

## **Nutrients, Hypoxia and Mass Fishkill Events in Tapi Estuary, India**

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### **Abstract**

From 1983 to 2011, dissolved oxygen (DO) conditions in the Tapi Estuary changed from normoxic to hypoxic due to increased and untreated discharge of sewage. Both tidal and day-night variations of DO were best explained by hydrographic factors, sewage pollution and phytoplankton dynamics in upper, middle, lower estuary and the coastal water. Hypoxia/anoxia was associated with low-flow periods due to riverine restrictions and changing in climatic condition. The upper Tapi Estuary becomes anoxic during summer irrespective of tide while the middle estuary was anoxic ( $<0.2 \text{ mg O}_2 \text{ l}^{-1}$ ) during post and premonsoon seasons and hypoxic ( $<2.0 \text{ mg O}_2 \text{ l}^{-1}$ ) during monsoon season. Differences in the degree of stratification, sewage discharge and flushing accounted for differences in DO. Because of high nutrient concentrations (maximum  $\text{NO}_3^- \text{-N}$  103.1,  $\text{NO}_2^- \text{-N}$  26.0,  $\text{NH}_4^+ \text{-N}$  104.0 and  $\text{PO}_4^{3-} \text{-P}$  99.0  $\mu\text{mol l}^{-1}$ ), the lower estuary remains DO deficient between 2.0 and 5.0  $\text{mg O}_2 \text{ l}^{-1}$ , most of the time. The environmental condition of Tapi Estuary has impacted the coastal water of the Arabian Sea in recent years with fishkills attributed to its hypoxic/anoxic condition. Enhanced concentrations of nutrients and organic matter from indiscriminate discharge of sewage into the Tapi Estuary and restricted flushing as a result of construction of a series of dams in the catchment area of the estuary are the primary factors that have lead to the development of hypoxia.

Keyword: Tapi Estuary; hypoxia; anoxia; fish kill; nutrients

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## 1. Introduction

Coastal hypoxia (Dissolved Oxygen (DO)  $<2.0 \text{ mg l}^{-1}$ , or approximately 30% saturation) is emerging as a major threat to coastal ecosystems globally. More than 600 coastal and estuarine sites globally have developed hypoxia (Nixon, 2009; Diaz et al., 2010; Conley et al., 2011) which is an increase of approximately 5 %  $\text{y}^{-1}$  over the last 50 years. This is due mainly to the combined effects of the continued spread of coastal eutrophication reducing extent and deteriorating habitat quality for a wide range of organisms (Vaquer-Sunyer and Duarte, 2008). Hypoxia has been shown to trigger mortality events, resulting in a depletion of living organisms in the ecosystems, resulting in “dead zones” (Fischer et al., 1992; Breitburg, 1994; 2002; Shimps et al., 2005). Estuaries support a diverse range of biota and serve as habitat, breeding grounds and nursery areas for many economically and ecologically important species (Yukseket al., 2006). Anthropogenic effects are stronger in the estuaries because water exchange is usually limited than the open-shore coastal ecosystem (Villate et al. 2013). The flushing out of contaminants entering an estuary is further impacted due to impounding of water in dams, weirs and barrages for hydropower, navigation, aquaculture, diversion for urban water supply, agriculture, due to activities related to recreation, and the maintenance of biodiversity. Anthropogenic contaminants generated around the estuary by upstream development introduce significant quantities of organic matter and nutrients, typically through sewage releases, into rivers and estuaries. Such inputs accelerate hypoxia and the eutrophication processes (Hadwen and Arthington, 2007; Villate et al., 2013). Human activities that alter the amount of freshwater entering an estuary reduce the amount of mixing. Poorly-mixed waters lead to development of hypoxia (Villate et al., 2013). For instance the buildup of organic load that is ultimately discharged into estuaries facilitates developing the hypoxia as a consequence of remineralization processes.

Fish kills in tropical regions are frequently attributed to low DO concentrations. However, the circumstances bringing in these events vary considerably based on several environmental parameters and resident life forms (Townsend et al. 1992; San Diego-McGlone et al., 2008). In the marine environment chronic oxygen deficiency occurs when levels of DO fall between 2.0 and 6.0  $\text{mg l}^{-1}$  and acute deficiency occurs when DO is  $< 2.0 \text{ mg l}^{-1}$  respectively. Anoxic or ‘no-oxygen’ situations occur when levels of DO fall below  $0.2 \text{ mg l}^{-1}$ . Hypoxic condition can have adverse effects on marine organisms including slower growth rates, elevated stress levels and impaired productive capacity and, in severe cases, mortality (Baden et al. 1990; Rose et al., 2009).

Frequent fish kills are known to occur in Tapi Estuary. Though there are a number of reports available on environmental quality of Tapi (Sargaonkar 2006; Marathe et al. 2011; Varghese et al. 2011), there is no analyses on DO depletion over the years. The present paper is the first time

attempt looking at historical record of environmental parameters and relating it to fish kill events in the estuary. As such the existence of a variety of industries along the northern bank of the estuary that release effluents into the outer estuary complicate the decipherance of impacts from any single source. Furthermore disposal of a large volume of untreated or partly treated sewage from the Surat City in the inner estuary adds to the problem. We examine the issue which has resulted in considerable public concern. Based on intensive field studies in the estuary supported using results of long-term data collection from this estuary. Data sets of 1983-84 are used as baseline since there was no industrial development along the outer estuary and population of the surrounding region was several folds lower. We hope that the present work will provide better tools for management and restoration of such coastal environments.

## **2. Material and Methods**

### *2.1 Study area*

Tapi River, with a length of ~720 km and catchment area of 65,145 km<sup>2</sup>, empties into the Gulf of Cambay (Fig. 1). The shallow and wide lower segment of the river exhibits characteristics of a typical estuary with strong currents associated with tidal influence discernible 25 km upstream. The riverine discharge into the Arabian Sea is controlled by Ukai and Kakrapar dams constructed 141 and 115 km upstream respectively and a causeway just upstream of Surat City, which also limits the excursion of seawater. The basin receives most of the rainfall from the South-West monsoon which sets in by the middle of June and withdraws by the first week of October. June to September is the period of heaviest rain. The average annual rainfall in the Tapi basin is 1000 mm.

The river discharge of  $6.9 \times 10^8 \text{ m}^3 \text{ d}^{-1}$  during monsoon decreases to  $9 \times 10^5 \text{ m}^3 \text{ d}^{-1}$  during November and is almost negligible during May leading to stagnation in the inner estuarine segment. The tidal influence decreases with distance into the estuary with mean spring and neap tidal ranges of 2.3 and 0.4 m respectively at Surat (station 10) as against 5.7 and 4.3 m in the mouth (station 5). Though the outer estuary is well flushed during spring tide with a flushing time of 3 tide cycles, stagnation in the inner estuary is high at the neap tide with a flushing time of 68 tidal cycles (NIO, 2002) during the dry season.

### *2.2 Sampling strategy*

Water samples for analyzing inorganic phosphate ( $\text{PO}_4^{3-}\text{-P}$ ), nitrate ( $\text{NO}_3^-\text{-N}$ ), nitrite ( $\text{NO}_2^-\text{-N}$ ), ammonia ( $\text{NH}_4^+\text{-N}$ ), pH, salinity, DO, chlorophyll a (Chl-a) and phaeophytin were collected from 1983 to 2011 at sampling stations. Samples for biochemical oxygen demand (BOD) were collected occasionally. Depth-averaged data is presented in this paper to explain historical episodes of Tapi

Estuary. Massive fishkills were reported during October 2007, May-June 2009 and occasional events followed thereafter, though not on a large scale. The study was conducted including seasonal, spatial and temporal variations (including tidal as well as day-night variations) from September 2009 till December 2011. The study area and the positions of sampling stations located between the latitudes 21°00'49.83"-21°13'07.5"N and longitudes 72°38'22.01"-72° 48'23.3"E are shown in Fig. 1. Surface water samples were collected by clean polythene bucket and bottom samples by using Niskin water sampler. For clarity, the results are presented in segments of upper estuary (stations 9-11), middle estuary (stations 6-8), lower estuary (stations 2-5) and coastal water/offshore zone (station 1). Since the DO was depleted almost completely up to station 6, which represents the mid-section of the estuary, a 24h, diurnal sampling every 2h was carried out from station 6 during September 2009 (monsoon), November 2009 (post monsoon) and April 2010 (premonsoon). Such diurnal sampling was extended for the lower segment during premonsoon (May 2011), monsoon (August 2011) and post monsoon (December 2011) period.

### 2.3 Analyses

Temperature was measured by a hand held thermometer with an accuracy of  $\pm 0.1^{\circ}\text{C}$  accuracy and pH with a microprocessor controlled pH meter with an accuracy of  $\pm 0.01$  unit. The instrument was calibrated before use with standard buffer solutions (pH 4.0, 7.0 and 9.2). The DO was fixed immediately after collection and measured by Winkler's method. Salinity was determined by Mohr titration (Grasshoff et al., 1983). Nutrient analysis was carried out within 6 h of collection. Analysis of nutrients was done, following Strickland and Parsons (1972) and Grasshoff et al. (1983). Measurement of ammonia as the sum of ionized ammonia ( $\text{NH}_4^+\text{-N}$ ) and unionized ammonia ( $\text{NH}_3\text{-N}$ ) was carried out following protocols of (USEPA 1985; Grasshoff et al. 1983; Batley and Simpson 2009). Chl-*a* was measured following Strickland and Parsons (1972) essentially using a Turner Fluorometer (Turner Designs, USA)

## 3. Results and discussion

### 3.1 Temperature

The mean annual depth-averaged water temperature in the Tapi Estuary ranged between  $22.3^{\circ}\text{C}$  and  $31.5^{\circ}\text{C}$ . The average winter temperature (November-February) was respectively in the range  $22.0\text{-}27.8^{\circ}\text{C}$ ,  $22.1\text{-}27.0^{\circ}\text{C}$ ,  $22.7\text{-}28.7^{\circ}\text{C}$  and  $22.5\text{-}28.9^{\circ}\text{C}$  in the upper, middle, lower estuary and the coastal waters. Similarly, during summer (March-June) it was in the range of  $28.5\text{-}33.0^{\circ}\text{C}$ ,  $26.2\text{-}31.6^{\circ}\text{C}$ ,  $29.5\text{-}31.5^{\circ}\text{C}$  and  $28.2\text{-}30.3^{\circ}\text{C}$  (Fig. 2). Its diurnal variation during monsoon (September 2009 and August 2011) ranged from  $26.4$  to  $29.6^{\circ}\text{C}$ ; in winter (November 2009 and December

2011) from 21.3 to 30.0°C and the summer (April 2009 and May 2011) 28.0 to 31.5°C. Day-night differences during summer and monsoon were minor unlike those observed during winter. As can be expected in the shallow estuarine region, no distinguishable difference was discernible for surface and bottom samples.

### *3.2 Salinity*

Depth-averaged, long term variations in salinity indicate its increase in upper zone for recent years. It rose from its 1983-1984 levels of ~0.1 (post monsoon) and 1.9 and (premonsoon) psu to 3.8 psu during April (premonsoon) 1995. Notably, the average salinity was 17.1 psu in December 2011 in the upper segment. However, during August 2011, 0.1 psu salinity was observed, as a result of fresh water flux to the Tapi Estuary during rainy season (Fig. 2). An increase of average salinity was also evident in the middle segment. A causeway cum weir commissioned during 1995 (Varghese et al. 2011), which reduced the inflow of freshwater in the estuary was probably responsible for the trend of increasing salinity. High salinity recorded during April 1992 (26.0 psu) prior to the commissioning of a weir may be due to restriction of freshwater during construction of the weir. However, salinity of coastal water remained more or less unaffected and ranged between 22.7 and 34.5 psu, with distinct seasonal fluctuations.

Tidal variation of salinity in the middle estuary (station 6) recorded during September 2009 (monsoon) varied between 0.4-4.4 psu and increased to 16.1-26.9 psu and 25.7-33.4 psu during November 2009 (post monsoon) and April 2010 (premonsoon) respectively (Fig. 3 & 4). In the lower estuary (station 5) too it co-varied with changing seasons and tides. For instance, during May 2011 (premonsoon), August 2011 (monsoon) and December 2011 (post monsoon) it respectively was in the range of 32.0-33.3, 14.7-29.3 and 28.4-33.0 psu (Fig. 5). There was no significant difference in surface and bottom salinity indicating well mixed water column during the dry season. However, during August 2011 (Monsoon) there was vertical salinity stratification. A distinct difference in surface (14.7-16.4 psu) and bottom (27.8-29.3 psu) was evident suggesting high influx of freshwater tongue inducing to density gradient during monsoon.

### *3.3 Dissolved oxygen*

#### *3.3.1 Historical variation*

During 1983 the depth-average concentration of DO was 8.4, 8.1, 6.7 and 6.3 mg l<sup>-1</sup> with saturation level of 99, 97, 86 and 89% in the upper, middle, lower estuary, and coastal water respectively, indicating good oxygen concentrations which continued until 1999 (Fig. 2). The DO concentrations decreased substantially in the upper estuary after 1999 barring occasional highs due

to fresh water discharge. The sudden decrease in DO concentration during 2000 and 2001 in most segments is attributable to low precipitation during these years throughout the west coast, hence, no replenishment of DO (Naqvi et al. 2009). Rain droplets bring atmospheric gases dissolved in it as well as it increases the solubility of oxygen in water due to low salinity and decreased temperature. Maximum average concentration of  $9.1 \text{ mg l}^{-1}$  in middle estuary during May 2003 (summer season) could be attributed to increased photosynthesis, as high chl-a ( $142.5 \text{ mg m}^{-3}$ ) in the mid estuary (Fig. 6).

As per the survey carried out by Surat Municipal Corporation (SMC) during 2001, upstream of weir at Rander, around  $5.2 \times 10^3 \text{ m}^3$  per day of domestic waste is discharged to the Tapi River through 28 discharges (Varghese et al. 2011). Downstream, there are several point and non-point discharges of sewage. The population of Surat, which was 2.8 million during 2001, has increased to 4.9 million in 10 years (Census of India, 2011). Domestic sewage (around  $3.4 \times 10^5 \text{ m}^3 \text{ d}^{-1}$ ) generated is discharged to the estuarine region both through point and non-point discharges (CPCB 2005).

Before construction of the weir near Surat City, the wastewater discharged would get flushed out into the ocean during the low tide. The weir restricts the flow of fresh water after monsoon and on daily basis, the excursion of at least a portion of tidal water. Hence, the organic waste discharged through different sources accumulates in the upper (down to weir) and mid-estuarine zones. The DO is used up for oxidation of organic matter, leading to hypoxic ( $<2.0 \text{ mg l}^{-1}$ ) and anoxic ( $<0.2 \text{ mg l}^{-1}$ ) conditions in the estuary especially during summer (March-May). However, during monsoon when the weir overflows, efficient flushing of estuary takes place and replenishes the DO in particular with influx of rainwater. However, the mid estuary remains hypoxic/anoxic most of the time (Fig. 2). In general, the lower estuary mostly sustains normoxic (90-100% saturation) condition. Normally, the concentration of DO is inversely proportional to salinity and water temperature but decomposition of organic matter lowers oxygen well below saturation. Water temperature varied seasonally but average salinity in the upper estuarine region increased after 1995 due to the construction of the weir, which restricts the freshwater flow causing seawater intrusion in the upper estuarine region. DO was negatively correlated with salinity in upper estuary ( $r=-0.66$ ;  $p<0.007$ ) likely because of salinity stratification and consumption during oxidation of organic matter. The DO was negatively correlated with temperature in lower estuary and coastal region.

### *3.3.2 Spatial and diurnal variation*

Following the summer 2009 fishkill, a study was conducted during postmonsoon, premonsoon and monsoon periods and two stations (one in middle estuary and the other in lower

estuary) were sampled for 24 h to determine tidal as well as day night variations. The concentration of DO at stations 1 to 4 was between 6.0 to 8.0 mg l<sup>-1</sup> representing the normoxic condition (90-100% saturation). Though DO value recorded at station 5 showed some fluctuations depending upon the season; overall, the water of Tapi Estuary from station 5 to 8 was seasonally under oxygen deficient conditions (Fig. 7). The concentration of DO decreased at station 6 substantially showing hypoxic and anoxic conditions. The water upstream of station 7 was anoxic for most of the study period (Fig. 7).

During the September 2009 24-h study, station 6 was hypoxic 44% of the time and oxygen deficient (< 4.0 mg l<sup>-1</sup>) the rest of the time (Fig 3). A clear tidal trend of DO was recorded at station 6 (Fig. 4), with minimum concentration (1.0 mg l<sup>-1</sup>) recorded at night (0300 h) in the bottom probably owing to net heterotrophy during hours of darkness. After withdrawal of the monsoon, the DO became deficient ushering in anoxic (< 0.2 mg l<sup>-1</sup> of DO) condition though for a short period in the month of November 2009 (Fig. 3). A similar trend was recorded during summer (April 2010). High concentration of chl- a recorded during April 2010 might have facilitated an increase in DO concentration. Concentration of DO recorded at station 5 (Fig. 5) during premonsoon was much better than that at station 6 (Fig. 3 & 4). However, during night, lower concentration (3.6-4.8 mg l<sup>-1</sup>) of DO was recorded. Premonsoon and monsoon DO concentrations were similar with depletion during low tide due to the flushing of waters from upper estuarine region into the lower reaches. Similar eutrophication and hypoxic condition due to restricted river flow and sewage discharge has been reported for Bilbao Estuary (Villate et al., 2013).

Our DO data indicate that long reaches (upper and middle segments) of Tapi Estuary were deficient in oxygen at all stages of tide, which was replenished during monsoon (Figs.3 & 5). The fresh water discharge from a weir constructed near Surat City and downstream of Tapi Estuary is given in Table 1. Since the weir overflows only during monsoon (mid June to mid October), the data is recorded only for this period. From the Table it is clear that there is no fresh water discharge during dry season (November-mid June). The BOD in the upper and middle estuarine segment was found to be high (Table 2) indicating high load of organic waste from sewage discharge.

### 3.4 Nutrients

Concentration of PO<sub>4</sub><sup>3-</sup>-P, which was 0.3 μmol l<sup>-1</sup> in upper estuarine segment during November 1983, varied widely during recent years and the high concentration of PO<sub>4</sub><sup>3-</sup>-P (99.0 μmol l<sup>-1</sup>) was recorded in upper estuary (station 11) during April 2010. The impact of increase of PO<sub>4</sub><sup>3-</sup>-P in estuarine zone has influenced the coastal water off Tapi estuary (Fig. 2).

The diurnal variation recorded in the middle estuary (Station 6) during all three seasons implies high concentration of  $\text{PO}_4^{3-}\text{-P}$ , with no clear tidal trend (Fig. 3 & 4). Negative correlation of  $\text{PO}_4^{3-}\text{-P}$  with chl-*a* during November 2009 ( $r = -0.3846$ ;  $p < 0.064$ ) and May 2011 ( $r = -0.5812$ ;  $p < 0.003$ ) in the lower estuary indicate its uptake of  $\text{PO}_4^{3-}\text{-P}$  by phytoplankton. The observed concentrations are quite lower than expected from its inputs from several sources (Sargaonkar, 2006), which may be attributed to its precipitation forming different or insoluble phosphatic compounds in oxic conditions (Berner 1980).

During 1983 the depth-averaged concentration of  $\text{NO}_3^- \text{-N}$  were 8.3, 18.7, 13.8 and 13.4  $\mu\text{mol l}^{-1}$  in the upper, middle, lower estuary and coastal water respectively.  $\text{NO}_3^- \text{-N}$  varied in the range 0.1-103.1, 2.6-40.2, 9.1-46.3 and 7.9-36.7  $\mu\text{mol l}^{-1}$  in upper, middle, lower estuary and coastal water respectively showing its enhancement at various levels. Seasonal and diurnal variations in the mid estuary were higher due to its enhanced inputs via land runoff during monsoon compared to postmonsoon.

$\text{NO}_2^- \text{-N}$ , which is a transition phase in the oxidation-reduction between  $\text{NH}_4^+ \text{-N}$  and  $\text{NO}_3^- \text{-N}$  (Berner, 1980; Neil, 2005; Chen et al., 2012), varied significantly both in the estuarine and coastal waters. During November 1983, the depth-averaged concentration of  $\text{NO}_2^- \text{-N}$  was 1.1  $\mu\text{mol l}^{-1}$ , 0.6  $\mu\text{mol l}^{-1}$ , 2.0  $\mu\text{mol l}^{-1}$  and 0.3  $\mu\text{mol l}^{-1}$  in upper, mid, lower estuary and the coastal waters respectively. It increased considerably and averaged a maximum of 26.0  $\mu\text{mol l}^{-1}$  during June 2005 in the mid estuary (Fig. 2). In steady state  $\text{NO}_2^- \text{-N}$  is thermodynamically unstable and low in concentration ( $< 1 \mu\text{mol l}^{-1}$ ) in coastal water (Madison and Wang 2006; Flo et al. 2011). Many factors, such as pH, temperature, light, dissolved oxygen, organic matter discharged through agricultural, industrial and sewage effluents can cause an accumulation of nitrite in the coastal and estuarine waters (Razumov and Tyutyunova 2001; Philips et al. 2002; Chen et al. 2012). Such accumulation is attributed to the proliferation of certain autotrophic bacteria (*Nitrosomonas* sp.) and inhibition of *Nitrobacter* sp. (Weon et al., 2002). It has been shown that DO level  $< 0.5 \text{ mg l}^{-1}$  could also cause build up of  $\text{NO}_2^- \text{-N}$  (Hanaki et al., 1990). Since, concentration of DO in the upper and mid part of Tapi Estuary remains  $< 0.2 \text{ mg l}^{-1}$  for most of the time, this may be causing build up of  $\text{NO}_2^- \text{-N}$ .

Substantial increase of  $\text{NH}_4^+ \text{-N}$  has taken place in recent years and a depth-averaged concentration of 73.0  $\mu\text{mol l}^{-1}$  was recorded during May 2006 (premonsoon) in the upper estuarine segment, which is due to the buildup of organic load during summer as a result of insufficient flushing of the estuary. Accordingly depth-averaged concentration of  $\text{NH}_4^+ \text{-N}$  (19.8  $\mu\text{mol l}^{-1}$ ) recorded during August 2011 in the coastal region (Fig. 2) indicates that the estuarine water containing high concentration of  $\text{NH}_4^+ \text{-N}$  is flushed offshore. These results indicate poor water



quality up to station 6 during post and premonsoon seasons. There seems to be an extension of such retardation of quality well into the adjacent coastal area in recent years (Fig. 8). Diurnal study revealed maximum concentration of  $\text{NH}_4^+\text{-N}$  ( $90.5 \mu\text{mol l}^{-1}$ ) during low tide in April 2010 in the mid estuary. Significant negative correlation of  $\text{NH}_4^+\text{-N}$  with salinity ( $r=-0.61$ ,  $p<0.0001$ ;  $r=-0.59$ ,  $p<0.0001$ ) is attributable to nitrification, as a result of oxidation of organic waste in the upper estuary to  $\text{NO}_3^-\text{-N}$  with the ingress of seawater containing high concentration of DO. In general, the  $\text{NO}_3/\text{NH}_4$  ratio increased towards coast in the historical data. The diurnal study also showed low  $\text{NO}_3/\text{NH}_4$  ratio in the mid estuary as compared to lower estuary. This may be caused by decrease in  $\text{NH}_4^+\text{-N}$  and increase of  $\text{NO}_3^-\text{-N}$  in lower estuary due to nitrification. Correlation between  $\text{NO}_3/\text{NH}_4$  and Chl-a was negative ( $r=-0.53$ ,  $p<0.036$ ) during November 2009 and ( $r=-0.58$ ,  $p<0.02$ ) during April 2010 indicating the preference of  $\text{NH}_4^+\text{-N}$  over  $\text{NO}_3^-\text{-N}$  by phytoplankton. As Dortch (1990) indicated preferential utilization/uptake of  $\text{NH}_4^+\text{-N}$  vis a vis  $\text{NO}_3^-\text{-N}$  by some phytoplankton may also lead to such dynamic depletion of  $\text{NH}_4^+\text{-N}$ .

#### 4 Principle Component Analysis

Principle Component Analysis (PCA) has been shown to be a useful technique in the evaluation of environmental data (Clark, 1993; Zitko, 1994). Recently PCA has also been applied as a tool for water quality evaluation and management with special emphasis on the trophic potential (Parinet et al., 2004). Assessments of coastal eutrophication have also been based on PCA (Lundberg et al., 2005). To reduce the dimensionality of multivariate data set containing 10 variables that we have presented for 4 different zones along the Tapi estuary, Principal component analysis (PCA) (Mardia et al., 1979) was carried out. Before PCA, data was converted to a zero mean, unit variance equivalent to give each chemical parameter the same magnitude and variance and consequently the same influence in the PCA. Table 3 shows the weights for the first three principal components. The first three principal components account for over 53 % of the variability in the data set and we used these three components in the further analysis.

Principal component 1 (PC-1) showed positive weights for all parameters except salinity,  $\text{NO}_3^-\text{-N}$ , DO, and pH, which had a negative weight. Consequently, samples with elevated temperature,  $\text{NO}_2^-\text{-N}$ ,  $\text{PO}_4^{3-}\text{-P}$ ,  $\text{NH}_4^+\text{-N}$ , Chl.a and Phaeophytin tend to have high values of PC1. The large weights associated with  $\text{NH}_4^+\text{-N}$ , Chl. a and Phaeophytin are interpreted as due to high organic load associated with sewage discharge. In addition, if the samples had elevated concentrations of  $\text{NH}_4^+\text{-N}$  and Chl. a, the high PC1 value would also indicate eutrophication. Negative values of PC1 are mainly due to salinity stratification of upper estuary. PC-1 thus explained the formation of  $\text{NH}_4^+\text{-N}$  in the absence of DO with the consumption of  $\text{NO}_3^-\text{-N}$ , confirming denitrification in the upper estuary. PC-2 showed large positive weights for all the parameters and large negative

weight for  $\text{NH}_4^+\text{-N}$ . Samples with large negative values of PC-2 will generally have elevated DO, Chl.a and phaeophytin indicating aerobic conditions. Samples with large positive PC-2 values are interpreted as coming from upper estuary that have had significant amounts of degradation products. The negative weight associated with  $\text{NH}_4^+\text{-N}$  means that the concentrations are no longer elevated. PC-3 showed large positive weights for temperature,  $\text{NO}_3^-\text{-N}$  and  $\text{NO}_2^-\text{-N}$  and small negative weights for salinity, pH,  $\text{NH}_4^+\text{-N}$ , chl. a, phaeophytin, and DO. We interpret the samples with large positive values of PC-3 as being from zones with elevated quantities of nitrogen, and slightly low oxygen.

#### 4. Fish Kill in Tapi Estuary

Fishkills had taken place during October 2007, May-June 2009 and occasional events followed thereafter. *Liza persia*, *Arius dussumieri*, *Arius caelatus*, *Lepturacanthus savala*, *Muraenesox* sp. and *Puntius* sp. were found dead in the region. Several factors are known to cause fish kills such as hypoxia/anoxia, or the build up of high concentrations of ammonia or nitrite (Diaz and Rosenberg, 1995; Wetzel, 2001; Anderson et al., 2002; Breitburg, 2002, Camargo and Alonso, 2006). Our long term and extensive studies bring forth that most of the time the mid zone (Station 6) of Tapi Estuary is under hypoxic condition during monsoon and anoxic condition during postmonsoon and premonsoon seasons) (Fig. 3). The lower estuary (Station 5) experienced oxygen deficient condition ( $\text{DO} < 4.0 \text{ mg l}^{-1}$ ) even during monsoon. Nutrient inputs -through some  $2.5 \times 10^4$  MT of N and  $0.6 \times 10^4$  MT of P in agricultural fertilizers (CPCB 1994) from the Tapi Basin do induce eutrophication and subsequent hypoxic condition. Besides the  $3.4 \times 10^5 \text{ m}^3 \text{ d}^{-1}$  of sewage inputs downstream of the weir (CPCB, 2005), the lower estuary receives waste water from several multiple industrial units such as oil and gas, petrochemical, fertilizer plant, thermal power, heavy engineering and a steel plant situated in the Kawas-Hazira industrial belt. In the absence of efficient flushing, build up of organic load takes place in the upper estuary, which gives rise to nutrients after its oxidation, causing eutrophication, hypoxic and anoxia and ultimately dead zones in the estuary.

Fish mortality caused by natural and anthropogenic hypoxia has been reported in several coastal and estuarine waters and bays since 1900 (Diaz and Rosenberg 2008; Broszeit et al., 2013). Depending on the fish species, mortality can take place if oxygen levels drop below a certain critical concentration. Several studies have shown threshold level of  $\text{DO} < 2.0 \text{ mg l}^{-1}$  to cause mortality of several species (Fischer et al., 1992; Breitburg, 1994; 2002; Shimps et al., 2005). Higher temperatures, as are prevalent in this part of the world, can exacerbate the situations. It has been shown that most fish will suffocate, if DO is below  $1 \text{ mg l}^{-1}$  (Liu et al. 2005) as was also noted by us from Tapi Estuary during September 2009. Mainly catfish were seen gasping at the surface between 3 to 4 am in the morning. The DO concentration at this time was minimal ( $1 \text{ mg l}^{-1}$ ). Carruthers et

al. (1959) have reported that fish move away from the oxygen minimum zone to avoid this. However, in shallow, confined water systems it may be difficult for the fish to escape. It is also possible that fish were carried by the flood wave ahead of the hypoxic/anoxic water and were trapped at the outflow where the watercourse constricts to a small set of rapids (Townsend et al. 1992). As suggested by Shimps et. al. (2005) and Vaquer-Sunyer and Duarte, (2008), though some species of fish can acclimate to hypoxia, direct mortality is most likely to occur in the field when DO concentrations are far low akin to our recorded ones or, when the DO decreases are very rapid.

## **5. Conclusion**

Long term data on DO and nutrients reveal that substantial increase of nutrients, in particular of  $\text{NH}_4^+\text{-N}$  and  $\text{NO}_2^-\text{-N}$  have taken place in Tapi Estuary. The estuary remains hypoxic for most of the time followed by anoxia during low tide times. Such condition is the result of inhibition of flushing of the estuary after construction of a series of dams and increased level of domestic and industrial wastes. Increased industrialization and human population of Surat City and discharge of their waste waters have given rise to organic loading beyond the assimilation capacity of the estuary. The hypoxia, which was initially limited to the upper and middle estuarine segment, has extended to the lower region. High concentration of  $\text{NH}_4^+\text{-N}$  and low values of DO observed in most recent studies in the coastal region are of serious concern. We attribute the fishkills in Tapi Estuary to hypoxia/anoxia, caused by the indiscriminate release of domestic and industrial wastes and to restricted flushing owing to the building of barrages midstream which have not only impeded the natural tidal flushing and exchanges but also seem to have caused certain retention of high tide ingressions. Flushing is to be maintained and discharging of wastes containing high organic loads should be regulated/treated/prevented so as to reinstate normalcy in this once healthy coastal body.

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## Legend to the Figures

Fig 1: Map showing sampling locations in the Tapi Estuary.

Fig 2: Depth-averaged variation of temperature, pH, salinity, DO,  $\text{PO}_4^{3-}\text{-P}$ ,  $\text{NO}_3^-\text{-N}$ ,  $\text{NO}_2^-\text{-N}$ , and  $\text{NH}_4^+\text{-N}$  in Tapi Estuary from 1983 to 2011.

Fig 3: Variation of water quality at station 6 during September 2009 to April 2010.

Fig 4: Variation of water quality at station 5 during May 2011 to December 2011.

Fig 5: Diurnal Variation in water quality parameters (— S and ---- B) at station 6 during April 2010

Fig 6: Depth-averaged variation of DO (----), chl. *a* (—●—) and phaeophytin (—) in Tapi Estuary from 1983 to 2011.

Fig 7: Spatial variation of DO (----) and  $\text{NH}_4^+\text{-N}$  (—) during different seasons.

Fig 8: Depth-averaged variation of  $\text{NH}_4^+\text{-N}$  (—) and  $\text{NH}_3\text{-N}$  (----) in Tapi Estuary from 1983 to 2011.

Table 1: Fresh water discharge at the weir point near Surat City and downstream of Tapi Estuary recorded during monsoon months of year 2010 (Source: Surat Municipal Corporation) – indicating no discharge

Day	Average Fresh Water Discharge (Cusecs)				
	June	July	August	September	October
1	-	8852.12	11655.5	95420.31	11857.24
2	-	8755.614	13782.21	72430.71	14364.99
3	-	8698.284	14048.35	108653	15152.76
4	-	8690.64	13753.47	59965.2	15165.95
5	-	8640.954	13890.91	51495.79	15203.48
6	-	8794.79	13797.2	51636.06	15238.98
7	8981.112	8982.068	12667.39	60253.76	15275.49
8	9060.419	9914.626	14274.36	86137.69	15339.39
9	9117.749	11049.1	22840.95	107835.4	15366.78
10	9145.458	11176.34	19709.11	997154	15396.19
11	9175.079	11120.17	16313.9	497251.6	14942.8
12	9179.856	11213.02	14275.76	74994.38	15538.19
13	9126.826	11147.68	12988.46	88898.71	15585.87
14	9043.22	11088.08	13052.89	46727.49	15590.94
15	9063.285	11159.15	16233.28	41169.56	15607.17
16	10943.64	11058.27	16165.03	41742.83	15590.94
17	11423.94	11067.44	14729.07	41967.49	-
18	11151.12	11038.79	11301.29	40968.14	-
19	11090.37	11242.83	11383.82	40859.68	-
20	11119.03	11409.04	11131.64	41611.13	-
21	11152.27	11495.01	11235.95	28383.79	-
22	11112.15	11660.08	11488.14	27640.01	-
23	11008.98	11210.73	11125.9	32955.17	-
24	10976.89	11428.53	11002.1	16070.7	-
25	10925.3	14048.69	11121.32	11336.82	-
26	10822.14	15063.8	11076.61	11019.3	-
27	10689.16	16599.15	22702.03	11015.86	-
28	9518.681	15437.28	69158.9	11127.05	-
29	9080.484	13468.98	71730.72	11383.82	-
30	8972.513	11310.46	59931.9	11285.24	-
31	-	11190.1	111324.7	-	-



Table 2: Spatial variation of BOD (mg/l) in Tapi Estuary during different sampling events.

Station	Apr10	May11	Dec11
1	2.7	6.0	3.0
2	3.2	5.5	0.7
3	3.2	5.3	3.3
4	3.8	4.2	1.7
5	2.0	6.0	3.2
6	71.0	2.9	2.5
7	25.3	-	12.2
8	-	-	10.0
9	82.0	-	1.2
10	130.0	112.8	40.0
11	-	104.5	37.5

Table 3: Principal component weights for each variable obtained from  
PCA analysis of complete data set.

<b>Variables</b>	<b>Principal component weights</b>		
	<b>PC-1</b>	<b>PC- 2</b>	<b>PC- 3</b>
Temp	0.17769	0.02405	0.46895
Salinity	-0.31963	0.19769	-0.15068
pH	-0.10280	0.17441	-0.09890
NO <sub>2</sub> <sup>-</sup> -N	0.22197	0.06935	0.67911
NO <sub>3</sub> <sup>-</sup> -N	-0.12959	0.30360	0.40709
PO <sub>4</sub> <sup>3-</sup> -P	0.18117	0.18236	0.06332
NH <sub>4</sub> <sup>+</sup> -N	0.38878	0.42784	-0.17593
Chlorophyll <i>a</i>	0.49810	0.41452	-0.19798
Phaeophytin	0.52672	0.36768	-0.20131
DO	-0.28306	0.55644	-0.07747
<b>Eigen value</b>	2.35165	1.68147	1.32963
<b>Variance (%)</b>	23.531	16.825	13.304
<b>Cumulative Variance%</b>	23.531	40.356	53.66

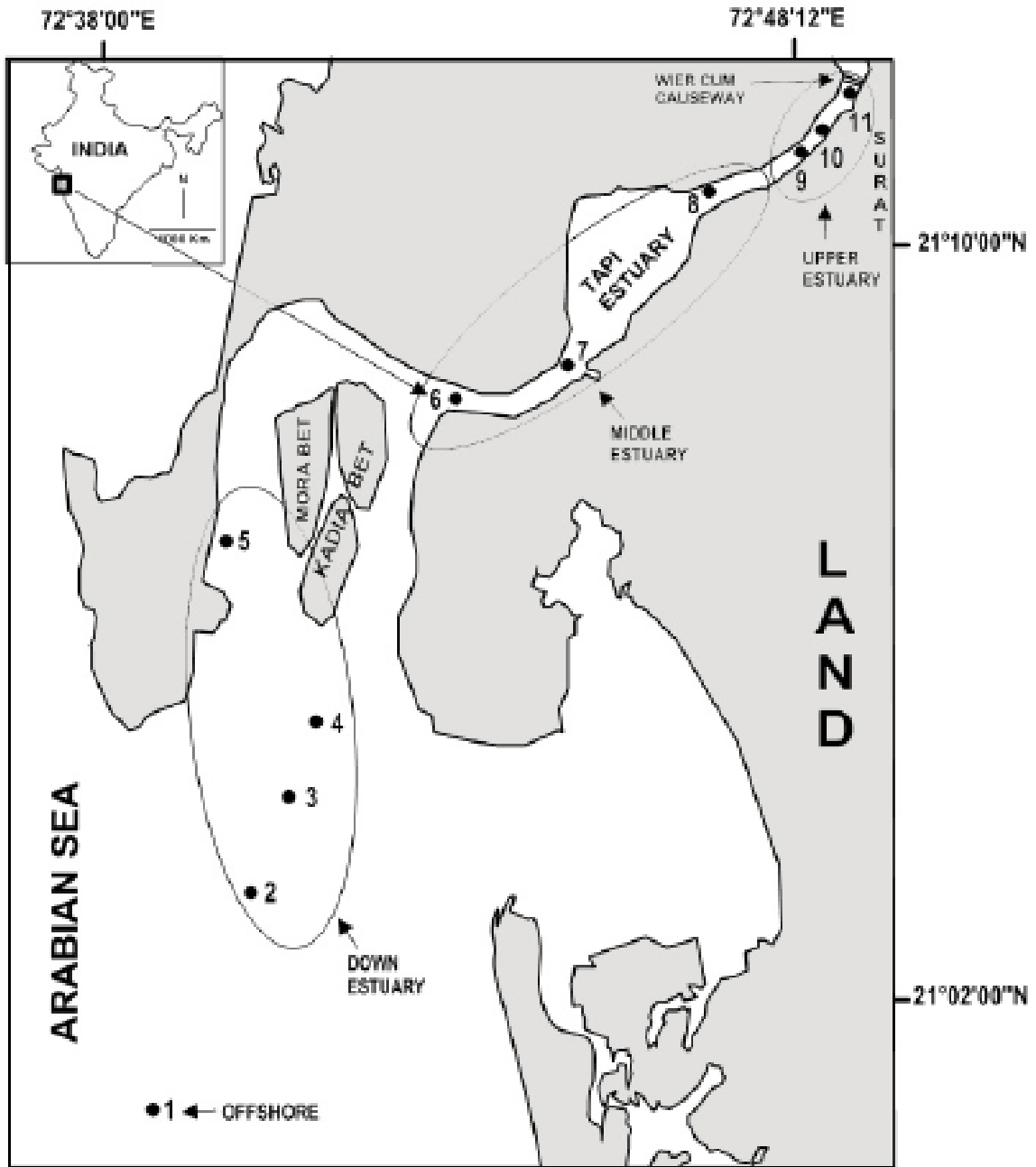


Fig. 1

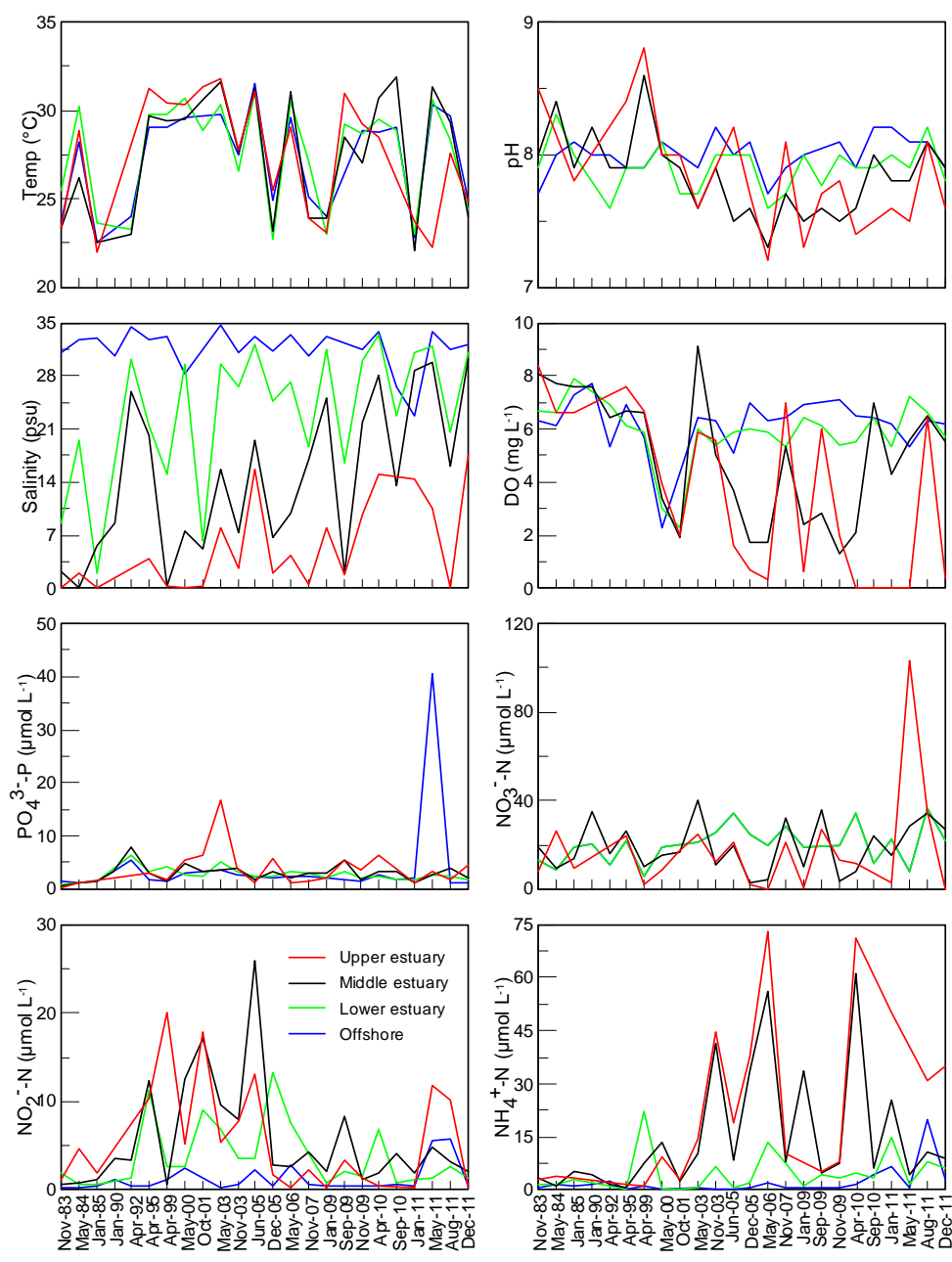
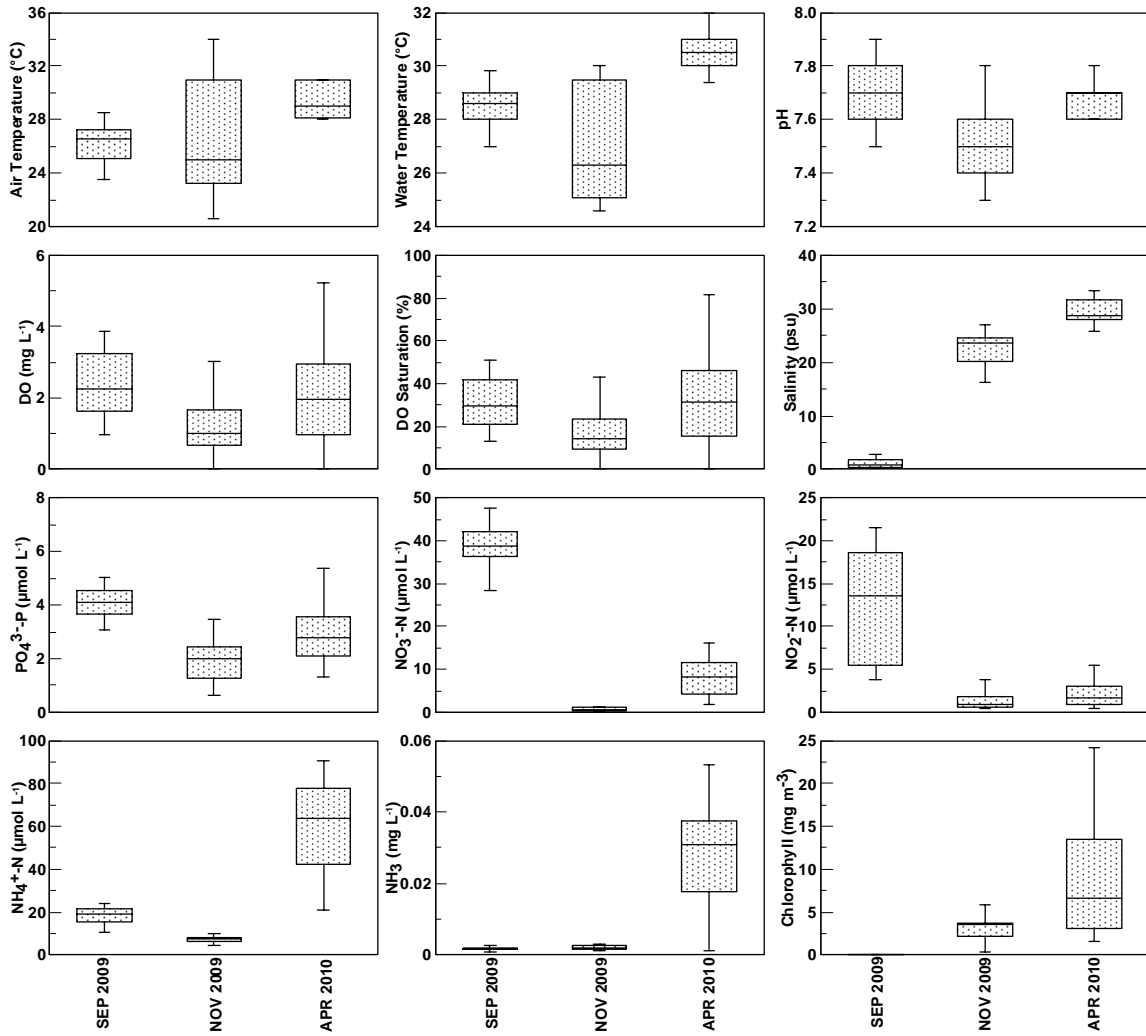


Fig. 2



**Fig. 3**

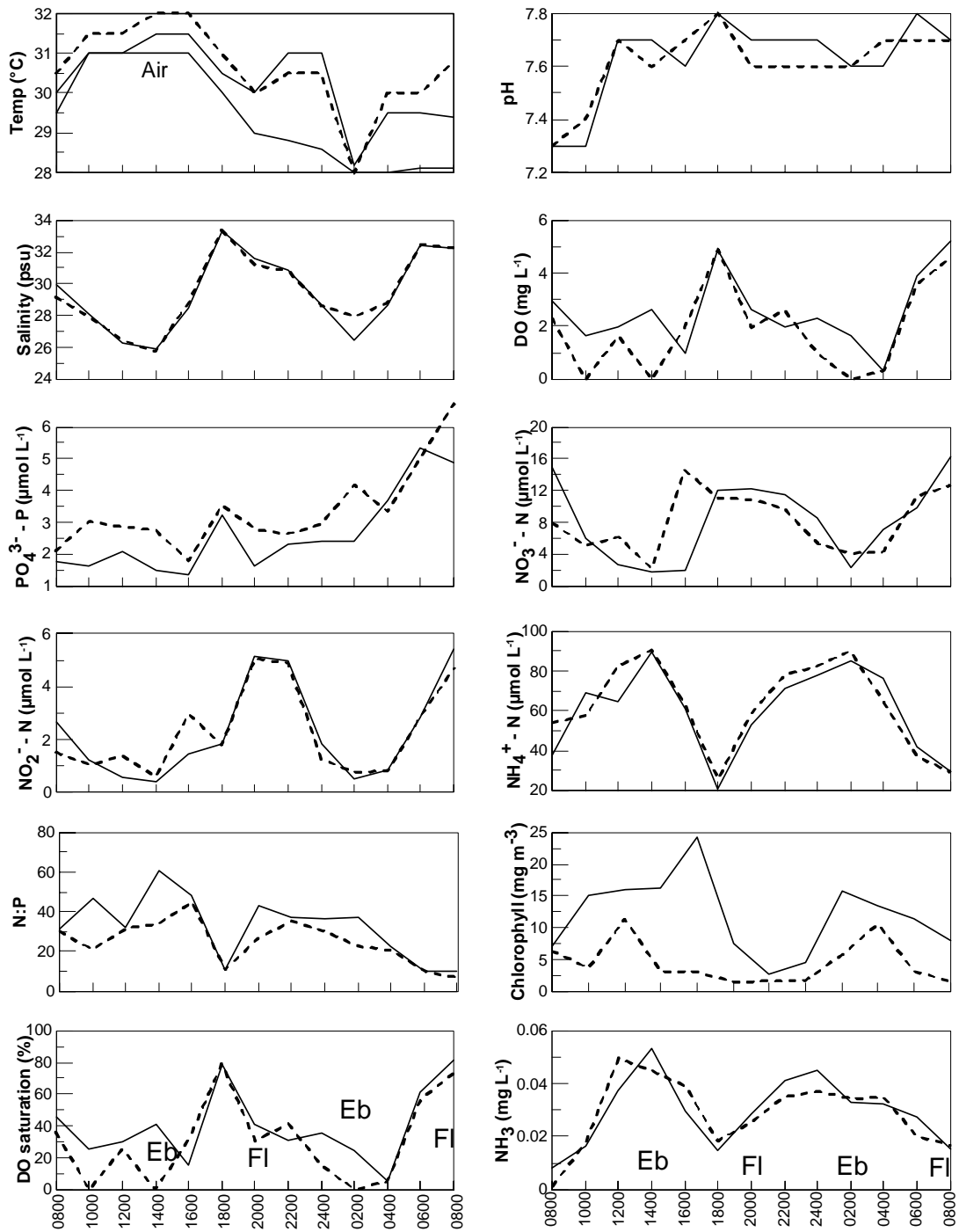


Fig. 4

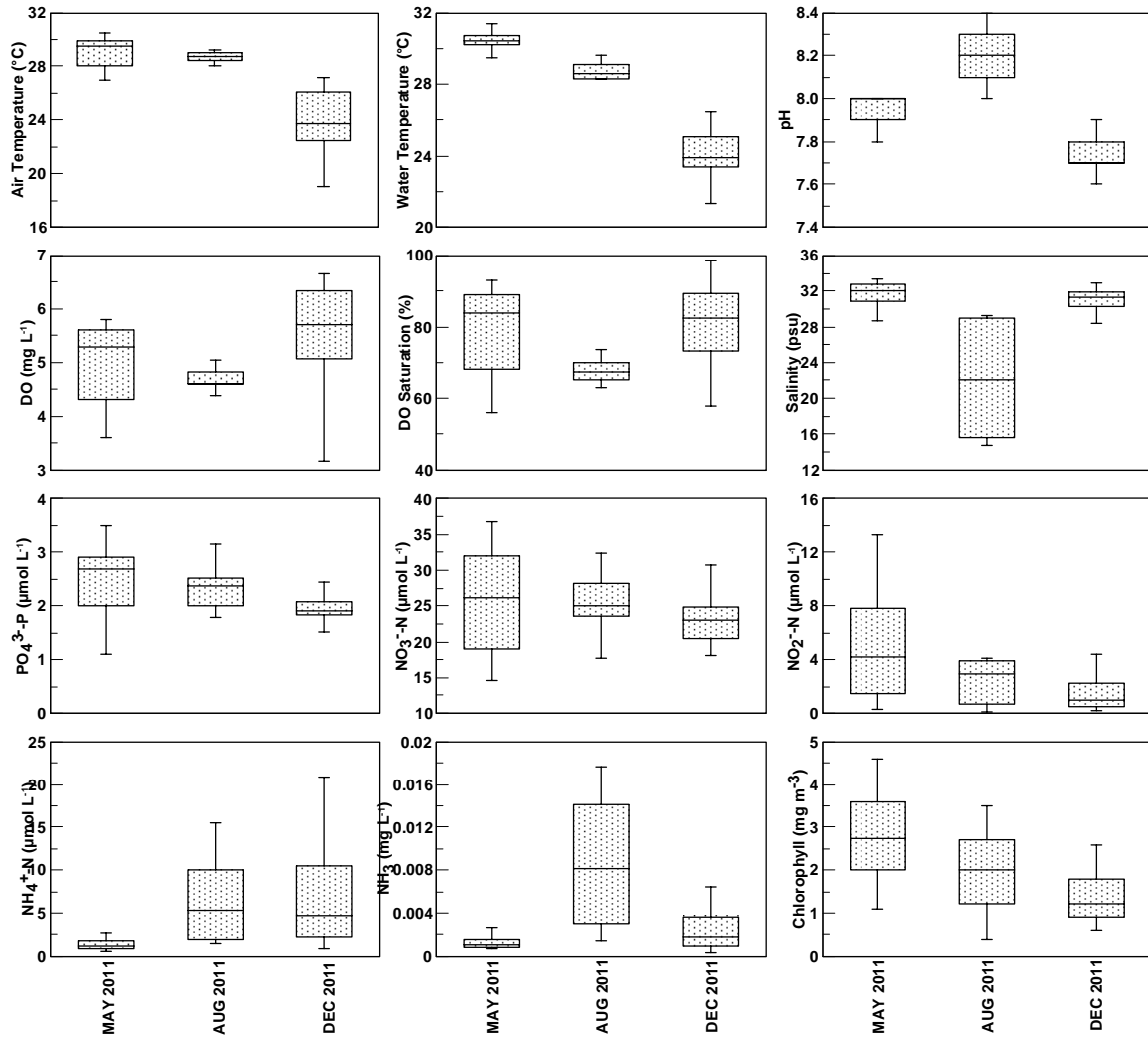


Fig. 5

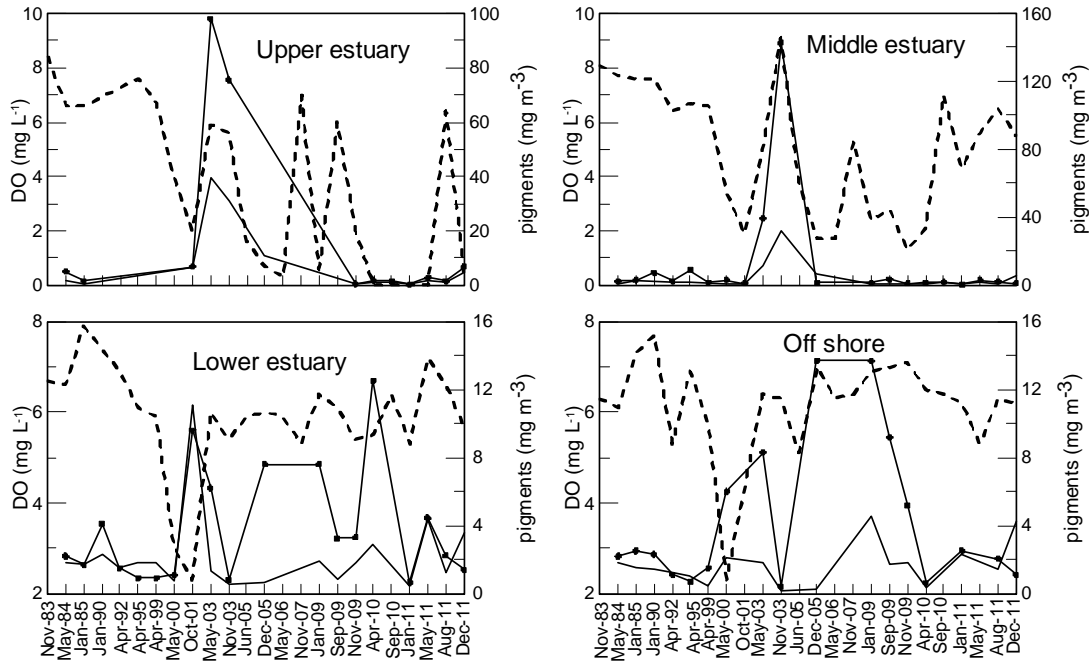


Fig. 6

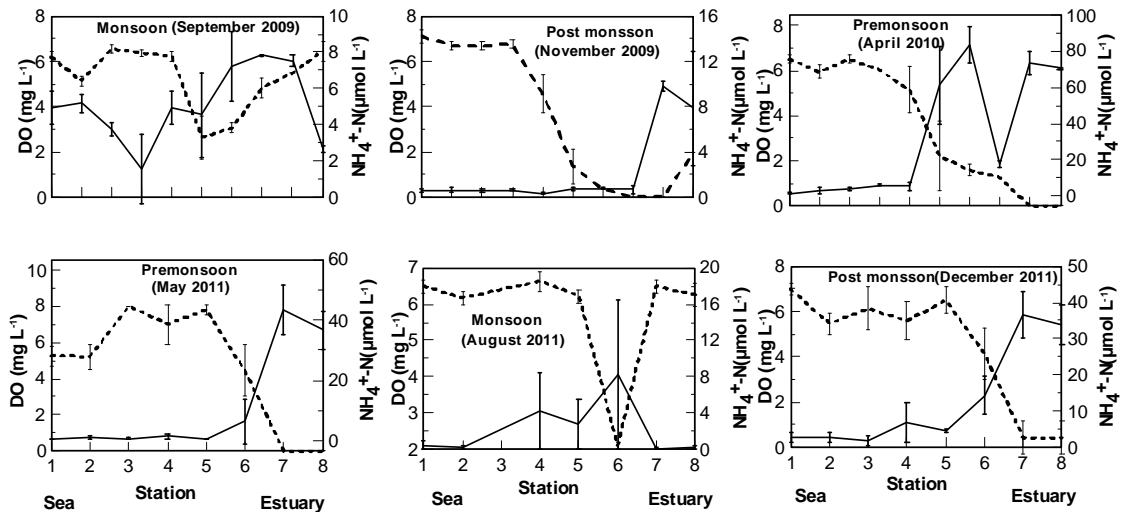


Fig. 7



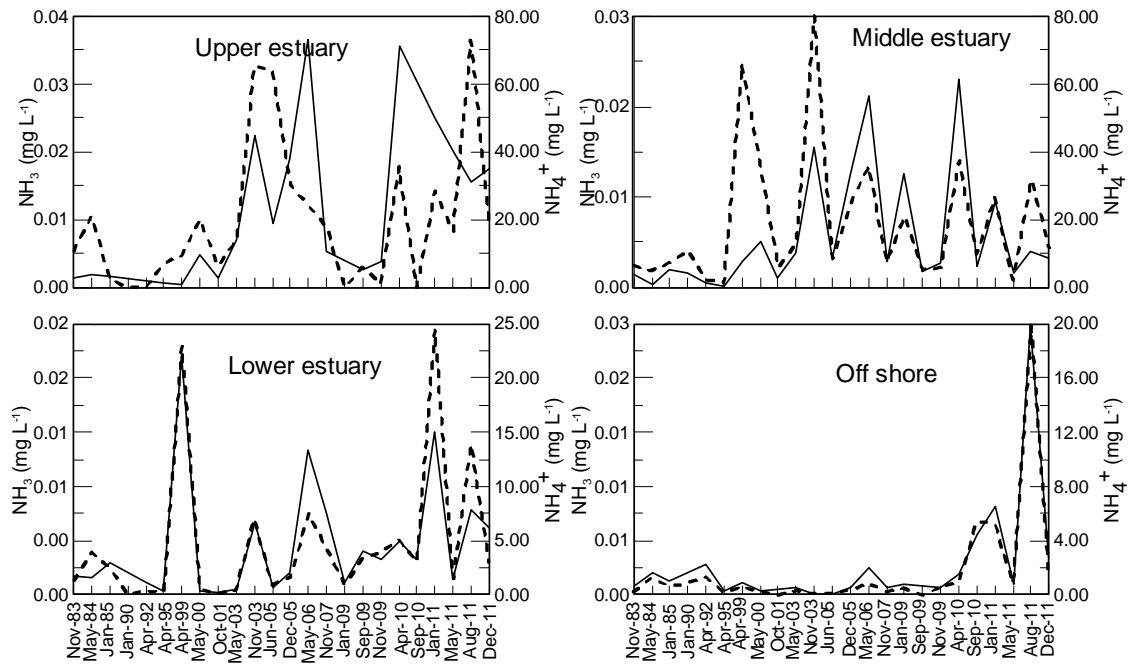


Fig. 8