si}(\text{OH})_4$ during d) no discharge, e) moderate discharge and f) peak discharge periods. Straight line in the graph represents Redfield ratio of N:P=16 and Si:N=1.

Figure 6: Influence of nutrients on Chl-*a* during *in vitro* experiment. Open diamonds – control, closed diamond – $\text{Si}(\text{OH})_4$ added, plus – PO_4 added, open circle – NO_3 added and closed circle – ammonium added.

Figure 7: Schematic diagram of nutrients flow in the Godavari river during (a) summer (peak discharge), (b) fall (peak bloom and moderate discharge), and (c) winter and spring (no discharge) periods. Size of the boxes represents magnitude of source or sink.

Table 1: Monthly mean (\pm SD) nutrients ($\mu\text{mol L}^{-1}$) and their ratios in the estuarine and upstream Godavari river.

Month	Estuary							Upstream					
	Salinity	NO ₃ +NO ₂	NH ₃	PO ₄	Si	N/P	Si/N	NO ₃ +NO ₂	NH ₄	PO ₄	SiO ₄	N/P	Si/N
Sep07	0.080 \pm 01	30.4 \pm 6.4	3.5 \pm 1.8	1.9 \pm 1.0	86.4 \pm 24	25.0 \pm 18	2.7 \pm 1.1	50.8 \pm 24	2.5 \pm 2.6	1.6 \pm 1.0	184.3 \pm 34	46.0 \pm 17	15.5 \pm 5
Oct07	0.08 \pm 0.02	14.3 \pm 8.8	4.2 \pm 1.4	1.0 \pm 0.4	55.1 \pm 23	23.6 \pm 17	3.7 \pm 2.5	16.6 \pm 11	4.5 \pm 1.6	1.1 \pm 0.4	61.3 \pm 15	26.3 \pm 23	0.6 \pm 0.3
Nov07	2.34 \pm 0.98	3.6 \pm 1.0	7.2 \pm 5.5	1.5 \pm 2.5	47.1 \pm 20	16.3 \pm 15	5.3 \pm 3.8	4.9 \pm 2.2	6.7 \pm 5.1	1.6 \pm 2.4	51.1 \pm 14	16.8 \pm 12	1.0 \pm 0.6
Dec07	11.66 \pm 3.3	7.4 \pm 1.5	4.7 \pm 2.9	0.6 \pm 0.2	36.6 \pm 21	25.6 \pm 11	3.0 \pm 1.8	10.0 \pm 2.4	5.9 \pm 4.9	0.6 \pm 0.3	41.5 \pm 22	26.3 \pm 16	0.8 \pm 0.6
Jan08	20.36 \pm 2.3	3.4 \pm 2.6	7.7 \pm 4.2	0.2 \pm 0.2	28.2 \pm 40	47.6 \pm 22	2.1 \pm 2.6	3.3 \pm 1.4	9.7 \pm 10	0.4 \pm 0.2	34.2 \pm 25	35.9 \pm 21	2.7 \pm 1.4
Feb08	23.13 \pm 1.7	4.0 \pm 1.2	2.4 \pm 1.1	0.2 \pm 0.2	10.8 \pm 4	44.0 \pm 23	1.5 \pm 0.7	4.1 \pm 1.4	4.1 \pm 5.7	0.6 \pm 0.3	68.9 \pm 33	11.4 \pm 8	5.7 \pm 1.2
Mar08	22.98 \pm 6.9	2.7 \pm 1.2	4.2 \pm 3.7	0.3 \pm 0.2	17.2 \pm 16	24.4 \pm 18	2.3 \pm 1.3	4.4 \pm 1.7	5.5 \pm 3.4	0.9 \pm 0.8	52.7 \pm 22	15.0 \pm 11	6.6 \pm 5.7
Apr08	18.81 \pm 5.7	4.5 \pm 1.9	7.4 \pm 5.3	0.4 \pm 0.2	21.5 \pm 16	32.7 \pm 20	2.3 \pm 2.8	8.1 \pm 2.8	10.1 \pm 11	0.5 \pm 0.2	57.9 \pm 29	34.2 \pm 17	4.0 \pm 3.3
May08	18.35 \pm 4.2	2.7 \pm 0.8	3.3 \pm 2.2	0.8 \pm 0.7	40.9 \pm 23	16.6 \pm 14	6.9 \pm 4.5	3.1 \pm 0.9	3.9 \pm 2.5	0.9 \pm 0.5	85.1 \pm 51	12.6 \pm 14	3.9 \pm 1.0
Jun08	17.07 \pm 4.7	9.5 \pm 4.8	5.2 \pm 4.3	1.0 \pm 1.6	20.5 \pm 23	29.9 \pm 19	1.9 \pm 3.0	12.1 \pm 8.4	4.1 \pm 2.1	0.5 \pm 0.3	33.3 \pm 26	33.5 \pm 19	3.2 \pm 3.0
Jul08	6.21 \pm 7.1	25.8 \pm 2.3	8.9 \pm 7.9	2.3 \pm 2.0	38.5 \pm 36	17.5 \pm 9	1.7 \pm 1.3	16.3 \pm 9.5	7.5 \pm 5.8	3.2 \pm 3.2	31.1 \pm 35	10.8 \pm 8	1.4 \pm 1.8
Aug08	0.09 \pm 0.07	35.7 \pm 2.9	6.5 \pm 5.5	6.7 \pm 6.8	79.9 \pm 49	27.9 \pm 24	0.9 \pm 0.6	48.2 \pm 5.3	6.5 \pm 5.7	5.9 \pm 6.4	131.0 \pm 48	42.2 \pm 25	1.2 \pm 1.4
Sep08	0.16 \pm 0.19	35.6 \pm 2.9	2.5 \pm 1.0	1.0 \pm 0.5	73.7 \pm 41	45.2 \pm 17	2.3 \pm 2.4	29.1 \pm 6.1	2.9 \pm 1.7	1.2 \pm 1.4	71.0 \pm 51	21 \pm 38	8.1 \pm 4
Oct08	3.00 \pm 2.4	12.1 \pm 4.4	2.1 \pm 2.6	0.8 \pm 0.5	58.3 \pm 36	23.2 \pm 16	2.8 \pm 1.8	10.2 \pm 2.45	1.8 \pm 2.1	0.8 \pm 0.5	67.9 \pm 39	22.1 \pm 8	9.5 \pm 2
Nov08	3.22 \pm 2.1	2.5 \pm 1.4	2.5 \pm 1.0	1.5 \pm 2.8	52.8 \pm 30	19.4 \pm 13	4.7 \pm 3.4	2.8 \pm 2.5	1.6 \pm 0.9	1.4 \pm 1.2	63.8 \pm 31	15.2 \pm 3	8.5 \pm 6

Table 2: Mean (\pm SD) nutrients ($\mu\text{mol L}^{-1}$) concentrations and their ratios during different river discharge periods in the Godavari estuary and upstream.

Discharge ($\text{m}^3 \text{s}^{-1}$)	Estuary							Upstream					
	Salinity	NO_3+NO_2	NH_3	PO_4	$\text{Si}(\text{OH})_4$	N/P	Si/N	NO_3+NO_2	NH_3	PO_4	$\text{Si}(\text{OH})_4$	N/P	Si/N
0	22.30 \pm 4	3.6 \pm 2	4.5 \pm 3.6	0.3 \pm 0.2	18.9 \pm 24	32.0 \pm 20	2.1 \pm 2	5.3 \pm 2	5.8 \pm 7	0.7 \pm 0.6	48.5 \pm 31	19.9 \pm 17	13.9 \pm 18
<2000	9.96 \pm 8	11.7 \pm 7	5.1 \pm 5	1.0 \pm 1.4	41.9 \pm 28	26.0 \pm 19	3.6 \pm 3	11.3 \pm 18	5.3 \pm 6	1.1 \pm 1.3	43.1 \pm 43	23.1 \pm 19	7.6 \pm 7
>2000	0.07 \pm 0.01	30.5 \pm 8	5.2 \pm 4	4.8 \pm 6	92.2 \pm 40	20.6 \pm 21	2.2 \pm 2	36.1 \pm 22	5.5 \pm 5	4.2 \pm 5	121.8 \pm 72	39.7 \pm 22	11.0 \pm 7

Table 3: Rank correlation matrix (Spearman's r_s) of main physical and chemical parameters measured in the estuary (n=1229) of Godavari river; *** $p < 0.001$, ** $p < 0.01$, * $p < 0.05$.

Parameter	Temp	Salinity	SSM	DO	NH ₄	NO ₃ +NO ₂	PO ₄	Si(OH) ₄	Chl <i>a</i>
Discharge	-0.10	-0.86***	0.68***	0.23***	0.002	0.69***	0.66***	0.57***	-0.13*
Temp		0.28***	0.32***	-0.24***	0.05	-0.42***	-0.06	0.09	0.14*
Salinity			-0.68***	-0.27***	0.02	-0.72***	-0.67***	-0.63***	0.28***
SSM				0.21***	-0.01	0.52***	0.34***	0.24***	-0.20***
DO					-0.12*	0.18**	0.14**	0.005	0.04
NH ₄						-0.03	0.12*	-0.01	-0.14**
NO ₃ +NO ₂							0.56***	0.40***	-0.42***
PO ₄								0.51***	-0.18**
Si(OH) ₄									-0.04

Table 4: Rank correlation matrix (Spearman's r_s) of main chemical and biological parameters measured in the upstream (n=430) of Godavari river; *** $p < 0.001$, ** $p < 0.01$, * $p < 0.05$.

Parameter	SSM	DO	NH ₄	NO ₃ +NO ₂	PO ₄	Si	Chl <i>a</i>
Discharge	0.62***	-0.004	-0.05	0.316***	0.37***	0.60***	-0.2***
SSM		0.18***	-0.03	0.62***	0.28***	0.28***	-0.24***
DO			-0.07	0.17**	-0.003	0.04	0.02
NH ₄				-0.13*	0.013	0.01	-0.01
NO ₃ +NO ₂					0.05	-0.52***	-0.44***
PO ₄						-0.06	-0.17*
Si							0.27***

Table 5: Changes in nutrients (μmol) and Chl *a* (mg m^{-3}) concentrations during *in vitro* incubation experiment.

Conditions	Before incubation experiment					24h after incubation experiment				
	NO ₃	NH ₄	PO ₄	SiO ₄	Chl <i>a</i>	NO ₃	NH ₄	PO ₄	SiO ₄	Chl <i>a</i>
Initial/control	2.61	3.92	0.36	17.2	1.78	1.62	2.73	0.14	16.9	2.29
NO ₃ added	10.6	3.92	0.36	17.2	1.78	7.81	1.84	0.21	15.2	3.99
NH ₄ added	2.61	10.2	0.36	17.2	1.78	2.44	3.92	0.18	15.4	3.78
PO ₄ added	2.61	3.92	5.62	17.2	1.78	0.36	2.11	3.22	14.9	9.56
SiO ₄ added	2.61	3.92	0.36	30.1	1.78	1.83	2.62	0.16	16.7	2.50

Figure 1

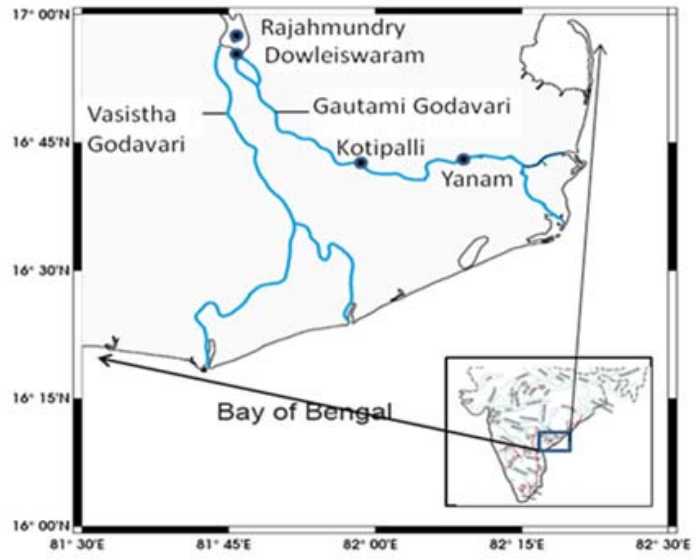


Figure 2

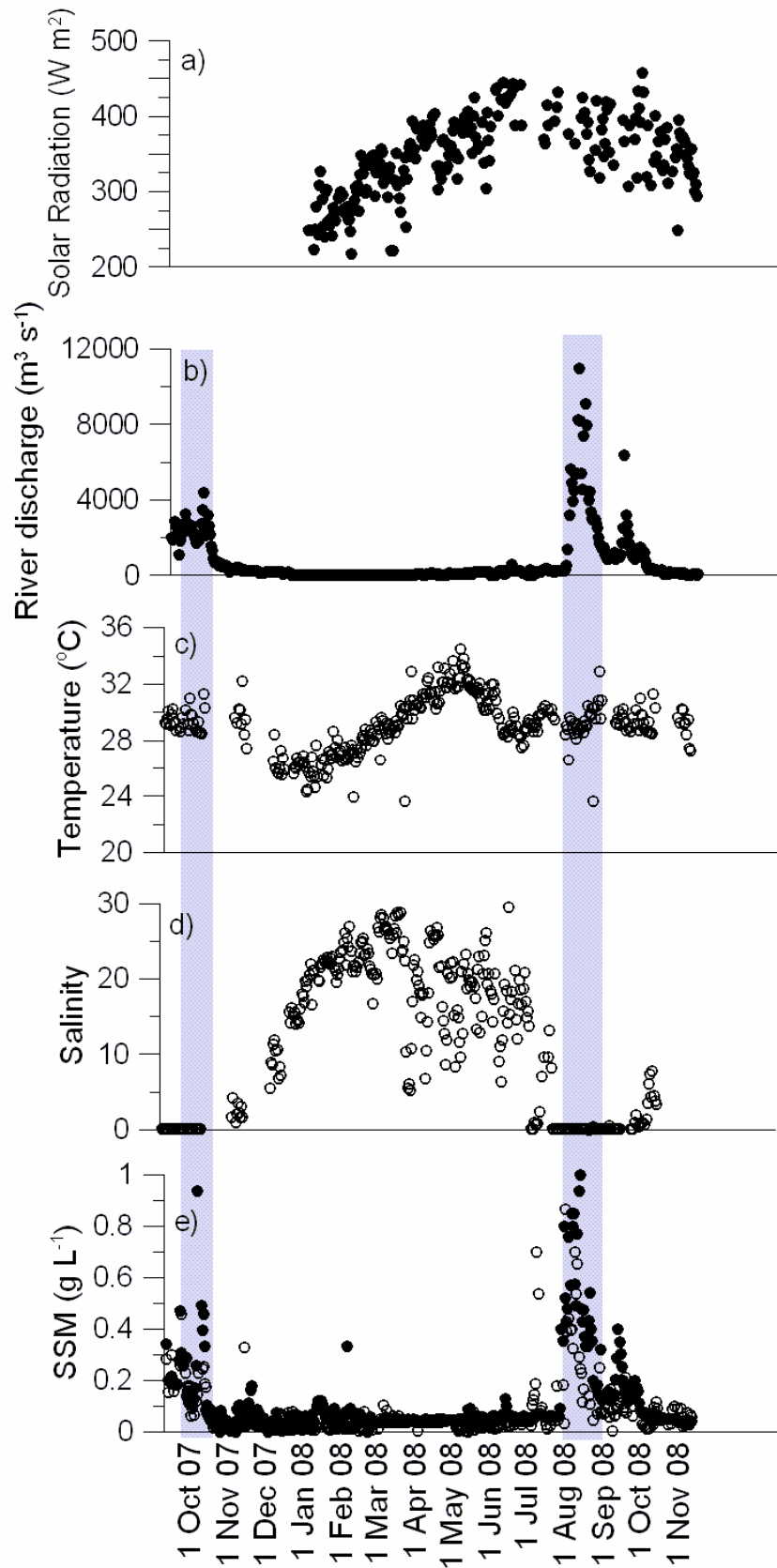


Figure 3

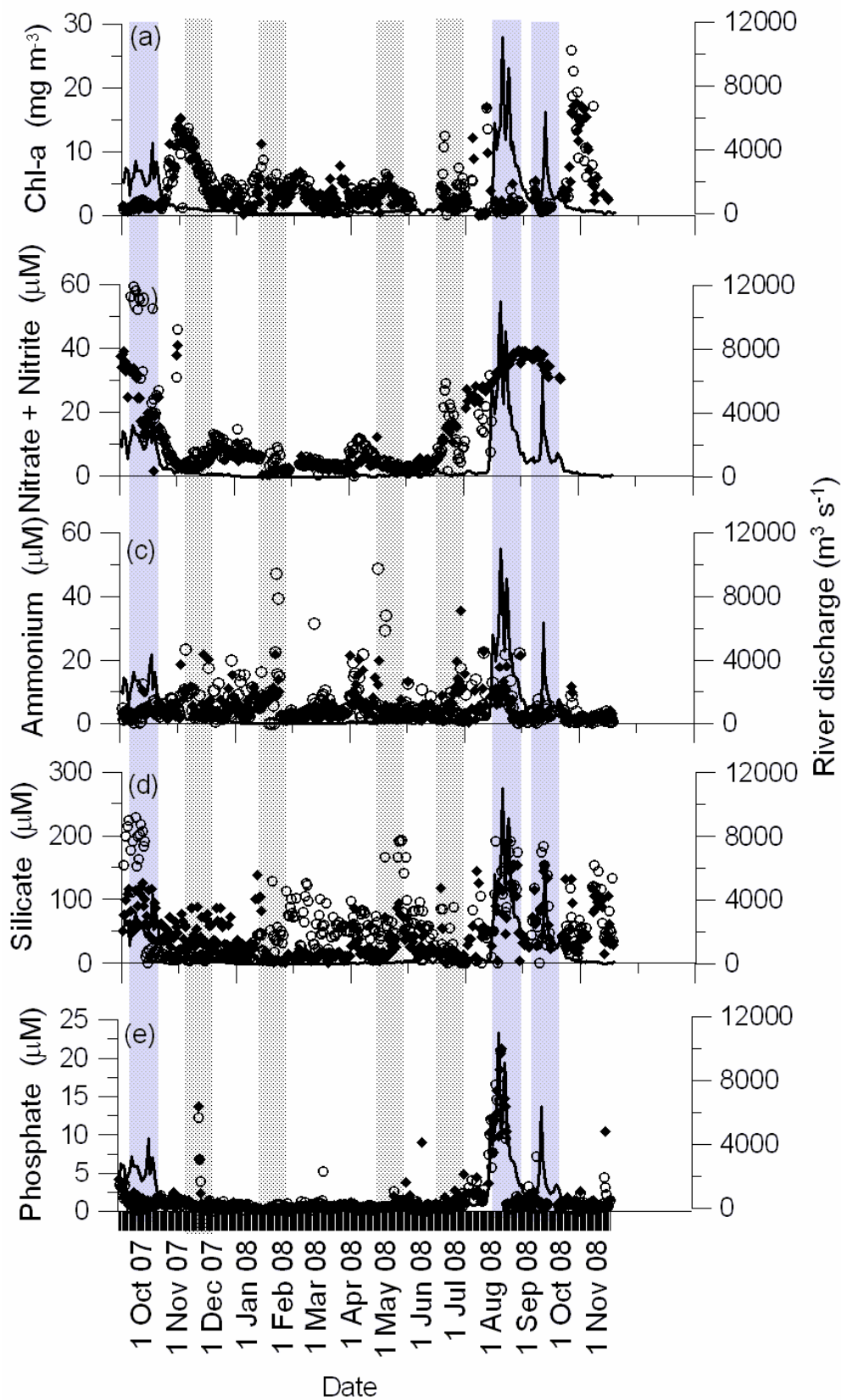


Figure 4

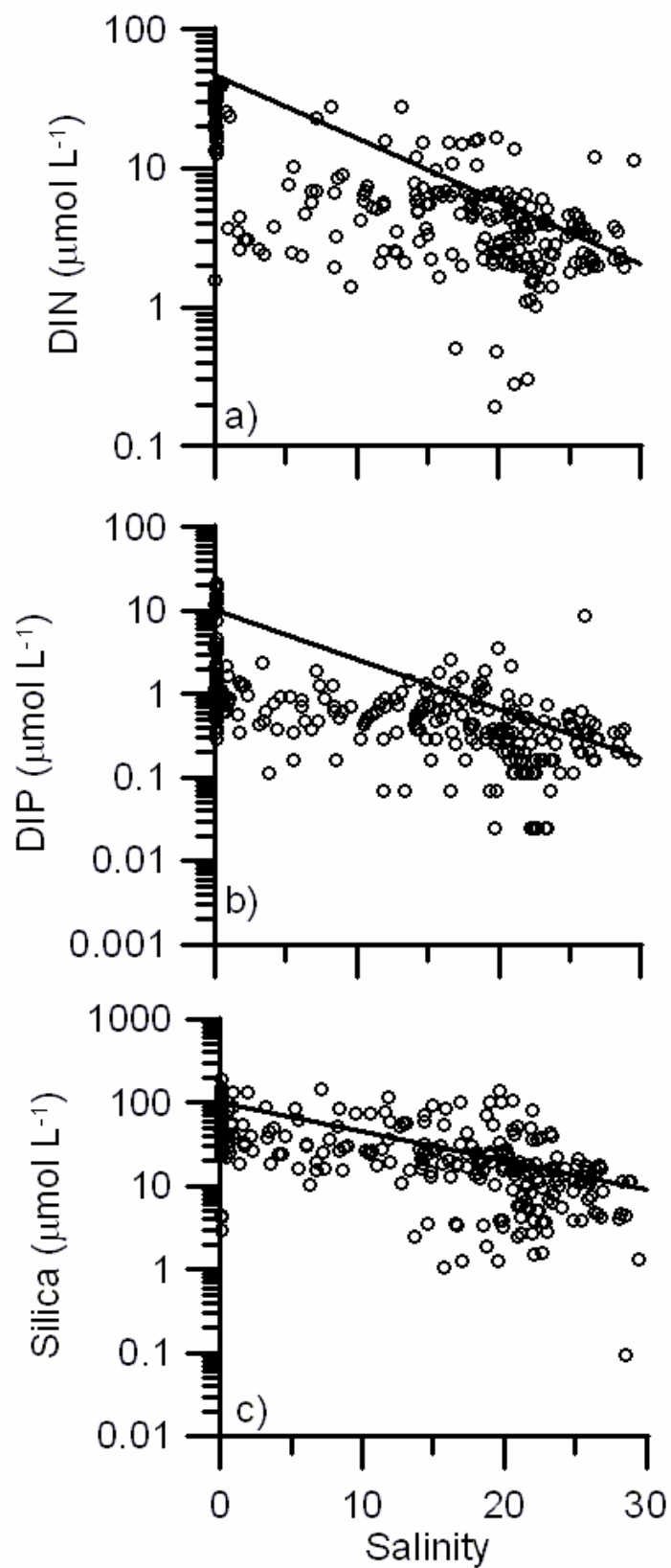


Figure 5

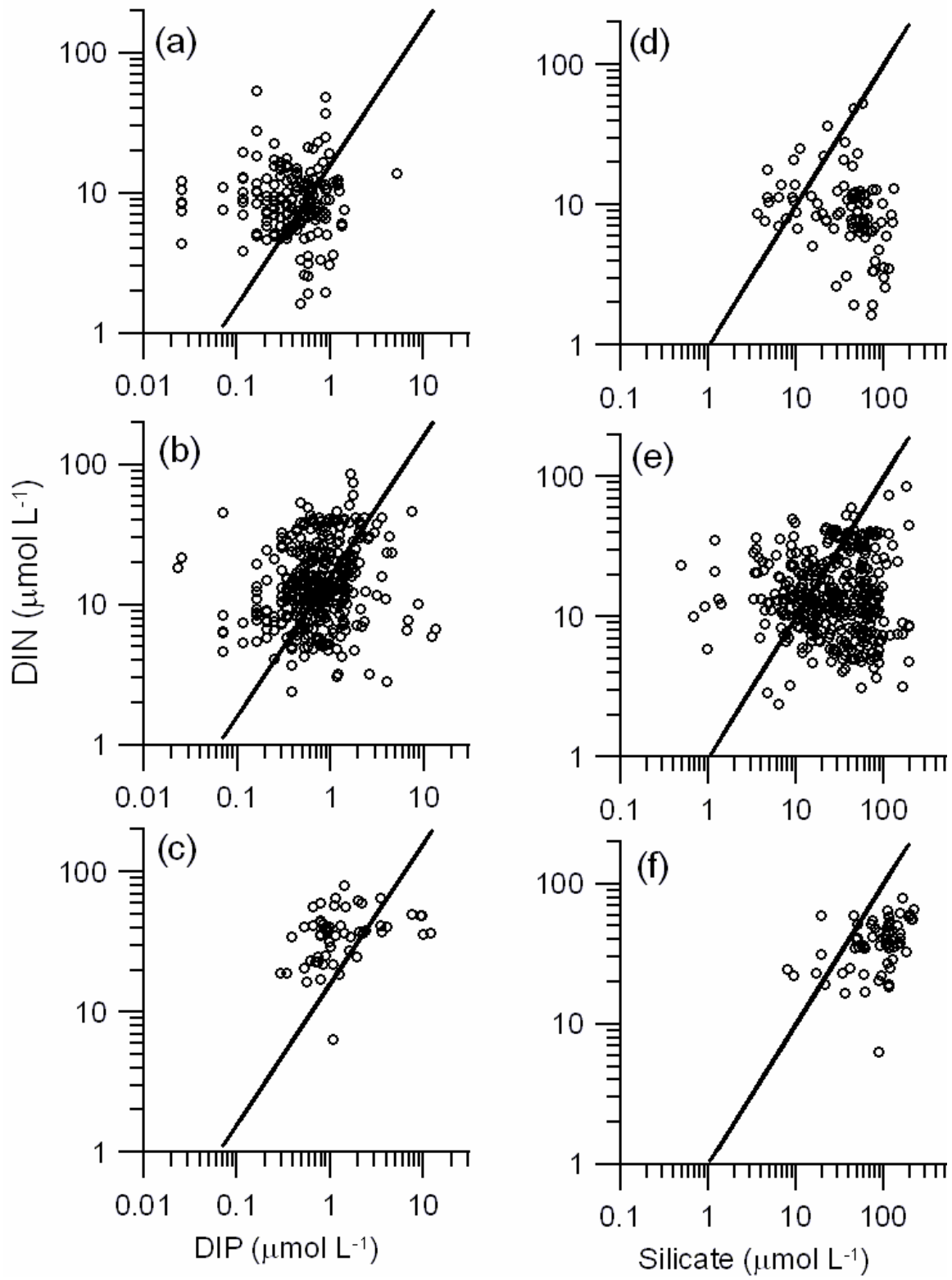


Figure 6

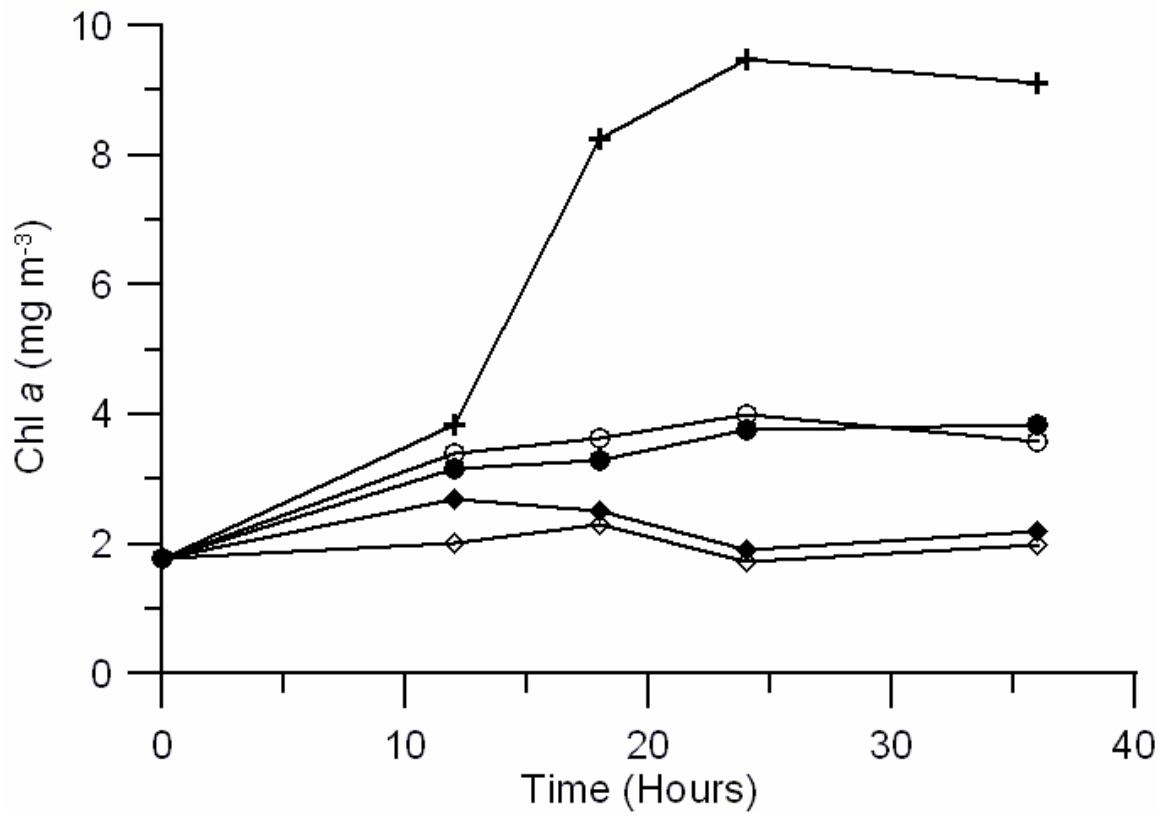


Figure 7

