

## CHAPTER - IV

### EXCHANGE OF BIOGENIC ELEMENTS ACROSS THE SEDIMENT-WATER INTERFACE

#### **4.1. Introduction**

Benthic environment is an important part of shallow water systems like estuaries, lagoons, nearshore and shelf environments. Since most of the organic matter produced in the system by phytoplankton or derived from land runoff sinks to the underlying sediment benthic regeneration and subsequent flux of nutrients exert a major control on the nutrient availability and in turn primary productivity of the pelagic system. Rowe *et al.* (1975) stated that if there were no benthic efflux of nitrogen (mainly  $\text{NH}_4^+$ ) in a shallow water environment, the system could lose its feedback and the primary production would solely be dependent on water column regeneration and thus would be reduced to rates similar to those found in the open ocean. In order to understand the role of benthic fluxes in estuarine and coastal ecosystems of Goa, flux measurements were undertaken in the estuarine and shelf region of Goa.

#### **4.2. Mechanisms and factors controlling benthic exchange**

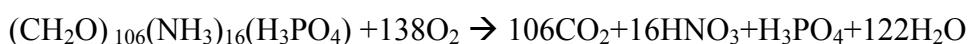
Several factors are responsible for exchange of nutrients and other solutes across the sediment water interface. A brief overview of those factors is as follows.

##### **4.2.1. Benthic mineralization**

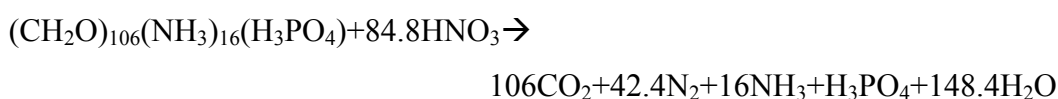
Benthic nutrient regeneration and metabolism are controlled by the supply of labile organic matter to the sediments. In estuarine and coastal systems degradable material enters the benthic system from terrestrial, littoral, pelagic sources and occasionally from *in-situ* production (Hartwig, 1978) which makes sediments of shallow water systems organic rich. Increasing primary productivity and subsequent sedimentation favours the preservation of more labile organic matter. Muller & Suess (1979) observed that a 10 -

fold increase in sedimentation rate led to the doubling of sedimentary organic carbon. Moreover, estuarine and coastal sediments have an oxic surface layer, only a few mm thick (Jorgensen & Revsbech, 1985). Hence the organic matter is mostly degraded by the anoxic mineralization process. However, since anoxic decomposition is a slow and less efficient process compared to oxic decomposition, it results in increased preservation of the organic matter and in turn, higher organic matter in the sediment. Organic matter decomposition is strongly temperature dependent (Nixon *et al.*, 1976) which is reflected in the seasonality of the benthic respiration rate. Benthic macrofauna can also influence both the magnitude and timing of decomposition (Rhoads, 1974; Aller, 1980, 1982; Rudnick & Oviatt, 1986). The oxidation of organic matter in the bottom sediments is stoichiometrically and sequentially coupled to the consumption of  $O_2$ ,  $NO_3^-$  and  $SO_4^{2-}$  according to mineralization models suggested by Redfield *et al.* (1963) and Richards (1965).

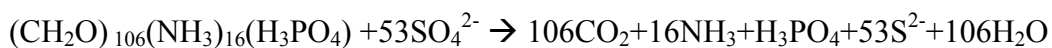
Under oxic condition oxygen is used by heterotrophic bacteria to decompose organic matter.



In the suboxic zone underlying the upper oxic layer  $NO_3^-$  is used up in the decomposition process.



In the anoxic zone sulphate acts as the terminal electron acceptor after oxygen and nitrate are exhausted.



Most of the organic matter including organic carbon, nitrogen and phosphorus that is deposited in the sediment is again mineralized. The products  $HCO_3^-$ ,  $NH_4^+$  and  $HPO_4^{2-}$  are released to the pore water and ultimately recycled into the overlying water by molecular diffusion, turbulent mixing, bioturbation etc. Only a small percent of the remineralized C, N and P are permanently buried.

#### 4.2.2. Diffusion

Aerobic degradation in the upper few mm and anoxic degradation in the underlying sediment layer releases the nutrients; N in the form of  $NH_4^+$ , P in the form of  $PO_4^{3-}$  and

silicate to the pore water. Due to this release, a concentration gradient is set up with increasing concentration with depth and this leads to the diffusion of these solutes across the gradient into the overlying water. Some fraction of  $\text{NH}_4^+$  undergoes adsorption onto clay minerals (Rosenfeld, 1979). Some part of  $\text{PO}_4^{3-}$  also remains adsorbed onto and/or precipitated with ferric minerals in the oxidized surface sediment (Krom & Berner, 1980). Similarly,  $\text{SiO}_4^{4-}$  has been found to be exchanged with different clay minerals (Siever & Woodford, 1973). But in spite of these geochemical processes within the sediment column, benthic efflux of these nutrients due to diffusion is still found to be significant in many estuarine and coastal systems. Oxygen from the overlying water generally diffuses to the sediment and used up in the aerobic degradation of organic matter. But because of low permeability and high respiration rate of the benthic community, it gets used up quickly resulting in only a few mm of the surficial sediment which is in direct touch with oxic overlying water being oxygenated.  $\text{NO}_3^-$  exchange shows dynamic variability in the direction of the flux. Some systems have been found to exhibit  $\text{NO}_3^-$  release from sediment whereas in the other systems  $\text{NO}_3^-$  diffusion to the sediment has been observed. However, since the coupling of nitrification and denitrification has been found in many coastal systems (Jenkins & Kemp, 1984), it means that the  $\text{NO}_3^-$  diffusing from the overlying water and produced from nitrification in the oxidized surficial sediment, gets denitrified in the suboxic zone just below the thin, oxic sediment layer. Molecular diffusion is an important process for transport of biogenic elements from sediment to the overlying water (Manheim, 1970; Li & Gregory, 1974; Lasaga, 1979; Katz & Ben-Yaakov, 1980).

#### **4.2.3. Activities of benthic animals**

Many organic rich coastal sediments are inhabited by a large number of benthic macro fauna and meiofauna feeding on deposited organic matter. These animals profoundly affect the transport processes. Various infaunal animals disturb the sediment structure differently, depending upon their specific feeding behavior, mobility and life cycle. Sediment reworking by feeding, burrowing and construction activity influence particle transport (Rhoads, 1974; Yingst & Rhoads, 1980) while water and nutrient transport are affected mostly by ventilation (Kristensen, 1984). The consequent physical and chemical

changes in the sediment enhance microbial activities and growth rates (Frenchel, 1972; Hylleberg, 1975; Hargrave, 1976; Rhoads *et al.*, 1977; Kristensen *et al.*, 1985) which in turn may control sedimentary nutrient cycling and thereby its exchange with overlying water.

#### *Bioturbation*

Spatial reworking of the sediment layer by diverse groups of benthos is called bioturbation. Thus the sediment particles in the upper layer which is inhabited by macrobenthos are subjected to continuous transfer. The zone affected by bioturbation generally reaches 5-10cm, rarely even up to 15cm below the sediment surface (Aller, 1988, 1990, 1994; Dicke, 1986). This mixing of sediment by benthic organisms homogenizes the sediment in turn destroying the existing vertical biogeochemical zonation. As a result, the porewater in the deeper sediment layer gets mixed with the overlying water thereby directly transferring biogenic elements to the latter. Bioturbated zone remains oxic and therefore several geochemical processes affect the pore water element concentration thereby changing the rate of diffusive flux between sediment and overlying water.

#### *Bioirrigation*

The process by which benthic organisms actively transport bottom water through their habitats is known as bioirrigation. In this case oxygen rich overlying water is usually pumped into the sediment and water with less oxygen getting pumped out. Typical conveyor belt feeders, such as polychaetes are intense pertubers (Rhoads, 1974). They live head down in permanently vertical burrows feeding on deposited organic matter. Burrows and tubes carry oxygen rich overlying water and this ventilation is a major factor in controlling biogeochemical processes occurring in sediments (Kristensen, 1984, 1985). Infaunal ventilation activity usually produces an increased transport of water and solutes in and out of the sediment. Penetrating oxic bottom water distorts the biogeochemical zones in the sediment and oxidizes reduced end products of anoxic mineralization such as  $H_2S$  and  $NH_4^+$  occurring at depth. Glud *et al.* (1994) detected an open cavity at a depth 80-90 mm full of oxygen rich bottom water. It has been shown that the flux induced by bioirrigation is several times larger than diffusive flux. Bioirrigation is volumetrically much greater than bioturbation. Goldhaber *et al.* (1977), Grundmanis &

Murray (1977), Aller & Yingst (1978), Hammond & Fuller (1979) and McCaffrey *et al.* (1980) have reported the enhancement of benthic exchange by macrobenthic irrigation in the sediment. Significant transport of solutes through the bubble tubes created by benthic organisms has also been found by Martens *et al.* (1980) and Klump & Martens (1981).

#### **4.2.4. Resuspension of surficial sediment**

Strong bottom currents and turbulent mixing cause disturbance in the water column also resulting in resuspension of the surficial sediment and consequently releasing nutrient rich pore water to the overlying water (Hammond *et al.*, 1977; Vanderborght *et al.*, 1977).

#### **4.2.5. Advection of pore water**

Movement of pore water from the sediment to the overlying water column is termed as advection. This type of physical transport of pore water occurs because of three different processes.

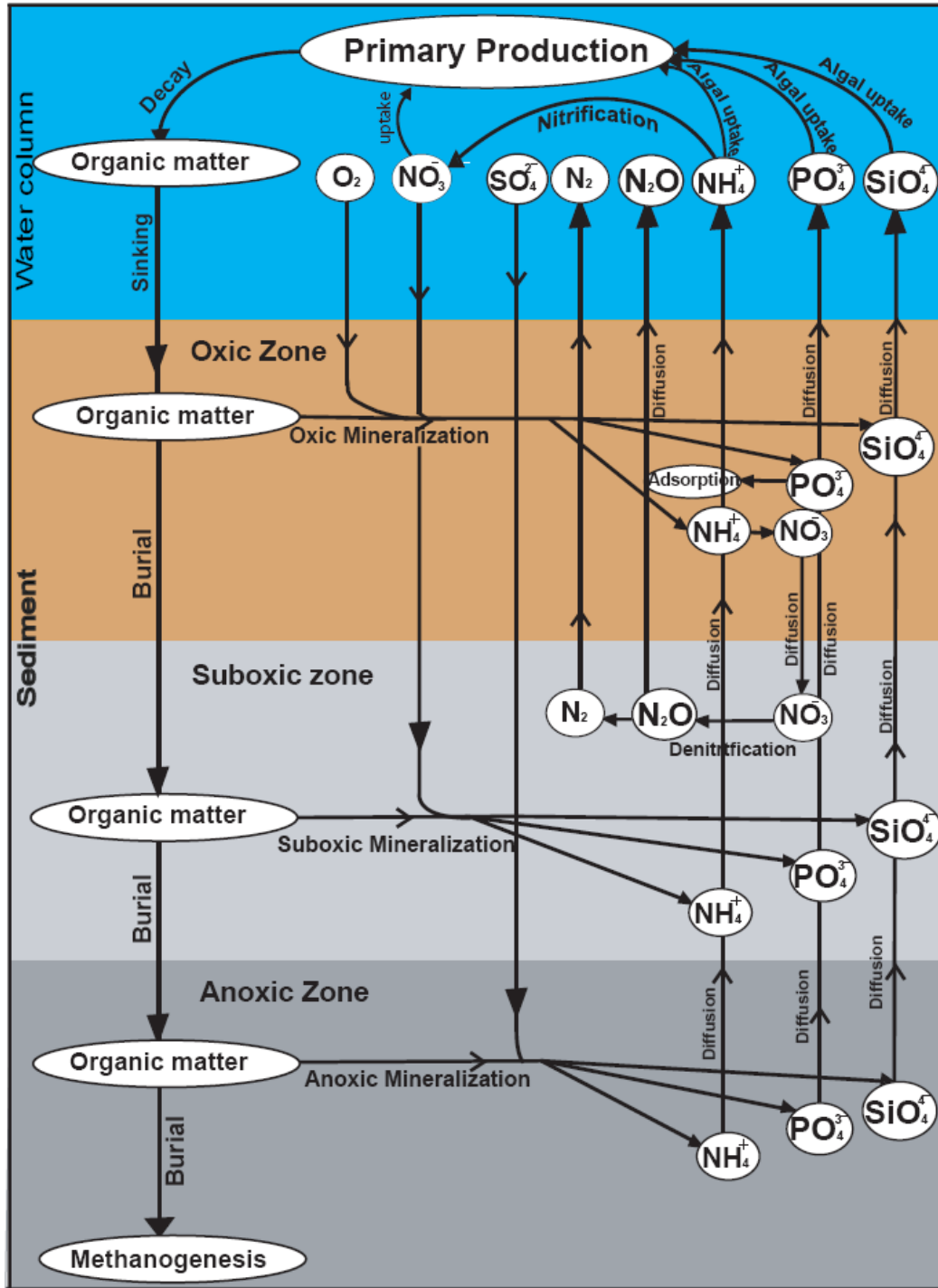
(1) Sediment compaction because of hydrostatic pressure and resulting flow of pore water towards the sediment surface (2) seafloor areas with warmer currents and a resulting upward directed pore water flow. (3) Currents in bottom water that induce pressure difference at the luv and lee sides of uneven patches on the sediment surface.

In response to the above phenomena pore water is released to the overlying water. Marinelli *et al.* (1998) observed a significant advective pore water transport in the upper 4-8cm of the permeable sediment of the US continental shelf. Huettel *et al.* (1996) found the advective pore water flow to be enhanced by increasing porosity of the sediment and flow velocity of overlying water.

#### **4.2.6. Evaporation during low tide and subsequent flushing:**

Oppenheimer and Ward (1963) described an additional mechanism of nutrient release from intertidal sediment. Intertidal sediments are periodically exposed during low tide. Interstitial water is drawn to the surface by capillary action caused by evaporation. The evaporation of pore water leaves the nutrient salts behind on the sediment surface and during high tide they are dissolved in the overlying water which ultimately transports the porewater nutrients and other solutes to the overlying water column.

The released nutrients from sediment are distributed in the overlying water by molecular diffusion and more predominantly by vertical mixing induced by upwelling or winter



**Fig. 4.1:** Benthic mineralization and nutrient release in coastal systems.

cooling. There exists a layer of a few mm just above the sediment-water interface called the *benthic boundary layer* through which transport takes place only by molecular diffusion.

### 4.3. Methodology

Benthic flux measurements were carried out by the following two methods:

(1) *In-situ* measurement by deploying a benthic chamber on the sediment (Devol, 1987; Devol & Christensen, 1993; Callender & Hammond, 1982; Jahnke, 1990; Jahnke *et al.*, 2000, Hammond *et al.*, 1985; Boynton & Kemp, 1985; Teague *et al.*, 1988; Nowiki & Nixon, 1985, Klump & Martens, 1981; Hopkinson Jr, 1987)

(2) Intact core incubation method where freshly collected sediment core is incubated in the laboratory at nearly *in-situ* temperature (Hammond *et al.*, 2004; Trimmer *et al.*, 1999; Cook *et al.*, 2004; Hopkinson Jr *et al.*, 2001; Banta *et al.*, 1995; Berelson *et al.*, 1998).

#### 4.3.1. *In-situ* incubation of sediment

##### 4.3.1.1. *Design of the benthic chamber*

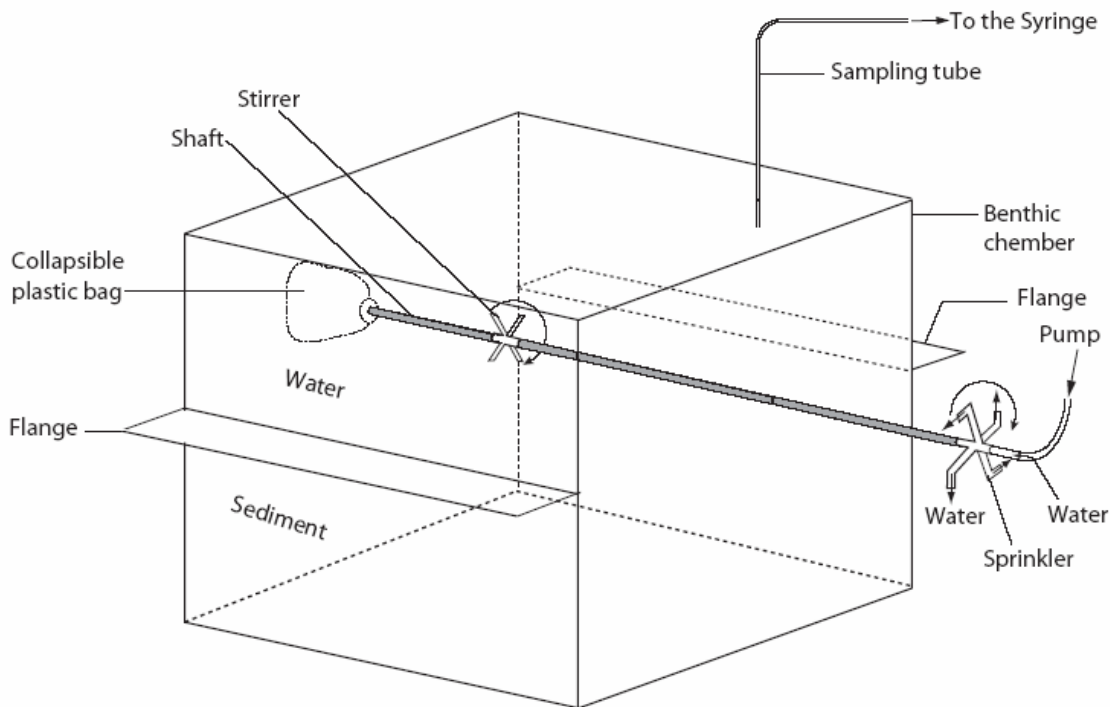
The benthic chamber was indigenously made using translucent acrylic sheet of 1.3 cm thickness having inner length, breadth and height 38.7, 38.7 and 36.2 cm respectively. Flanges were attached to two opposite outer walls of the chamber at a distance of 23 cm from the top in order to restrict excessive penetration of the chamber into the sediment during emplacement. Average depth of penetration in the sediment was 15 cm. The chamber covered an area of 0.15 m<sup>2</sup> of the sediment surface during deployment. Total volume of the chamber was ~54 L, but it encompassed an average ~31 L of water when deployed. Enclosed water was stirred by an acrylic stirrer mounted on a stainless steel shaft fixed to the chamber through two opposite walls. By this design the stirrer remained approximately 15 cm above the sediment. Stirring is necessary to create effective mixing inside the chamber during incubations and also to create an artificial bottom current to mimic the processes occurring in the natural environment so that advective pore water transport is not arrested in the chamber. To rotate the stirrer a water sprinkler was attached to the shaft outside the chamber and outside seawater was pumped through the sprinkler which causes the water to come out of the sprinkler thereby making the sprinkler rotate. This ultimately rotates the coupled stirrer inside the chamber thereby ensuring effective mixing of the overlying water. To control the water flow into the sprinkler, so that speed of the inside stirrer could be adjusted, a tap was connected to the outlet tube of the pump *i.e.* between the sprinkler and the pump. To increase the rotation

of the stirrer, the tap was closed further so that the increased water flow increased the stirring speed. Similarly, to decrease the rpm of the stirrer, more water was released through the tap by opening it further.

#### 4.3.1.2. Deployment and sampling

The benthic chamber was deployed in the month of February, March, April and August 2004. The chamber was deployed in the subtidal zone of the Mandovi estuary during the lowest low tide time for a period of 2-3 days, so that the chamber always remained at least one meter below the water surface. During emplacement of chamber, utmost care was taken to minimize disturbance of the surficial sediment. A pair of metallic weights was attached to two opposite sides of chamber to prevent its lateral displacement by the water currents during the incubations.

Samples were collected through a nylon tubing inserted into the chamber and the sample drawn was replaced by the initial ambient water enclosed in a collapsible plastic bag attached to the outer wall of the chamber.



**Fig. 4.2:** Schematic diagram of the benthic chamber.

First sampling was done immediately after deployment of the chamber *i.e.* at time zero and subsequent samples were taken at intervals of 4 hour for at least 24 hours. Dissolved



oxygen sample was collected in a gastight Hamilton glass syringe while other samples such as for N<sub>2</sub>O and nutrients were collected in B-D plastic syringes. At each sampling up to 150 ml of sample was withdrawn. Thus considering its replacement by same amount sample from the plastic bag, the dilution was 0.4% which was negligible. During sampling the tubing was ensured to be air bubble free. Oxygen samples were immediately fixed by adding Winkler's A and Winkler's B solutions (Grasshoff *et al.*, 1983) through a fine needle attached to 1ml syringes containing Winkler's solutions. N<sub>2</sub>O samples were immediately poisoned by adding saturated HgCl<sub>2</sub> solution to stop further growth of bacteria. Nutrient samples were immediately frozen at -20°C to arrest microbial growth. After 24-48 hrs of this *in-situ* incubation experiment, the benthic chamber was removed and two sediment cores, one for porosity and the other for pore water analysis were collected in a 30cm long, 54 mm ID acrylic liners. These liners were inserted into the sediment slowly with simultaneous removal of headspace air through a syringe attached to the top cap, in order to minimize compaction of sediment column. After collection, the cores were kept in dark and at -20 °C until further analyses.

### **4.3.2. Intact core incubation in the laboratory**

#### *4.3.2.1. Experimental design*

A 10 cm ID and 48 cm long acrylic liner fitted with a magnetic stirrer was used for this experiment. Two such liners were fabricated indigenously. These liners were fitted with nylon caps at both the ends. The top cap was attached to two 1.5 mm ID nylon tubings through the holes, fitted with 3-way luer locks. These caps had appropriate size O-rings to make the system completely air-tight. Two 60ml plastic BD syringes were directly attached to the liner so as to contain overlying water and replacing when samples were withdrawn. Two more tubings were attached through holes roughly at the centre of the liner which were used for drawing sample. The sediment column occupied half (22 cm) of the length of the liner and was overlain by ~22 cm high water column. A Teflon coated magnetic stirrer was positioned at 10cm above the sediment surface and was rotated at 60 rpm so as not to disturb the surficial sediment but ensure effective mixing in the water column. The stirrer was rotated by coupling it with another rotating bar magnet kept outside but close to the liner. A motor was used to rotate this bar magnet.

#### 4.3.2.2. *Sampling and incubation*

Sediment cores were collected in May 2006 from the intertidal zone of Mandovi estuary as well as from a coastal station (G5) on different dates. In the estuary collection was done during low tide when the sediment was exposed. At G5 where the depth is 27 m, core was collected by a SCUBA diver. After collection cores were brought to the laboratory and kept in dark at a temperature close to that of the estuarine water or the coastal water. The bottom water collected from the same location was then introduced slowly over the sediment and the attached syringes were also filled with the same water. The liner was closed properly by the caps ensuring that there was no headspace above the water. The rpm of the stirrer was adjusted to 60 since at that speed; the mixing did not disturb the sediment. The incubation was carried out for 48 hours with regular sampling at 6 hourly intervals. At  $T_0$  the volume of the overlying water including that in two attached syringes was  $\sim 2$  L. After the syringes became empty, the replacement during sampling was done by attaching an aluminium bag containing zero grade helium gas. Each time a total of 25 ml of the sample was withdrawn. As the samples were withdrawn, the plungers of attached syringes moved inside. This ensured again that the system was completely air-tight.

Initial samples were collected for dissolved oxygen,  $N_2O$  and nutrients in syringes through the attached nylon tubing. Oxygen sample was fixed,  $N_2O$  sample was poisoned and nutrients sample was frozen at  $-20^\circ C$  immediately as described before.

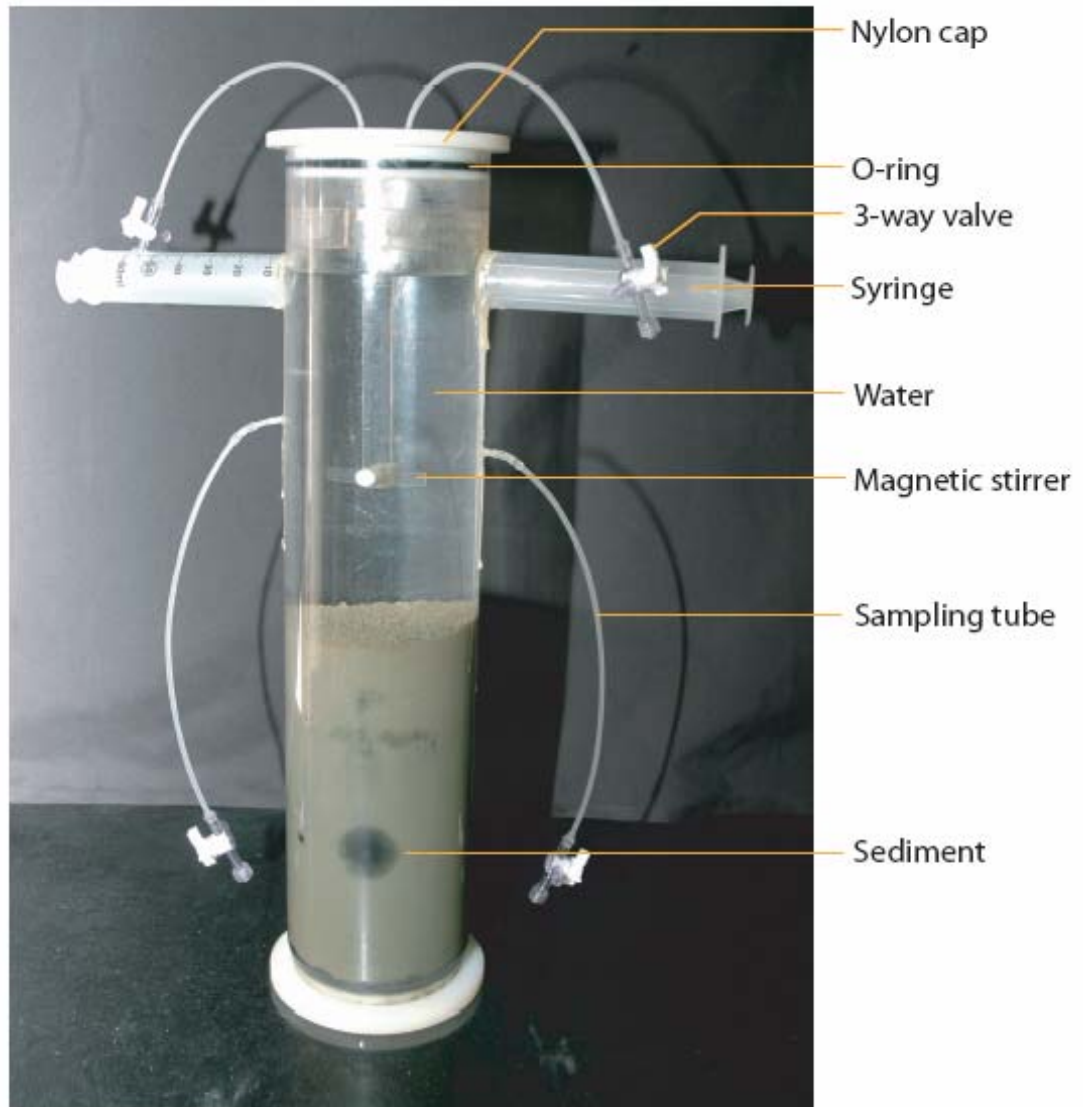
Two extra sediment cores, one for porosity and the other for pore water analysis were also collected from the same site, in 30 cm long, 54 mm ID acrylic liners. These liners were inserted into sediment slowly with simultaneous removal of headspace air through a syringe attached to the top cap, in order to minimize compaction of sediment column. After collection, the cores were kept in dark and at  $-20^\circ C$  until further analyses.

#### **4.3.3. Flux calculation**

The rate of concentration change in the overlying water of a core or benthic chamber depends on the ratio of flux per unit area to effective water height.

In the benthic chamber water column remained constant through out the experiment and dilution factor was negligibly 0.4%. Moreover, since average change in the volume of

water column at the end of the experiment was only 3%, the plot between concentration against time was found to be linear and thus benthic flux was calculated as follows.



**Fig. 4.3:** Photographic image of the core liner used in laboratory incubations.

$$F = (V/A) \times (dC/dt) \times (24/1000)$$

Where V is the volume of the overlying water column

A is the surface area of the sediment

dC/dt is the slope of the linear regression of concentration ( $\mu\text{M}$ ) versus time plot.

Finally after multiplying with 24 and dividing with 1000 flux is expressed in  $\text{mmol m}^{-2} \text{d}^{-1}$

<sup>1</sup>. But in case of core incubation experiments, water height changed by 1.7% at each sampling and the total change in the volume of overlying water was 15% on an average. This introduces a curvature in a plot of concentration versus time. So as suggested by Hammond *et al.* (2004), the ratio of time/height for each sample interval was calculated and concentration of overlying water was plotted against the sum of elapsed time/height for all preceding intervals.

$$F = dC/dT_h$$

Where  $dC/dT_h$  is the slope of the plot between concentration and sum of time/height.

Thus the slope of the plot directly gave the flux in  $\text{mmol m}^{-2} \text{d}^{-1}$ .

In case of nutrients slope of the linear regression fit was considered for flux calculation but in case of dissolved oxygen, slope of the polynomial fit at time 0 ( $dy/dx$  at  $x = 0$ ) was used for that purpose since curvature appears usually after a concentration of  $\sim 100 \mu\text{M}$ . (see Fig. 4.4, 4.5, 4.6, 4.7)

#### **4.4. Results & discussion**

Benthic exchange studies were carried out at two stations one in Mandovi estuary, where river influence varies with season, by *in-situ* benthic chamber method and another at G5, a coastal station off Goa, where there is no river influence, by core incubation method.

##### **4.4.1. Benthic exchanges in the Mandovi Estuary**

###### **4.4.1.1. Seasonal variability of fluxes**

Temperature is the major physical factor which affects benthic remineralization rate in coastal and estuarine systems. Biological rates increase exponentially with temperature, generally showing a two or four fold increase for every  $10^\circ\text{C}$  temperature rise. Microbially mediated regeneration processes, pore water profiles, concentration gradients, fluxes and transport processes are all strongly influenced by seasonal temperature variations (Nixon *et al.*, 1976; Aller, 1977; Goldhaber *et al.*, 1977; Martens *et al.* 1980; Klump, 1980). However factors causing seasonality in benthic exchange rates may vary from place to place depending upon the geographical setting, hydrography and climate of the area of study. The seasonal variability of benthic fluxes in Mandovi estuary was found to be significant.

#### 4.4.1.1.1. *Benthic respiration rate*

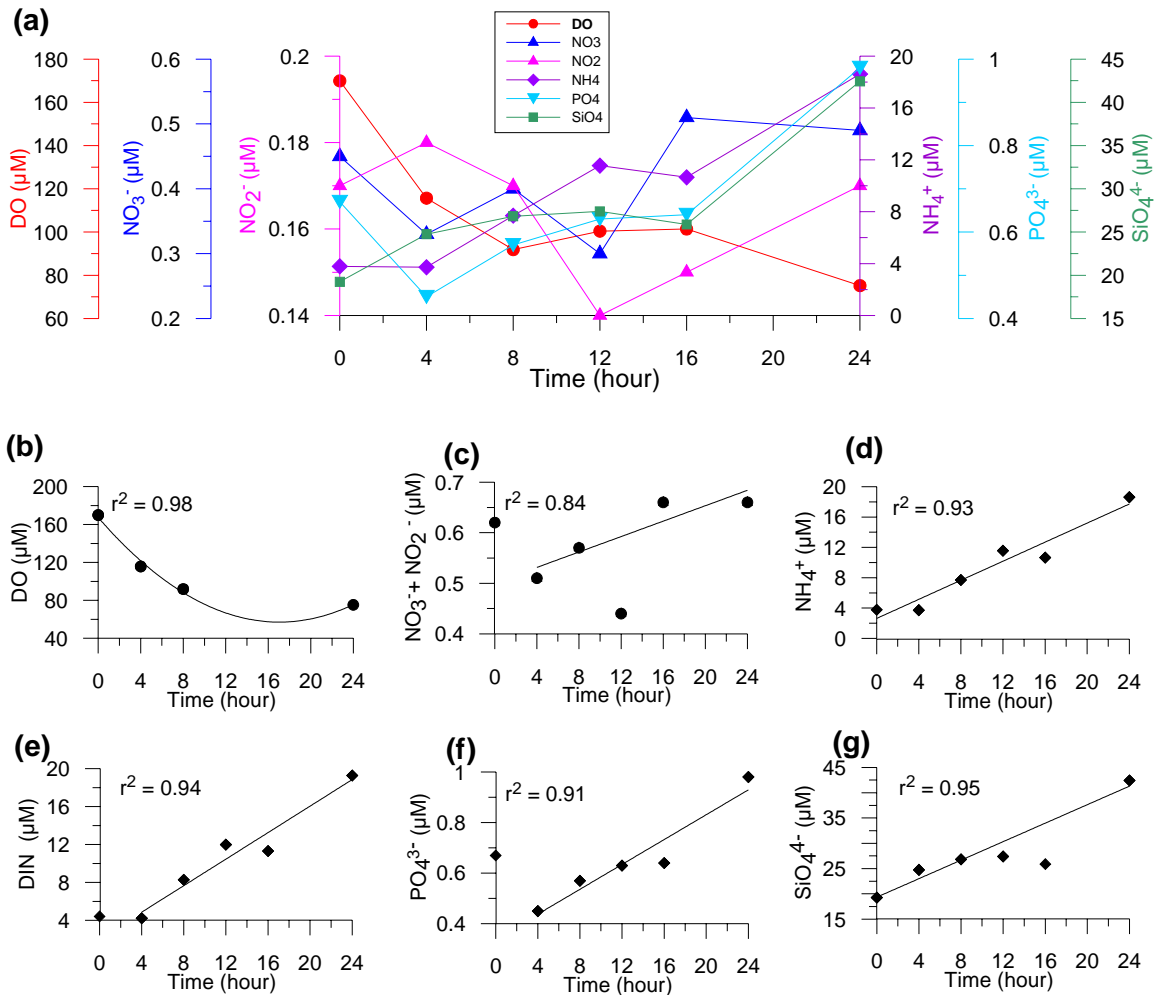
Benthic respiration or benthic oxygen uptake is a good proxy for the numerous microbial reactions and processes responsible for the decomposition of organic matter in marine sediments. Benthic respiration rates, which include both the oxygen consumption by aerobic organisms and oxidation of reduced compounds carried out by anaerobic microbes (Jorgensen, 1982; Mackin & Swider, 1989), closely reflect rates of oxic and anoxic decomposition in sediment overlain by oxic waters.

Oxygen uptake pattern remains approximately linear at the beginning of the experiment, but once oxygen level in overlying water comes down to 100  $\mu\text{M}$ , it starts decreasing in a logarithmic fashion. The pattern has been observed by many authors (Sundby *et al.*, 1986), Revsbech *et al.* (1988) and is typical of these experiments reflecting the gradual decrease of concentration gradient across the diffusive boundary layer at the sediment-water interface. The diffusive boundary layer (DBL) is the region near the sediment surface where solute transport takes place via molecular diffusion rather than via eddy diffusion. The thickness of this layer is of the order of a few millimeters or fraction of a millimeter. However Sundby *et al.* (1986) suggested two reasons for observed logarithmic curvature in oxygen versus time plot (decreasing oxygen flux into the sediment with time). The first is that the concentration gradient across the boundary layer decreases with the decreasing oxygen concentration in the water column and the second is that the thickness of surficial oxic sediment layer decreases, thereby reducing the number of oxygen respiring microorganisms.

Since the Mandovi estuary is a well mixed tidal dominated estuary, the estuarine water column remains well oxygenated throughout the year but since water column salinity exhibits considerable seasonal variation in a year owing to varying fresh water runoff, dissolved oxygen also undergoes seasonal variation (Fig. 2.3), reaching a maximum during the southwest monsoon (June-September) *i.e.* 254  $\mu\text{M}$  and a minimum of around 169  $\mu\text{M}$  in winter (February) (as observed during the study). Though pore water oxygen profile could not be obtained because of logistic reasons, pore water  $\text{NO}_3^-$  indirectly showed the oxygen penetration depth in the sediment.

Also a very thin brown layer of < 0.5 cm thickness was conspicuous on visual

observation in the surficial sediment in the collected cores which clearly indicated that the oxidized surficial sediment layer was very thin. Pore water  $\text{NO}_3^-$  in the upper part of sediment remained close to the overlying water  $\text{NO}_3^-$  concentration but since oxygen decreases rapidly with depth and reaches suboxic level below few mm, microbial



**Fig.4.4:** Sediment-water exchange of oxygen and nutrients in the Mandovi Estuary during February.

decomposition of organic matter takes place through  $\text{NO}_3^-$  reduction which results in a rapid decrease in the pore water  $\text{NO}_3^-$ .

Oxygen exchange is controlled by sedimentary oxygen consumption which in turn

depends on several factors such as bottom water oxygen content, organic load, benthic biomass and temperature. Oxygen penetration of the sediment goes down to between few mm and few cm in estuarine and coastal sediments (Revsbech, 1983; Sorensen *et al.*, 1984). TOC in the sediments of the Mandovi estuary has been found to be 0.1-3% being the highest at the mouth (Alagarsamy, 1991). In the month of April, the estuarine water temperature was at its peak (31°C) and high primary productivity because of spring phytoplankton bloom as reflected in high chlorophyll concentration (5.2 mg m<sup>-3</sup>) (Fig. 2.2c) appeared to lead to the highest benthic respiration rate as indicated by peak benthic oxygen flux (- 98 mmol m<sup>-2</sup> d<sup>-1</sup>) (Fig. 4.8a).

Trimmer *et al.* (1999) observed a substantial increase in benthic respiration rate following a spring bloom in the Irish Sea. Nixon *et al.* (1976) observed a strong positive correlation of organic matter decomposition with temperature. Bartoli (1996) and Officer *et al.* (1984) also found increases in sedimentary oxygen demand (SOD) with increasing temperature. Although the terrigenous organic loading through riverine discharge remains high during the monsoon period which leads to the highest organic carbon content in the estuarine sediment *i.e.* 3.27% (Nasolkar *et al.*, 1996), low temperature (~25°C) (Fig. 2.2a) seems to be a cause of slow benthic respiration rate and in turn low benthic oxygen influx in the estuary. Thus although the combined effect of temperature and organic load controls the sedimentary oxygen uptake, temperature seems to control the benthic respiration rate predominantly.

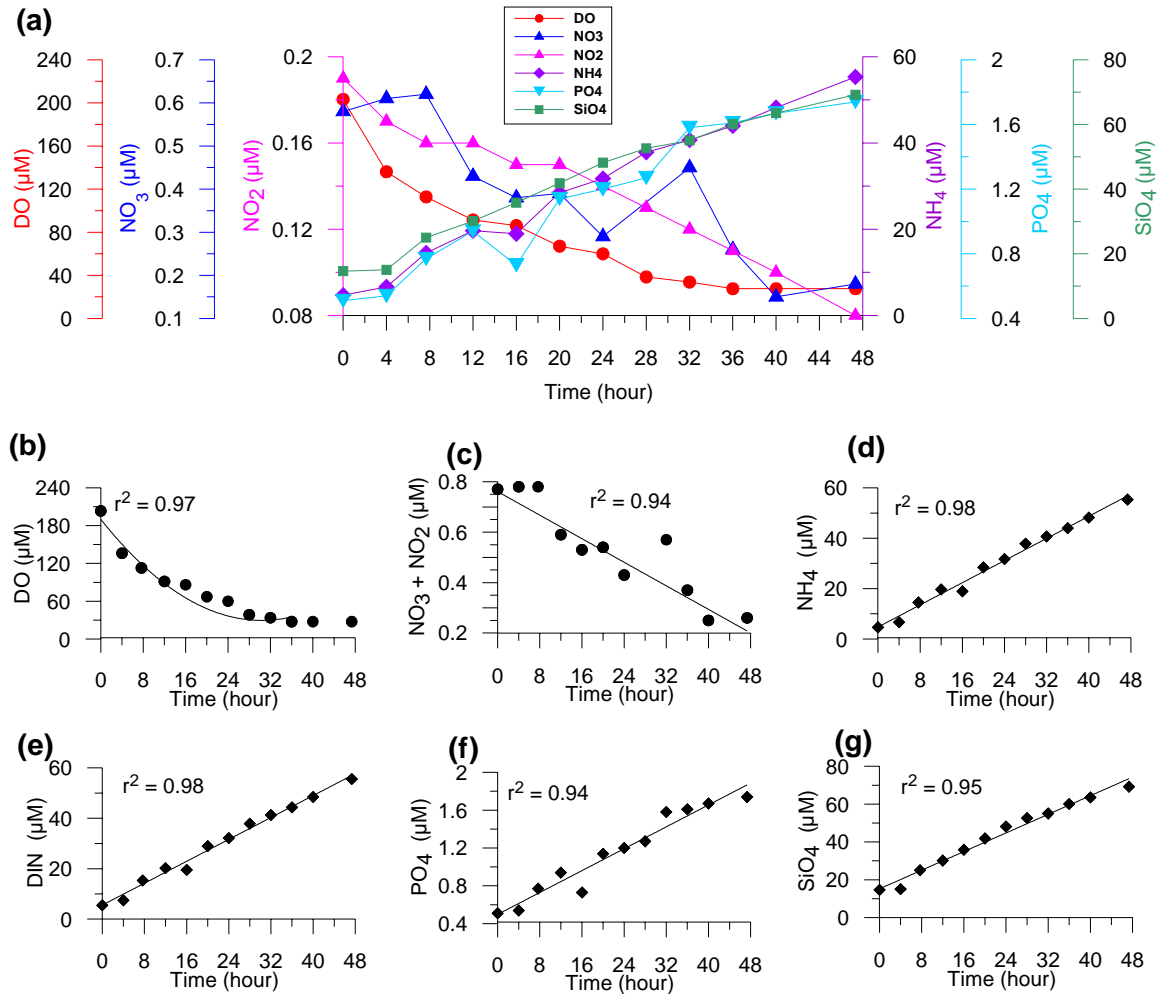
#### **4.4.1.1.2. Benthic nutrient fluxes**

##### *Nitrate and Nitrite*

Benthic NO<sub>3</sub><sup>-</sup> flux was always found to be directed towards the sediment indicating that estuarine sediment is a NO<sub>3</sub><sup>-</sup> sink which happens usually in organic rich environments where heterotrophic bacteria use NO<sub>3</sub><sup>-</sup> as a terminal electron acceptor after exhausting oxygen. NO<sub>3</sub><sup>-</sup> uptake by sediment was observed to be positively and significantly correlated with NO<sub>3</sub><sup>-</sup> concentration of the overlying water (Fig. 4.9b). NO<sub>3</sub><sup>-</sup> in Mandovi estuary remained highest (~12 µM) during monsoon owing to high riverine discharge which resulted in the highest observed benthic NO<sub>3</sub><sup>-</sup> flux in August (-1.06 mmol m<sup>-2</sup>d<sup>-1</sup>)

whereas the premonsoon value was much lower ( $-0.05 \text{ mmol m}^{-2}\text{d}^{-1}$ ) (Fig. 4.8b) during which water column nitrate remained apparently low ( $0.1\text{-}0.8 \mu\text{M}$ ).

$\text{NO}_2^-$  is an intermediate product of both nitrification and denitrification processes. So its observed concentration was interplay between its production and oxidation/reduction

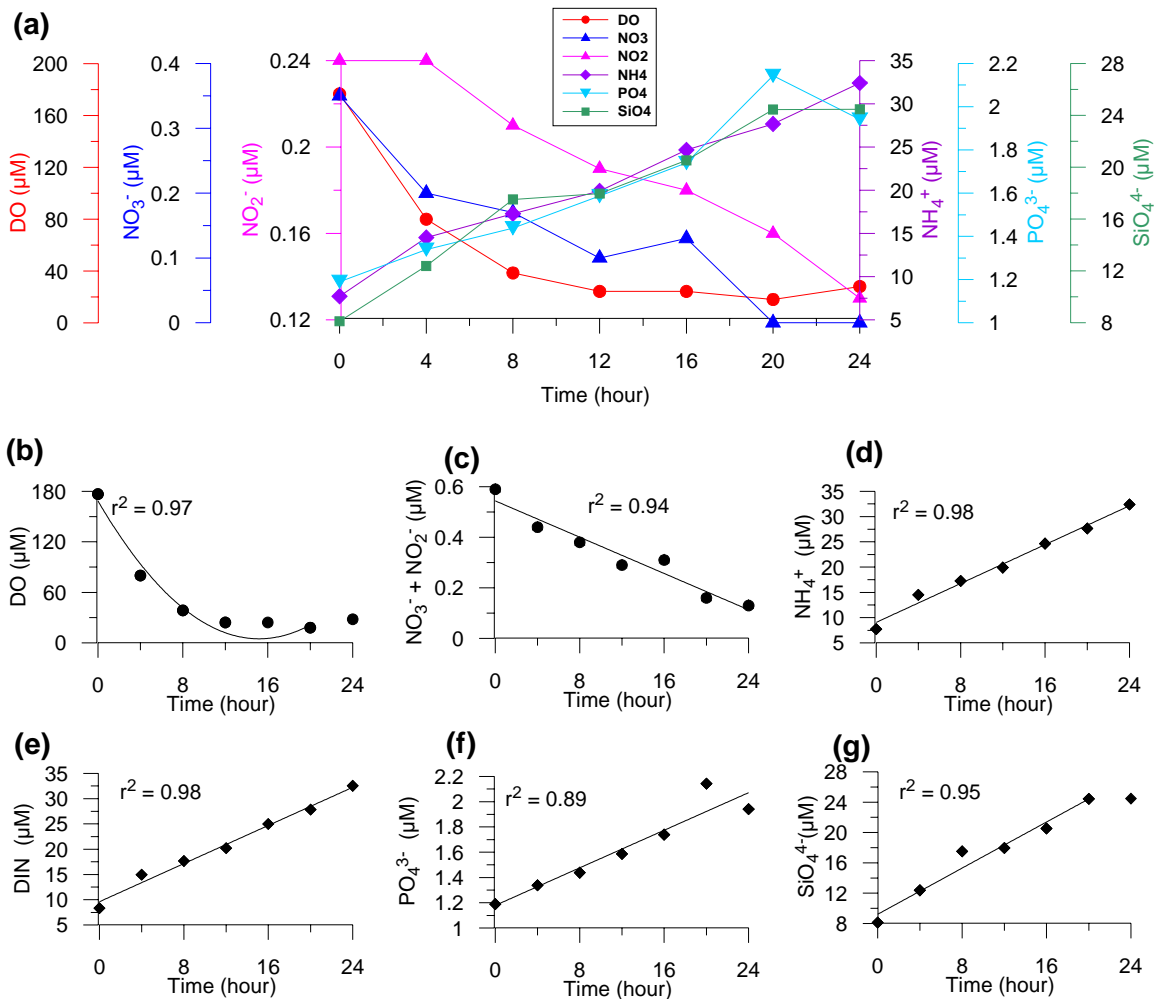


**Fig.4.5:** Benthic exchange of oxygen and nutrients in Mandovi estuary during March.

by heterotrophic bacteria.  $\text{NO}_2^-$  concentration in the estuary was low throughout the year ( $0.1\text{-}0.3 \mu\text{M}$ ) since the water column remained oxic. However inside the chamber  $\text{NO}_2^-$  flux was directed towards the sediment in non-monsoon seasons but only in August its concentration increased with time within the chamber (Fig. 4.7 a) which may be because of its net release from the sediment as a reduced product of benthic denitrification since



$\text{NO}_3^-$  uptake was at its peak.  $\text{NO}_2^-$  concentration increased from its initial value of  $0.31 \mu\text{M}$  to  $1.7 \mu\text{M}$  after 24 hours and subsequently decreased to  $0.06 \mu\text{M}$  after 48 hours of experiment which indicates its diffusion to sediment and subsequent reduction to  $\text{N}_2\text{O}$  or  $\text{N}_2$  via the benthic denitrification process.

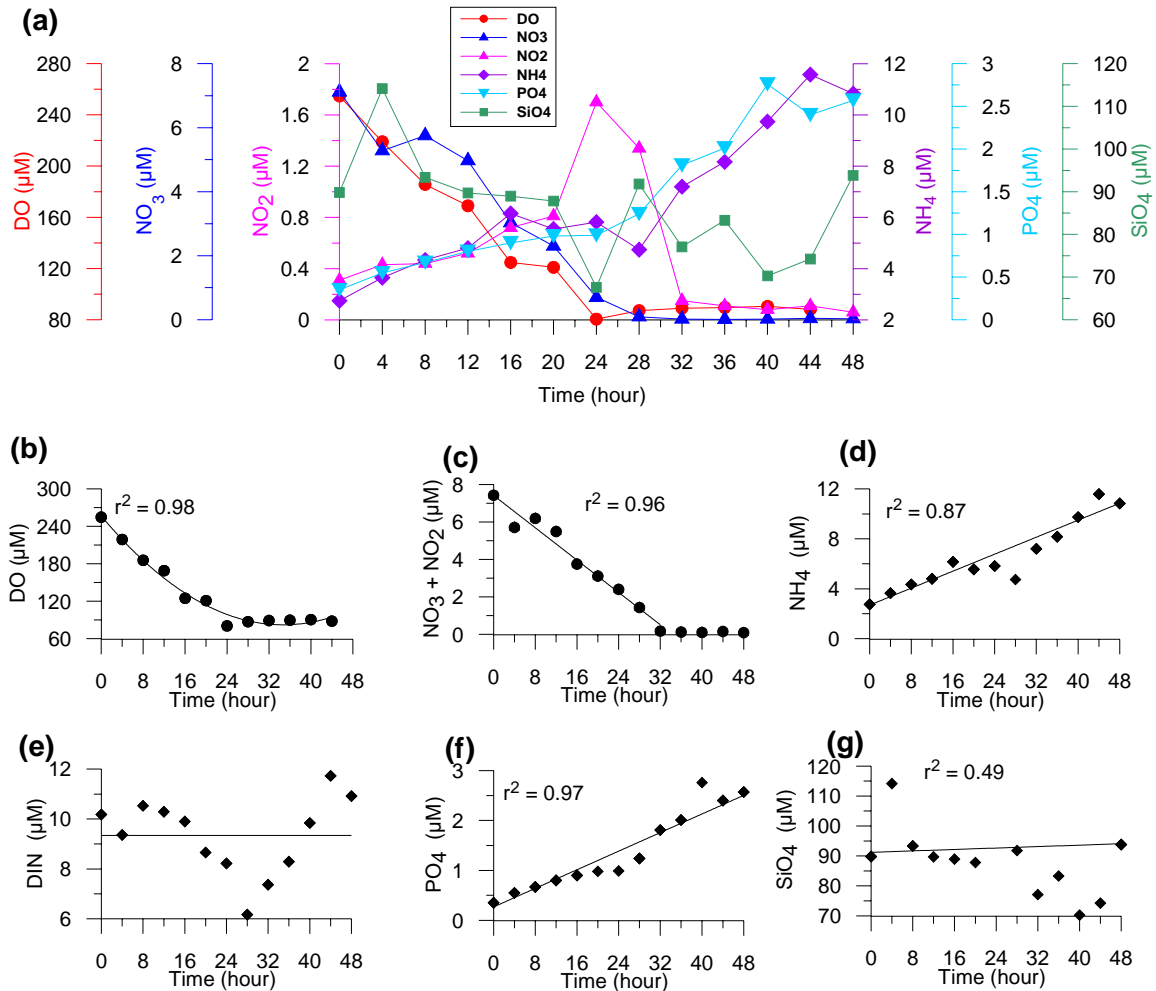


**Fig.4.6:** Benthic exchange of oxygen and nutrients in Mandovi estuary during April.

#### Ammonium

$\text{NH}_4^+$  produced from organic matter decomposition by heterotrophic bacteria, may either be used by phytoplankton or be further oxidized by microbes to nitrate *i.e.* nitrification (Henriksen & Kemp, 1988; Nishio *et al.*, 1983). Ammonium constitutes a substantial

portion of the sediment-water flux of nitrogen in estuarine and coastal environments (Blackburn & Henriksen, 1983; Nowiki & Nixon, 1985). Usually  $\text{NH}_4^+$  accumulates in very high concentrations in pore waters of estuarine and coastal sediments because sulfate reduction produces this species and it is not nitrified since pore water remains almost anoxic below upper few mm of sediment. Also the pore water  $\text{NH}_4^+$  was  $207 \mu\text{M}$

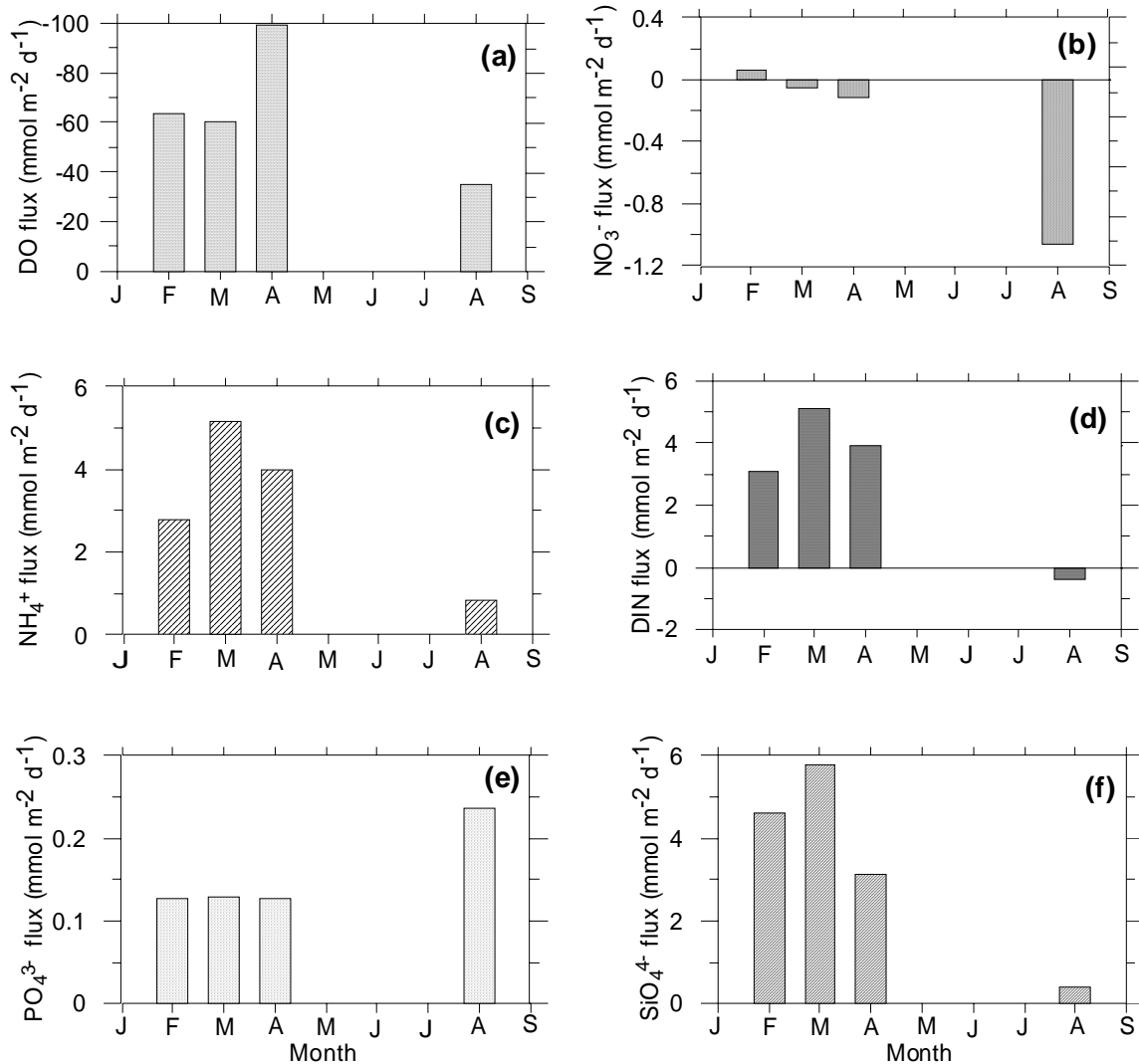


**Fig.4.7:** Benthic exchange of oxygen and nutrients in Mandovi estuary during August.

at 1-2 cm and increased to  $750 \mu\text{M}$  at 14-15 cm depth (Fig. 4.12e) whereas bottom water  $\text{NH}_4^+$  remained very low owing to rapid biological uptake and consequently this steep concentration gradient resulted in high diffusive  $\text{NH}_4^+$  flux to the overlying water.

However many competitive processes such as adsorption also take place along with

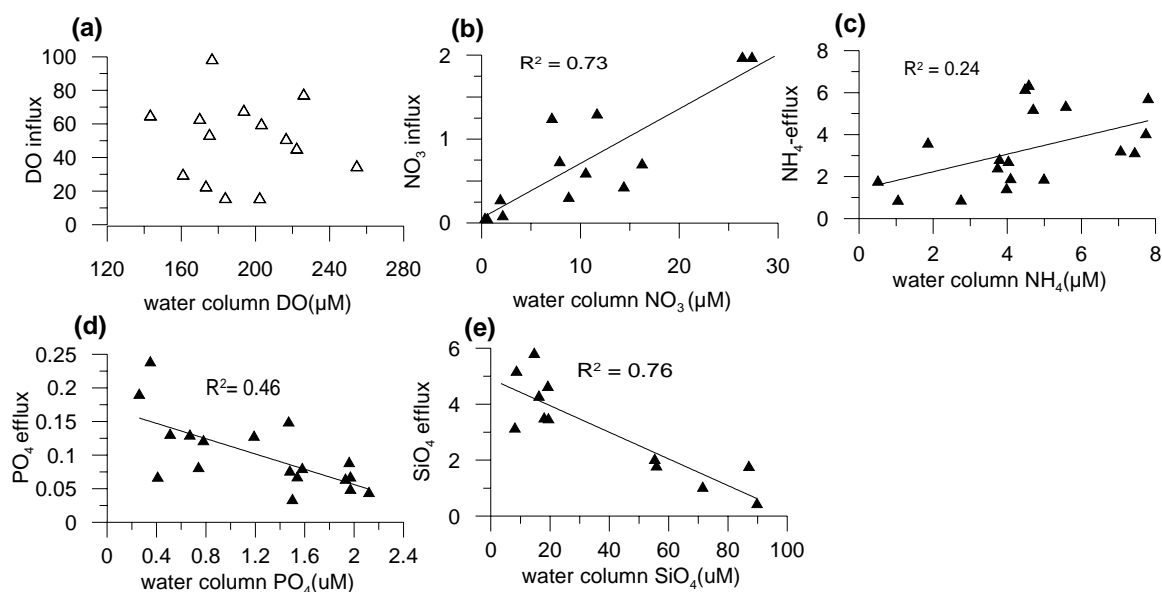
molecular diffusion which tend to act as sink for  $\text{NH}_4^+$ . Upward diffusing  $\text{NH}_4^+$  may be nitrified to  $\text{NO}_3^-$  in the upper oxic sediment layer and since this  $\text{NO}_3^-$  further diffuses to underlying suboxic zone and gets subsequently denitrified to  $\text{N}_2\text{O}$  and  $\text{N}_2$  as nitrification



**Fig. 4.8:** Seasonal variation of benthic flux of dissolved oxygen and nutrients in the Mandovi Estuary.

and denitrification remain tightly coupled in estuaries and coastal systems (Jenkins & Kemp, 1984).  $\text{NH}_4^+$  efflux was at a maximum in premonsoon season (March) (Fig. 4.8c) which may be due to high organic load following spring bloom and high rate of organic matter decomposition induced by high temperature. Lower temperature (25°C) during the

monsoon seems to be one of the possible reasons for the low rate of organic decomposition and in turn the lowest flux of  $\text{NH}_4^+$  as observed.



**Fig.4.9:** Correlation between benthic fluxes and water column concentration of Dissolved oxygen and nutrients. All fluxes are in  $\text{mmol m}^{-2} \text{d}^{-1}$ . Influx means flux into sediment and efflux denotes flux out of sediment.

Interestingly, Gardner *et al.* (1987) and Seitzinger (1988) observed very low  $\text{NH}_4^+$  release from fresh water sediments whereas Blackburn & Henriksen (1983) and Nowiki & Nixon (1985) observed  $\text{NH}_4^+$  to be the major form of released N from estuarine and coastal sediments. This comparatively much lower benthic release of  $\text{NH}_4^+$  from fresh water system was experimentally proved by Gardner *et al.* (1991) wherein they suggested that in saline environments cation exchange sites are mostly occupied by major ions (Boatman & Murray 1982) and ion pairing of remineralized  $\text{NH}_4^+$  with major ions of the salt water systems prevents its nitrification considerably in the upper oxic zone and facilitates its release to the overlying water. By contrast, in fresh water sediments most of the remineralized  $\text{NH}_4^+$  remains adsorbed to sediment particles as exchangeable  $\text{NH}_4^+$  which equilibrates with pore water (Rosenfeld, 1979) and undergoes substantial nitrification in the upper oxidized zone. In many fresh water systems with oxic bottom water, 80-100% of the net  $\text{NH}_4^+$  produced in the sediment is lost through nitrification and

subsequent denitrification whereas only 40-60% of remineralized  $\text{NH}_4^+$  is nitrified and denitrified in coastal marine sediments (Andersen, 1971, 1977; Gardner *et al.*, 1987; Seitzinger *et al.*, 1984, Seitzinger 1987, Henriksen & Kemp 1988, Kaspar *et al.*, 1985; Seitzinger, 1988). Nitrification acts as a major sink for  $\text{NH}_4^+$  since its coupling with denitrification ultimately removes  $\text{NO}_3^-$  from the system in the form of  $\text{N}_2$ . Effect of salinity on benthic  $\text{NH}_4^+$  release was also demonstrated in the lab experiments conducted in the present study where the estuarine sediment released more  $\text{NH}_4^+$  under highly saline condition (Details of this experiment have been described later). Mandovi estuary experiences highly variable salinity regime, being most saline in premonsoon (33.00 – 34.00) and displaying an almost freshwater-like condition in the monsoon season (0 – 4.00) (Fig. 2.2a) owing to heavy riverine inflow. Thus, the observed low  $\text{NH}_4^+$  efflux ( $0.83 \text{ mmol m}^{-2}\text{d}^{-1}$ ) in August and the highest flux ( $5.15 \text{ mmol m}^{-2}\text{d}^{-1}$ ) in March (Fig. 4.8c) can be attributed mainly to the above geochemical processes.

#### *Phosphate*

There are two major sources of  $\text{PO}_4^{3-}$  in the estuarine and coastal sediments, one is bacterial decomposition of organic matter and desorption and reductive dissolution of ferric oxides minerals. The latter process is geochemical in nature and becomes very significant when the environment becomes anoxic. Ferric oxides and ferric oxyhydroxides are major scavengers of dissolved  $\text{PO}_4^{3-}$ . Phosphate remains adsorbed and also co-precipitates with ferric oxide phases under oxic condition and dissolution of these minerals under anoxic condition mobilizes the bound phosphorus to the pore water (Krom & Berner, 1981, Sundby *et al.*, 1992). Therefore high  $\text{PO}_4^{3-}$  content of pore water is attributed to organic matter degradation and reductive dissolution of ferric minerals since pore water below few mm of interface remains anoxic. In spite of the high  $\text{PO}_4^{3-}$  content of pore waters and comparatively much lower  $\text{PO}_4^{3-}$  concentration of overlying water, the diffusive flux can be lower than expected. This is because much of the upward migrating  $\text{PO}_4^{3-}$  gets re-adsorbed and precipitates in the upper oxic sediment layer close to the interface. This was reflected in the high  $\text{NH}_4^+ : \text{PO}_4^{3-}$  flux ratio ( $>16$ , Redfield ratio of N: P=16:1) when the overlying water remained oxic in the benthic chamber. Significant increase of DIP flux in the monsoon season (Fig. 4.8e) may be because of the

resuspension of surficial sediment and consequent release of  $\text{PO}_4^{3-}$  rich pore water to the overlying water. In addition to this the higher allochthonous organic matter input to the sediment and its decomposition may shift the oxic-anoxic interface upward; closer to the sediment-water interface. Thus increasing the  $\text{PO}_4^{3-}$  production rate and geochemical release of adsorbed and mineral bound  $\text{PO}_4^{3-}$  from reductive dissolution of ferric minerals under anoxic condition in the sediment could result in higher benthic  $\text{PO}_4^{3-}$  release.

### *Silicate*

Estuarine and coastal sediment pore waters are usually rich in dissolved silicate since diatoms are the dominant group of phytoplankton in the water column and dissolution of their sinking siliceous frustules in sediment leads to this enrichment. Diatom dominance in algal community has been observed in the Mandovi estuary in previous studies (Devassy & Goes, 1988; Krishnakumari *et al.*, 2002). Apparently spring bloom in March, subsequent sinking of dead cells to sediment followed by the dissolution of opal must have enriched the pore waters with silicate as pore water (0-1 cm)  $\text{SiO}_4^{4-}$  in March was found to be 150  $\mu\text{M}$  (Fig. 4.12f) as compared to 66  $\mu\text{M}$  in April (Fig. 4.13f). This higher pore water  $\text{SiO}_4^{4-}$  led to steep concentration gradient between surficial sediment porewater and overlying water and ultimately resulting in highest  $\text{SiO}_4^{4-}$  efflux in March (Fig. 4.8f). Silicate efflux in monsoon was the lowest (0.416  $\text{mmol m}^{-2} \text{d}^{-1}$ ) which may be because the overlying water silicate was very high (89  $\mu\text{M}$ ) due to heavy fresh water flow in monsoon, and this value was probably very close to pore water silicate thereby eliminating the concentration gradient and thereby resulting in low flux of silicate between sediment and water.

### *Net DIN exchange*

Inorganic nutrients such as  $\text{NH}_4^+$ ,  $\text{NO}_3^-$  and  $\text{NO}_2^-$  play a very important role in benthic biogeochemistry because they are interconvertible depending on the redox conditions. Since the Mandovi estuary remains virtually N depleted throughout the year except during the monsoon season when enormous riverine flow increased  $\text{NO}_3^-$  concentration (12  $\mu\text{M}$ ) in the estuarine water and the water column  $\text{NO}_3^-$  and  $\text{NO}_3^-$  influx were strongly correlated, very low  $\text{NO}_3^-$  influx (0.05-0.07  $\text{mmol m}^{-2} \text{d}^{-1}$ ) occurred in winter and premonsoon. Only during the monsoon  $\text{NO}_3^-$  flux was significantly higher (-1.26  $\text{mmol}$

$\text{m}^{-2} \text{d}^{-1}$ ). However  $\text{NO}_3^- + \text{NO}_2^-$  flux was always directed downward indicating intense benthic denitrification in the estuary. Overall benthic DIN exchange was dominated by  $\text{NH}_4^+$  in non-monsoon period which always fluxed out of the sediment at a significantly higher rate ( $2.7\text{-}5.1 \text{ mmol m}^{-2} \text{d}^{-1}$ ). Net DIN flux was directed towards the water column in winter and premonsoon seasons with the peak value ( $5.09 \text{ mmol m}^{-2} \text{d}^{-1}$ ) occurring in March and then linearly decreased to  $-1.065 \text{ mmol m}^{-2} \text{d}^{-1}$  in August (Fig. 4.8d), indicating its net uptake by sediment which implies that estuarine sediments of the Mandovi are a net seasonal sink of DIN as net loss of combined N to sediment was found to be  $229 \text{ } \mu\text{mol m}^{-2} \text{d}^{-1}$ . Only in February the sediment behaved as a source of  $\text{NO}_3^- + \text{NO}_2^-$  (Fig. 4.4a & c) but the magnitude of the flux was very small ( $0.06 \text{ mmol m}^{-2} \text{d}^{-1}$ ) (Fig. 4.8b).  $\text{NH}_4^+$  efflux comprised  $\sim 70\%$  of the total benthic DIN release in winter (February).  $\text{NO}_2^-$  flux was also observed to be always directed towards the sediment (Fig. 4.4a, 4.5a & 4.6a) since it was consumed along with the  $\text{NO}_3^-$  in benthic denitrification process, but only in August with increased denitrification in sediment, initially its production rate exceeded its consumption rate in the first 24 hours of incubation, resulting in an efflux from sediment as it attained a peak value ( $1.7 \text{ } \mu\text{M}$ ) at 24 hours and decreased to  $0.06 \text{ } \mu\text{M}$  at 48 hours (Fig. 4.7a). This indicates its uptake by sediment due to denitrification. Thus its net contribution to overall DIN release was very negligible, making  $\text{NH}_4^+$  again the dominant fraction of released DIN in the estuary. Overall  $\text{NH}_4^+$  was the major form of released DIN from sediment, accounting for 70-100% of DIN released from benthic remineralization.

#### **4.4.1.2. Pelagic versus benthic remineralization**

In order to further confirm the role of estuarine sediment in changing the nutrient inventory of overlying water, a set of core incubation experiment was carried out in the laboratory. Two core liners were filled with estuarine water. In the first liner (Liner-A) the top valve was kept open so that the outside air would pass to keep the overlying water oxidic. The second core liner (Liner-B) was kept completely air-tight. In the other two liners sediment cores were collected and overlain by the estuarine water. One core (Liner-C) was kept aerated and other one (Liner-D) was kept air-tight. The overlying waters of all cores were continually stirred by magnetic stirrers rotating at 60 rpm ensuring no

suspension of surficial sediment. All the four core liners with samples were maintained close to *in-situ* temperature and incubated together. Samples were collected for dissolved oxygen, N<sub>2</sub>O and nutrients at regular intervals. Oxygen and N<sub>2</sub>O samples were collected only from air-tight cores (Liner-B & D). Samples for N<sub>2</sub>O were collected both from the overlying water and the headspace over it. Results were shown in Fig. 4.10.

Unfortunately dissolved oxygen in the Liner-B (airtight estuarine water) could not be measured because of some technical problem. Nevertheless negligible variations in nutrients in this core between initial and final values indicates that oxygen consumption must have been very low.

#### *Nitrification and denitrification*

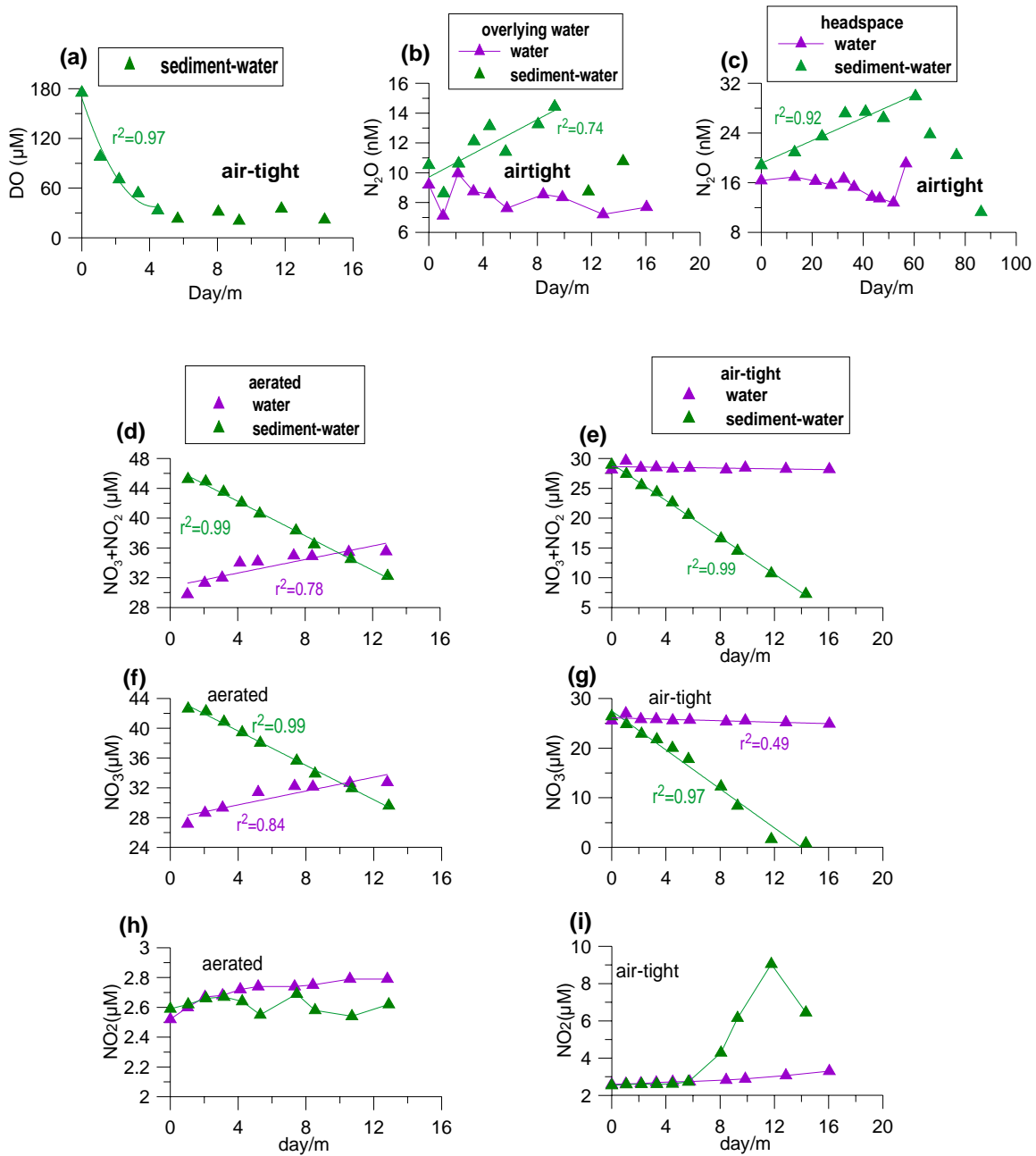
No significant change in NO<sub>3</sub><sup>-</sup> concentration was observed in the air-tight water system but increase was noticed in the aerated water system which can be due to nitrification of NH<sub>4</sub><sup>+</sup> since system was well oxygenated. Nitrification took place at a rate of 1.74 μmol L<sup>-1</sup>d<sup>-1</sup>. But both in aerated and air-tight condition there was significant uptake of NO<sub>3</sub><sup>-</sup> (Fig. 4.10f &g) which indicates vigorous benthic denitrification.

NO<sub>2</sub><sup>-</sup> did not undergo much change in aerated water and sediment-water system (Fig. 4.10 h). ( $p > 0.05$ ). Even in airtight water system NO<sub>2</sub><sup>-</sup> change was very negligible whereas significant accumulation of up to 9 μM observed in airtight sediment-water system (Fig. 4.10i) followed by its decrease which could be due its further microbial reduction to N<sub>2</sub>O and N<sub>2</sub>. This confirms that the NO<sub>2</sub><sup>-</sup> accumulation in the overlying water was in fact due to its release from sediment as an intermediate product of benthic denitrification, rather than from pelagic denitrification. The observed net consumption of NO<sub>3</sub><sup>-</sup> + NO<sub>2</sub><sup>-</sup> in sediment-water systems (Fig. 4.10e) was apparently due to their loss in benthic denitrification rather than pelagic denitrification. Variation in NO<sub>3</sub><sup>-</sup> influx pattern between aerated and air-tight sediment-water system was statistically significant (ANOVA,  $p > 0.05$ ). For pelagic denitrification to occur the suboxic condition has to be attained which was not the case since oxygen in both air-tight water and sediment-water system was above 0.2 ml/L even at the end of the experiment. But because of limited penetration of oxygen to the sediment, existence of a suboxic zone just below the top thin oxic layer becomes permanent even though overlying water remains well oxygenated.

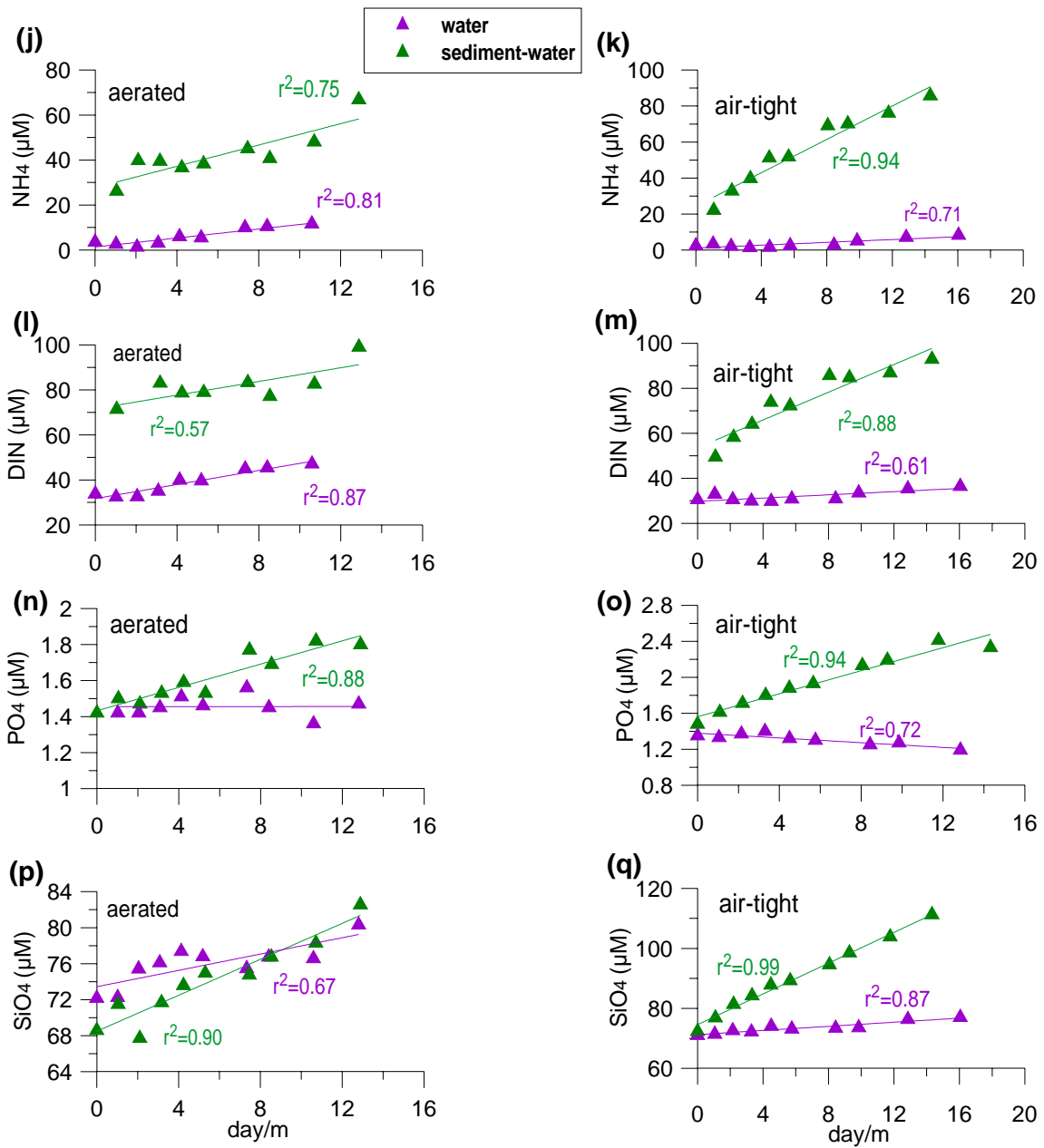


This results in greater downward diffusion of overlying  $\text{NO}_3^-$  and  $\text{NO}_2^-$  to the sediment and their consumption in benthic denitrification.

Accumulation of  $\text{N}_2\text{O}$  in the overlying water and the headspace was observed only in air-tight sediment-water system rather than in air-tight water system (Fig. 4.10 b & c). This indicates that the estuarine sediment is a source of  $\text{N}_2\text{O}$  to the water column.  $\text{N}_2\text{O}$  flux from sediment to the overlying water and water to the overlying air were calculated as 391 and 182  $\text{nmol m}^{-2} \text{d}^{-1}$  respectively. However its decrease after the peak value indicates its further reduction to  $\text{N}_2$ . The results show that benthic denitrification was the dominant process in the sediment-water system in controlling the pelagic inventory of nitrogenous species. Variation in concentration of nutrients between time zero and end (72 h) of both aerated and air-tight water experiment was statistically insignificant ( $p > 0.05$ ). Accumulation of  $\text{NH}_4^+$ ,  $\text{PO}_4^{3-}$  and  $\text{SiO}_4^{4-}$  in sediment-water systems was much higher than that in water system both under aerated and air-tight conditions (Fig. 4.10) which proves that a greater part of organic matter mineralization takes place in the sediment which leads to the flux of nutrients to the overlying water and in turn increasing the pelagic nutrient inventory.



(Fig. Contd...)



**Fig. 4.10:** Comparative regeneration of nutrients and gases in only water and sediment-water system in aerated and air-tight conditions.

#### 4.4.1.3. Stoichiometry of benthic fluxes

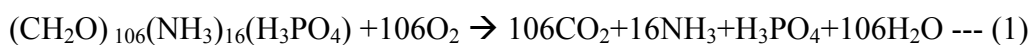
A very important aspect of the mineralization process in the sediment is the release of nutrients back into overlying water, which is essential to provide nutrients for primary production by the phytoplankton communities and thus maintain the element cycles of the ocean. The average C:N:P ratio in organic matter of phytoplankton has been found to be 106:16:1 (Redfield *et al.*, 1963). The ratio at which carbon ( $\text{CO}_2$  or  $\text{HCO}_3^-$ ), nitrogen ( $\text{NO}_3^-$  or  $\text{NH}_4^+$ ) and phosphorus ( $\text{PO}_4^{3-}$ )

**Table 4.1:** Comparative regeneration in water and sediment-water system. (Fluxes are in  $\text{mmol m}^{-2} \text{d}^{-1}$ ; Negative sign denotes consumption and positive sign means regeneration).

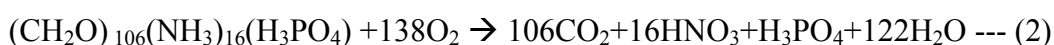
	Water system		Sediment-water system	
	<i>aerated</i>	<i>airtight</i>	<i>aerated</i>	<i>airtight</i>
DO flux	-----	-----	-----	-70.74
$\text{N}_2\text{O}$ flux	-----	-----	-----	0.003
$\text{NO}_3^- + \text{NO}_2^-$ flux	1.33	-0.019	-1.158	-1.593
$\text{NH}_4^+$ flux	1.244	0.583	2.474	4.263
DIN flux	1.709	0.602	2.312	2.706
$\text{PO}_4^{3-}$ flux	0.004	0.007	0.032	0.074
$\text{SiO}_4^{4-}$ flux	0.676	0.369	0.925	2.562

are assimilated into algal cell and ratio at which these biogenic elements are released back through remineralization, usually remain very close to the Redfield ratio in water column in steady state. Although the sinking organic matter to the sediment contains C, N and P in Redfield ratio, benthic release of these elements does not necessarily follow the same ratio because of fractionation (Suess & Muller, 1980), authigenic production of or interaction with sedimentary solids (Suess, 1979; Martens *et al.*, 1978) and other biogeochemical processes like benthic nitrification and denitrification.

In the oxic decomposition process, the nutrient release relative to the oxygen uptake at the surface should conform to the following reaction proposed by Redfield (1934) and Alvarez-Borrego *et al.* (1975) when  $\text{NH}_4^+$  is the immediate nitrogenous end product.



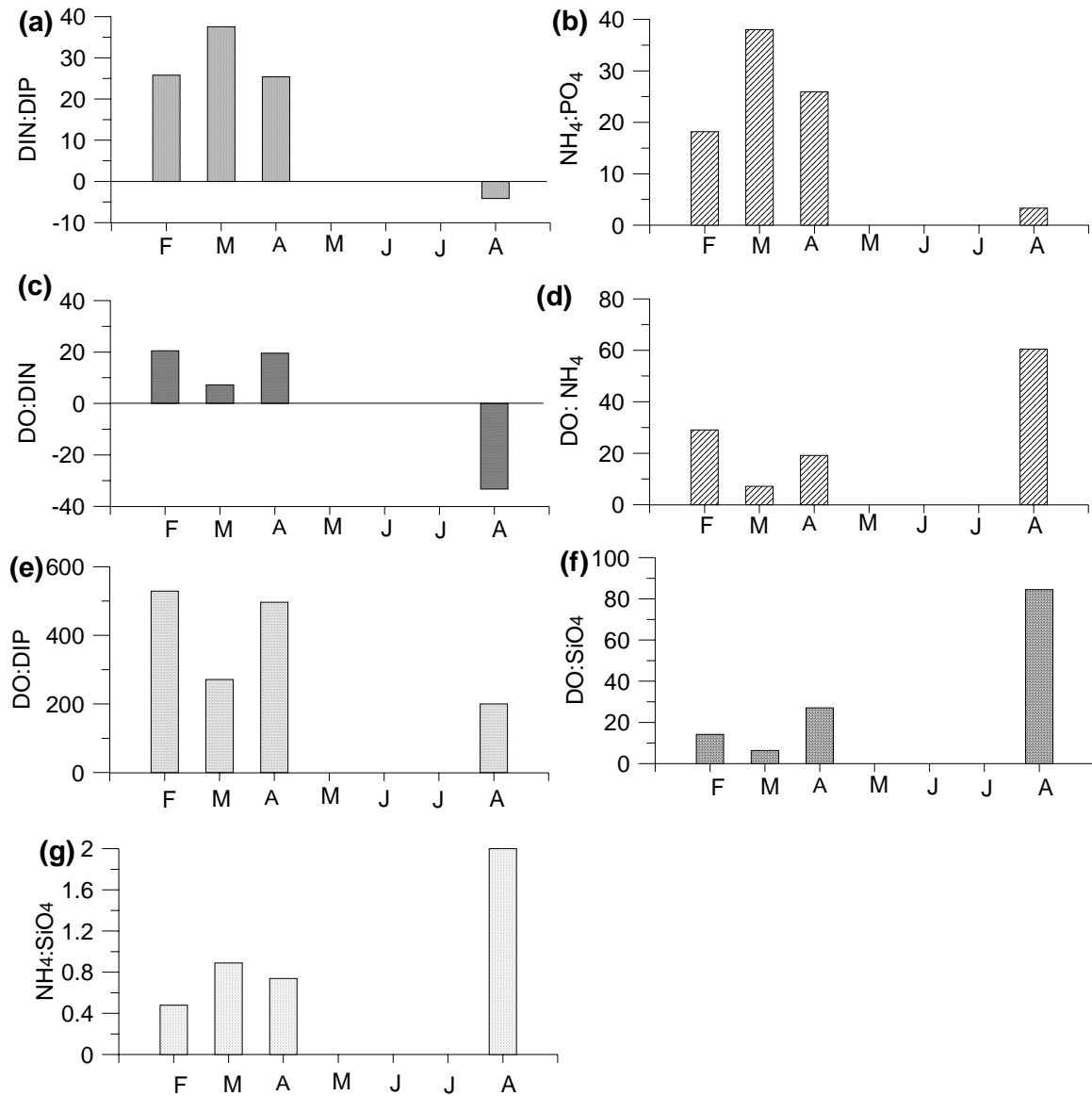
With the ultimate oxidation of  $\text{NH}_4^+$  to  $\text{NO}_3^-$  in which 138 moles of  $\text{O}_2$  are consumed instead of 106 moles in above equation-1. The degradation is represented by the following equation.



$\text{NH}_4^+$  is released from bacterial decomposition of organic matter as the first nitrogenous remineralized product (Eq-1) along with  $\text{PO}_4^{3-}$  and it usually accumulates in sediment pore water.

The benthic flux ratio between  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  varies from 3.5 in August to 39 in March (Fig. 4.11b). Such a large departure from the expected Redfield value (16:1) can be attributed to several geochemical processes which distort the release ratio such as adsorption of  $\text{NH}_4^+$  onto clay minerals (Rosenfeld, 1979) nitrification and subsequent denitrification because of their close coupling in sediments (Jenkins & Kemp, 1984), adsorption of  $\text{PO}_4^{3-}$  onto ferric oxides and also its co precipitation with ferric oxyhydroxides in upper oxic zone of the sediment (Krom & Berner, 1980). Similarly O:  $\text{NH}_4^+$  ratio remains close to the expected value in winter and premonsoon period but deviates considerably in August (Fig. 4.11d) which can be attributed to the lower salinity (Gardner *et al.*, 1991) in the estuary in monsoon season.  $\text{NH}_4^+ : \text{SiO}_4^{4-}$  shows a linear increase from 0.6 in February to 2.01 in August (Fig. 4.11g). The closeness of  $\text{NH}_4^+ : \text{SiO}_4^{4-}$  in winter and premonsoon to its theoretical value (1:1) indicates that the estuary was dominated by diatoms during these periods but the diatom population decreased towards August in turn reducing biogenic silica flux to the sediment. The decrease in diatom population has been observed in the estuary by Devassy and Goes (1988) in response to cloud cover and high turbidity in the estuary during the monsoon period. DIN:DIP ratio also showed a wide range of variation being high (24-31) during the premonsoon season but decreased to -1.7 in August (Fig. 4.11a) showing net

consumption of combined N and relatively higher release of  $\text{PO}_4^{3-}$  in monsoon. As discussed earlier the increase in  $\text{NO}_3^-$  fuels higher denitrification rates and the decrease in



**Fig.4.11:** Seasonal changes in benthic flux ratios in Mandovi estuary.

salinity favors low benthic release of  $\text{NH}_4^+$  thereby making the estuarine sediment a net sink of N in monsoon.

#### 4.4.1.4. Pore water nutrients

Sediment cores were collected in March and April immediately after benthic chamber deployment in the Mandovi estuary. Pore water profiles of nutrients are shown in Fig. 4.12 and 4.13. In March pore water  $\text{NH}_4^+$  (424  $\mu\text{M}$ ) and  $\text{SiO}_4^{4-}$  (150  $\mu\text{M}$ ) of the surficial sediment layer (0-1cm) were found to be higher than those observed in April *i.e.* 207  $\mu\text{M}$  and 66.75  $\mu\text{M}$  respectively for  $\text{NH}_4^+$  and  $\text{SiO}_4^{4-}$ . This would result in weaker concentration gradient between pore water and overlying water. This agrees with the flux data that show decreases in  $\text{NH}_4^+$  and  $\text{SiO}_4^{4-}$  efflux from March to April.  $\text{NO}_3^-$  in the pore water did not show any regular increasing or decreasing trend with depth. This also applied for  $\text{NH}_4^+$  and  $\text{SiO}_4^{4-}$ , particularly in March. But in April the observed trends were much better for  $\text{NH}_4^+$  and  $\text{SiO}_4^{4-}$ . Both showed increasing trends roughly linear with depth. Irregular pattern of  $\text{NO}_3^-$ ,  $\text{NH}_4^+$  and  $\text{SiO}_4^{4-}$  distribution in the sediment column in March may be attributed to higher abundance of benthic macrofauna (Ansari & Parulekar, 1993) which probably proliferated in response to higher organic matter loading, following spring bloom in March. These benthic organisms create burrows in the sediment through which the oxic overlying water penetrates to the deeper sediment layer. Some part of  $\text{NH}_4^+$  must have been nitrified to  $\text{NO}_3^-$  which is reflected in sudden increase in  $\text{NO}_3^-$  and decrease in  $\text{NH}_4^+$  in the pore water. Other benthos mix up the upper few cm of the sediments. Regular increasing trend of  $\text{NH}_4^+$  and  $\text{SiO}_4^{4-}$  in April may be due to relative decrease in macrofaunal population probably because of decrease in fresh organic matter in the sediment. However pore water concentration of  $\text{NH}_4^+$  and  $\text{SiO}_4^{4-}$  showed overall increases and  $\text{NO}_3^- + \text{NO}_2^-$  exhibited overall decrease with depth in both the months. Core collection was not possible in August.

#### 4.4.1.5. *In-situ* incubation versus laboratory incubation

Though no simultaneous flux measurements were made by the benthic chamber method and core incubation method, still the flux data from benthic chamber experiment in April, 2004 and core incubation in May, 2006 are compared (Table 4.2) assuming that the physical conditions of the estuary do not vary much in premonsoon months.

Higher uptake of  $\text{NO}_3^- + \text{NO}_2^-$  in case of core incubation could be because of the higher

water column concentration (28.9  $\mu\text{M}$ ) during the period of core collection as compared to much lower  $\text{NO}_3^- + \text{NO}_2^-$  (0.5  $\mu\text{M}$ ) in the overlying water during chamber experiment given that a positive correlation exists between the water column  $\text{NO}_3^-$  concentration and benthic  $\text{NO}_3^-$  uptake (Fig. 4.9b).  $\text{NH}_4^+$  flux values agreed reasonably whereas dissolved oxygen, phosphate and silicate fluxes were smaller by 28%, 41% and 17% respectively in the core incubation experiment.

**Table 4.2:** Comparison of fluxes measured by two different methods.

Parameter	Benthic flux ( $\text{mmol m}^{-2} \text{d}^{-1}$ )	
	by Benthic chamber	by Core incubation
DO	-98.91	-70.74
$\text{NO}_3^- + \text{NO}_2^-$	-0.121	-1.543
$\text{NH}_4^+$	4.002	4.263
DIN	3.927	2.706
$\text{PO}_4^{3-}$	0.127	0.074
$\text{SiO}_4^{4-}$	3.117	2.562

Higher fluxes of oxygen,  $\text{PO}_4^{3-}$  and  $\text{SiO}_4^{4-}$  were conspicuous in the benthic chamber experiment than those in core incubation experiment. Several factors may account for this discrepancy. Spatial heterogeneity in porosity and pore water nutrients may be one of them as the deployment site and core collection site are  $\sim 3\text{m}$  apart. Temperature change after core retrieval could also affect pore water silicate by 2.5% due to rapid adsorption/desorption (McManus *et al.*, 1995). Moreover, since the surficial sediment remains exposed to atmosphere for 5-10 minutes, the oxic layer might have thickened which probably enhanced  $\text{PO}_4^{3-}$  adsorption resulting in lower flux. Decrease in macro benthic activity in case of core incubation might also reduce the fluxes of oxygen and nutrients significantly (Hammond *et al.*, 2004).

#### 4.4.1.6. Calculated diffusive flux versus *in-situ* measured flux

The flux occurring only due to existing concentration gradient across sediment-water interface is termed as the diffusive flux since the exchange takes place solely by



molecular diffusion.

According to Fick's first law of diffusion, the diffusive flux is directly proportional to the concentration gradient under a steady state condition.

Diffusive benthic fluxes can be estimated using a modification of Fick's first law of diffusion appropriate for sediment (Berner, 1980)

$$F = -\phi \cdot D_s \cdot (\delta C / \delta x)_{x=0}$$

Where F is the diffusive flux ( $\text{mmol m}^{-2} \text{h}^{-1}$ )

$\phi$  is the the porosity of the surficial sediment (dimensionless),  
 $(\delta C / \delta x)_{x=0}$  is the concentration gradient across the sediment-water interface ( $\text{mmol/l/m}$ )  
 i.e. concentration difference between overlying water and pore water of surficial sediment.

and  $D_s$  is the whole sediment diffusion coefficient ( $D_0$ ) after temperature correction and tortuosity ( $\theta$ ) (Krom & Berner, 1980).

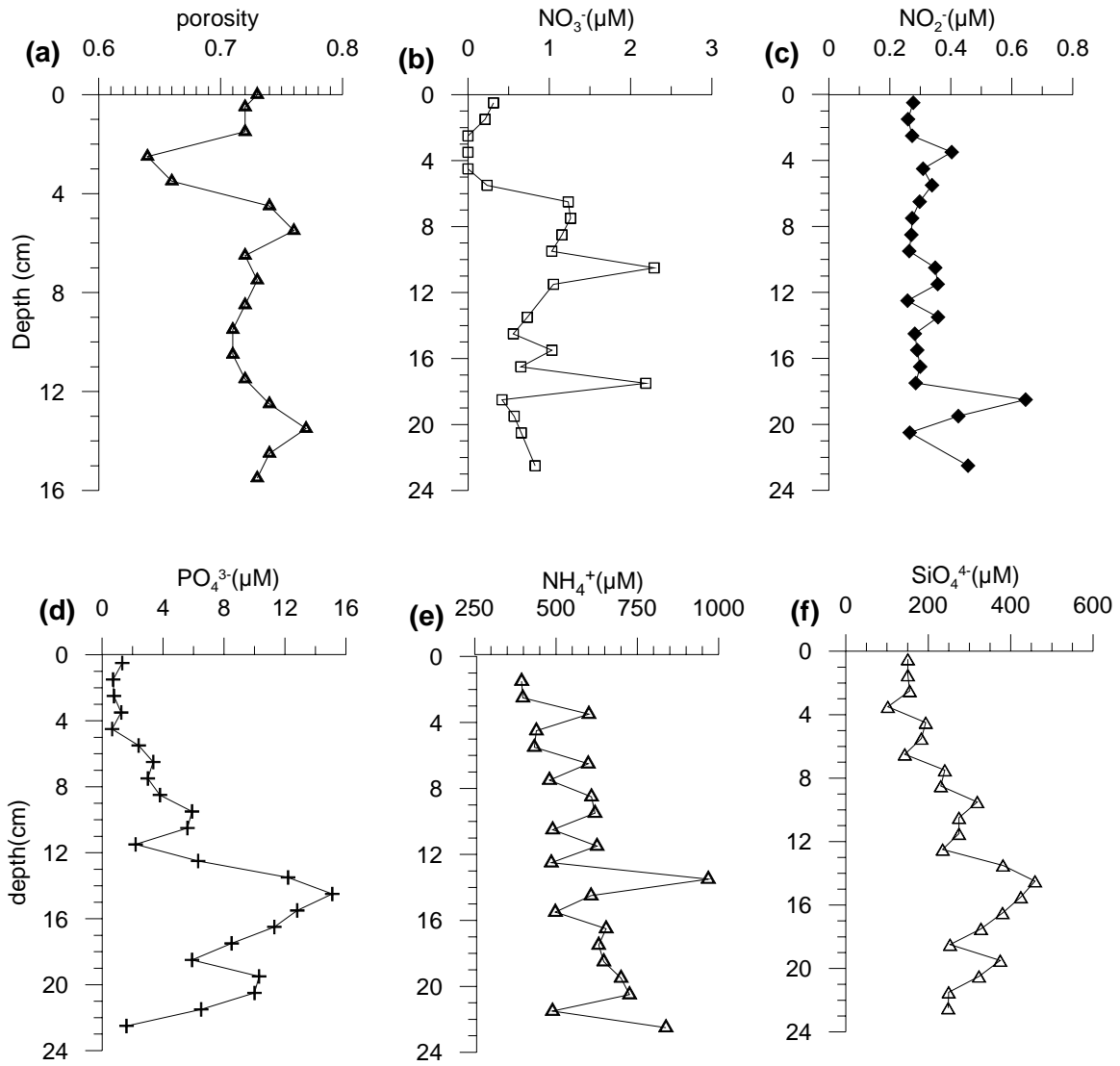
$$D_s = D_0 / \theta^2$$

where  $\theta$  is sediment tortuosity and can be expressed in terms of porosity *i.e.*

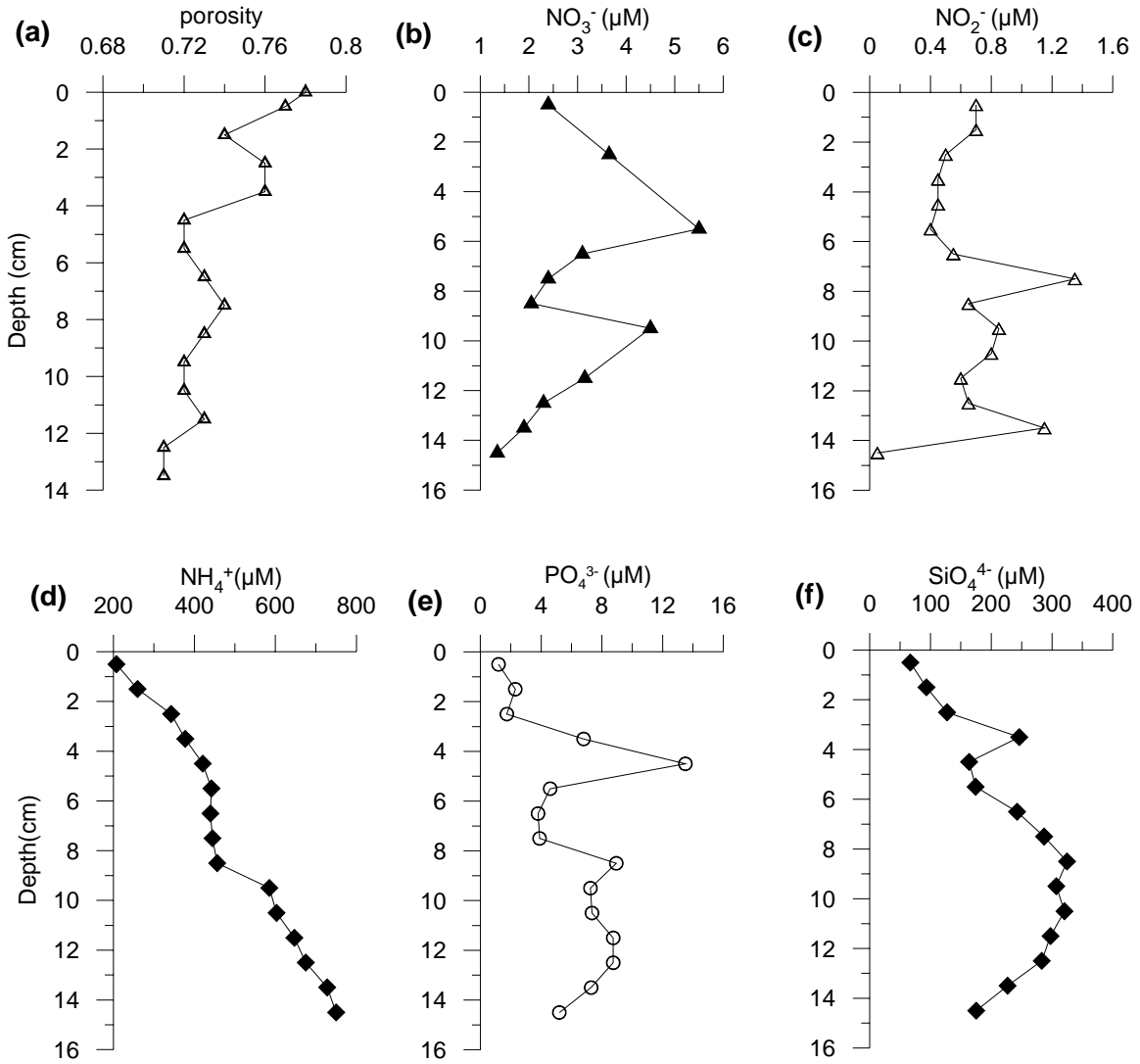
$$\theta = (1 - \ln \phi^2) \text{ (Boudreau, 1996)}$$

$D_0$  is measured at infinite dilution and 25 °C. As given by Boudreau (1997),  $D_0$  is  $1.85 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$  for  $\text{NH}_4^+$ ,  $5.77 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$  for  $\text{PO}_4^{3-}$ ,  $1 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$  for  $\text{SiO}_4^{4-}$ ,  $1.79 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$  for  $\text{NO}_3^-$ ,  $1.73 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$  for  $\text{NO}_2^-$  and  $2.13 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$  for  $\text{O}_2$ .

Porosity ( $\phi$ ) was determined as described in the section 3.4.2.6.



**Fig.4.12:** pore water profile of the estuarine sediment in March.



**Fig.4.13:** Pore water profile of the estuarine sediment in April.

**Table 4.3:** Comparison between diffusive flux calculated from pore water Concentration gradient and *in-situ* flux measured directly by incubation.

Nutrient	March		April	
	Diffusive flux (mmol m <sup>-2</sup> d <sup>-1</sup> )	<i>In-situ</i> flux (mmol m <sup>-2</sup> d <sup>-1</sup> )	Diffusive flux (mmol m <sup>-2</sup> d <sup>-1</sup> )	<i>In-situ</i> flux (mmol m <sup>-2</sup> d <sup>-1</sup> )
NO <sub>3</sub> <sup>-</sup>	-0.002	-0.037	----	---
NH <sub>4</sub> <sup>+</sup>	2.008	5.159	2.581	4.002
PO <sub>4</sub> <sup>3-</sup>	0.016	0.13	0.018	0.127
SiO <sub>4</sub> <sup>4-</sup>	1.221	5.78	0.167	3.116

Diffusive fluxes calculated from pore water concentrations are lower than those measured by direct incubation of sediment-water by benthic chamber. This indicates an apparent enhancement of benthic exchange rate across the sediment-water interface as observed by McCaffrey *et al.* (1980) in Narraganset Bay.

Various possible mechanisms that may be responsible for increasing the fluxes, are physical stirring by currents (Hammond *et al.*, 1977), benthic macrofaunal activity *i.e.* bioirrigation and bioturbation (Callender & Hammond, 1982), transport through abiogenic bubble tube structures (Martens *et al.*, 1980) and advective flows arising from bottom unevenness (Huettel & Gust, 1992; Huettel *et al.*, 1996). Physical reworking of the sediments whether by benthic organisms or waves and tidal, can also enhance the exchange of nutrients with the overlying water by increasing the mixing intensity of the sediment and pore water with the overlying water (Santschi *et al.*, 1990). Directly measured fluxes can be 2-10 times greater than the calculated diffusive fluxes under oxic condition, but under anoxic condition, diffusive fluxes can be closer to the measured benthic fluxes (Rutgers van der Loeff *et al.*, 1984). Studies conducted by Ansari *et al.* (1986) and Ansari & Parulekar (1993) show that sediments of the Mandovi estuary are inhabited by several groups of benthic macrofauna and meiofauna such as polychaetes, copepods and turbellarians with the highest abundance (60%) in the top 0-2 cm of the sediment. They found faunal population showing pronounced seasonality with maximal population during premonsoon and post monsoon periods. Visual observation showed burrows created by benthic organisms at the chamber deployment site in March and

April. Ansari & Parulekar (1993) reported an average density of the meiofauna  $1702 \times 10^3/m^2$  at a station very close to the deployment site. High rate of bioturbation and bioirrigation by such a large population of benthic organisms in the estuarine sediment seems to make *in-situ* measured flux rate much higher than the diffusive flux. In March diffusive flux contributed 4.8% of  $NO_3^-$ , 38.9% of  $NH_4^+$ , 12.3% of  $PO_4^{3-}$  and 21% of  $SiO_4^{4-}$  to the corresponding *in-situ* measured fluxes. In April these concentrations were 64.5%, 14% and 5.3% to the corresponding *in-situ* fluxes respectively. Callender & Hammond (1982) found diffusive fluxes of  $NH_4^+$ ,  $PO_4^{3-}$  and  $SiO_4^{4-}$  to be 66%, 30% and 15% of the corresponding measured flux rates in Chesapeake Bay. Several other authors such as McCaffrey *et al.* (1980), Hammond *et al.* (1985) and Miller-Way *et al.* (1994) also reported similar results. Possibility of other factors such as advective flow and transport through bubble tubes contributing to the enhancement of total measured flux also can not be ruled out in this study. The enhancement factor (ratio between measured fluxes and calculated diffusive fluxes) were 18.5, 2.56, 8.125 and 4.73 for  $NO_3^-$ ,  $NH_4^+$ ,  $PO_4^{3-}$  and  $SiO_4^{4-}$  respectively in March and 1.55, 7.05 and 18.65 for  $NH_4^+$ ,  $PO_4^{3-}$  and  $SiO_4^{4-}$  respectively in April. Qu *et al.* (2005) observed 1.9, 1.1 and 4.4 times enhancement of flux for  $NO_3^- + NO_2^-$ ,  $NH_4^+$  and  $PO_4^{3-}$  respectively. Kristensen & Hansen (1999) reported 2-4 fold increase in  $NH_4^+$  flux in bioturbated sediments. Callender & Hammond (1982) showed that bio-irrigation enhanced the flux of  $NH_4^+$  and  $SiO_4^{4-}$  by factor of 20 and 2 respectively.

#### **4.4.1.7. Effect of salinity on benthic fluxes**

Estuaries are dynamic environments where diurnal and seasonal changes in several physical, chemical and biological parameters are very prominent. The Mandovi estuary remains tidally dominated throughout the non-monsoon period, becoming highly saline (33.00 – 34.00) in March-May. Reduced riverine flow allows saline water penetration up to ~55 Km landward from the estuary mouth. But during monsoon season (June-September) heavy rainfall and increasing riverine outflow reduce the estuarine salinity to almost fresh water condition (0-4.0). With varying riverine freshwater flow nutrient concentrations in the estuary have been found to undergo significant variations. The

estuary remains highly enriched with nutrients during June to September because of heavy riverine inputs. To understand the geochemical control of salinity on benthic exchange the following core incubation experiments were carried out.

#### **4.4.1.7.1. Experimental set up**

A sediment core was collected from the estuarine site in May. It was first overlain by fresh water (0.00) of the Mandovi collected from the upper reaches of the river. The core was capped on both sides to make it airtight. The overlying water was stirred by a magnetically coupled *Teflon* coated stirrer inside the liner. Rotation was kept at ~60 rpm ensuring effective mixing of the overlying water but minimal disturbance of the surficial sediment. The core was incubated in dark at a temperature close the *in-situ* temperature. After 48 hours of incubation the overlying fresh water was siphoned off slowly and was replaced by water having salinity 12.00 and incubated in a similar manner and after this incubation the overlying water was again replaced by water with 24.00 and 33.00 salinity successively and incubation as in other two cases continued. Saline water of 12.00 and 24.00 were prepared by mixing required quantities of fresh river water and seawater collected from the coastal station (G5). This experiment allowed the investigation of the effect of sediment exposure to varying salinities in the estuary. The results are shown in Fig. 4.14 & Fig. 4.15.

#### **4.4.1.7.2. Nutrient fluxes**

##### *Silicate efflux*

As observed before silicate increased from 11  $\mu\text{M}$  in May to 89  $\mu\text{M}$  in August owing to heavy fresh water input from upstream and this apparently decreased benthic efflux of  $\text{SiO}_4^{4-}$  in August to 0.41  $\text{mmol m}^{-2} \text{d}^{-1}$  because of smaller concentration gradient between pore water and overlying water. This was further confirmed by above incubation experiment where the estuarine sediment collected in May was overlain by waters of different salinity from 0 – 33.00. No direct correlation was found to exist between benthic efflux of  $\text{SiO}_4^{4-}$  and salinity. Thus in the natural system  $\text{SiO}_4^{4-}$  concentration in the overlying water was indirectly correlated with salinity, since heavy fresh water flow during monsoon season decreases salinity and enriches estuary with  $\text{SiO}_4^{4-}$ . Moreover, benthic efflux of  $\text{SiO}_4^{4-}$  was found to have a significant inverse relation with ( $r^2=0.98$ ) with  $\text{SiO}_4^{4-}$  concentration in the overlying water (Fig. 4.15j), which indicates that

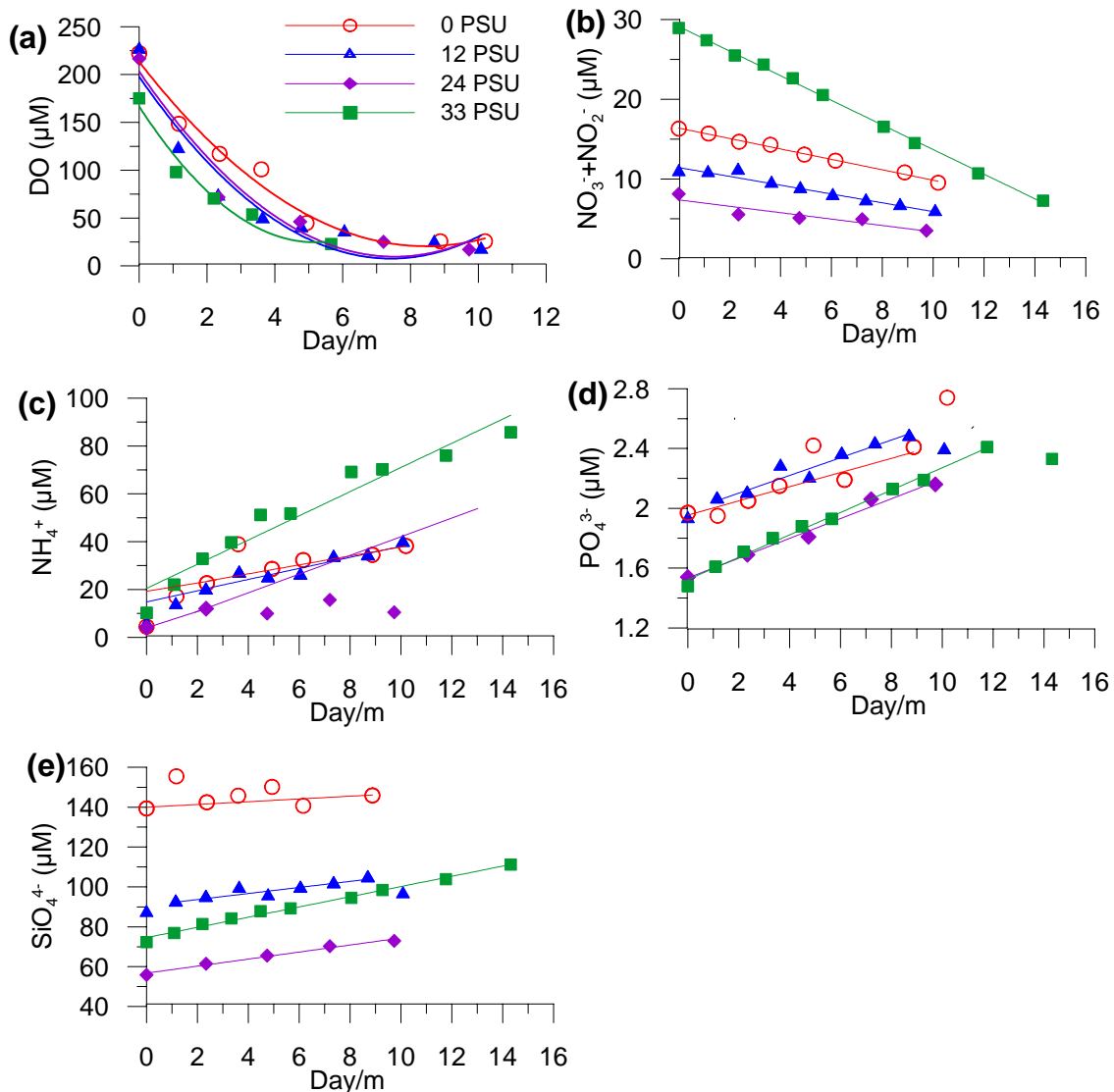
increasing water column concentration reduces silicate release from sediment considerably. Fluxes measured by *in-situ* benthic chamber in August and flux measured in this experiment at 0 salinity gave very low and of similar magnitudes *i.e.* 0.41, 0.69  $\text{mmol m}^{-2} \text{d}^{-1}$ . Similarly  $\text{SiO}_4^{4-}$  flux obtained from *in-situ* measurement ( $2.71 \text{ mmol m}^{-2} \text{d}^{-1}$ ) in April and that measured from this core incubation experiment ( $2.43 \text{ mmol m}^{-2} \text{d}^{-1}$ ) at salinity of 33.00, also agree well. Thus overall benthic flux of  $\text{SiO}_4^{4-}$  was observed to be correlated though indirectly but significantly with salinity of the water column in the estuary; however, the flux was considerably dependent on silicate concentration of the water column.

#### *Ammonium efflux*

$\text{NH}_4^+$  efflux was weakly correlated with its concentration in overlying water (Fig. 4.15f) but a strong correlation ( $r^2=0.96$ ) was found with salinity (Fig. 4.15e).  $\text{NH}_4^+$  flux increased significantly in a linear fashion from  $1.8 \text{ mmol m}^{-2} \text{d}^{-1}$  at 0.00 to  $4.1 \text{ mmol m}^{-2} \text{d}^{-1}$  at 33.00 salinity. Interestingly similar result was obtained from the benthic chamber where  $\text{NH}_4^+$  efflux was weakly correlated with the overlying concentration (Fig. 4.9c) and the highest flux ( $4 \text{ mmol m}^{-2} \text{d}^{-1}$ ) was observed in April when the condition remains highly saline and the lowest flux was observed in August (Fig. 4.8c) when low salinity prevails in the estuary. Since salinity does not change much from April to May, the  $\text{NH}_4^+$  flux at 33.00 salinity, obtained from this incubation experiment and  $\text{NH}_4^+$  flux measured directly from benthic chamber deployment in April agree very well. This further shows the closeness of flux values obtained from core incubation with benthic chamber measurement. The geochemical effect of increasing salinity on  $\text{NH}_4^+$  release was experimentally proved by Gardner *et al.* (1991). They demonstrated higher benthic  $\text{NH}_4^+$  release when salinity of overlying water was increased.  $\text{NH}_4^+$  in porewaters remains as free dissolved  $\text{NH}_4^+$  ion and in exchangeable form in sediment particles and equilibrates between pore water and sediment (Rosenfeld, 1979).

In fresh water sediment a major fraction of  $\text{NH}_4^+$  remains adsorbed to clay minerals as exchangeable  $\text{NH}_4^+$  (Seitzinger *et al.* 1991), since fresh water sediments have been found to contain lower porewater  $\text{NH}_4^+$  (Simon & Kennedy, 1987) and hence it gets nitrified and subsequently denitrified because of tight coupling of these two processes in estuarine and

coastal sediments (Jenkins & Kemp, 1984). Gardner *et al.* (1991) hypothesized that upon increasing salinity the major ions occupy cation exchange sites in sediment, also forming ion pairs with  $\text{NH}_4^+$ . Thus  $\text{NH}_4^+$  escapes nitrification and fluxes out to overlying water. The effect of fluctuating salinity in controlling  $\text{NH}_4^+$  adsorption capacity of sediments has also been well documented by Boatman & Murray (1982).



**Fig.4.14:** Oxygen consumption and nutrient exchange pattern at changing salinity of overlying water.

Boynton and Kemp (1985) also reported an increasing  $\text{NH}_4^+$  efflux along a gradient of increasing salinity in Chesapeake Bay. In the present experiment increasing salinity from



0 to 33 resulted in ~2 fold increase in benthic  $\text{NH}_4^+$  flux rate. Overall *in-situ* and core incubation experiment results agree well with the results obtained by Gardner *et al.* (1991) and other authors.

#### *Phosphate flux*

The  $\text{PO}_4^{3-}$  efflux tends to decrease with increase in  $\text{PO}_4^{3-}$  concentration in overlying water ( $r^2=0.82$ ) concentration (Fig. 4.15h) which is obviously because of weaker  $\text{PO}_4^{3-}$  concentration gradient between the pore water and the overlying water. This was also observed by Cowan *et al.* (1996). In this experiment  $\text{PO}_4^{3-}$  flux exhibited a significant positive correlation ( $r^2=0.99$ ) with salinity of overlying water (Fig. 4.15g). Tominaga *et al.* (1987) observed an increase in water column  $\text{PO}_4^{3-}$  concentration with increasing salinity. Clavero *et al.* (1990) also experimentally showed higher benthic release of  $\text{PO}_4^{3-}$  with the increase in water column salinity. Porewater  $\text{PO}_4^{3-}$  is geochemically controlled by its sorption and co precipitation onto ferric oxides (Fox, 1993; Sundby *et al.*, 1992; De Jonge *et al.*, 1993) under the oxic condition and release during anoxia following dissolution of ferric oxide and oxyhydroxides (Krom & Berner, 1981). The estuarine sediment was observed to be Fe rich since the iron content of the surficial sediment was 4.8 % (Fig. 4.18h) which indicates high  $\text{PO}_4^{3-}$  adsorbing capacity of the sediment. Increased pH of the water in contact with the sediment decreases the P-binding capacity of iron and aluminium minerals, primarily due to ligand exchange reactions in which  $\text{OH}^-$  ions replace  $\text{PO}_4^{3-}$  ions (Lijklema, 1977; Bostrom *et al.*, 1982). Froelich (1988), Hawke *et al.* (1989) further reported decreasing P adsorption onto ferric oxyhydroxide with increasing pH. Heavy rainfall accompanied by high river outflow during the monsoon obviously decreases salinity and pH of estuarine water. Sarma *et al.* (2001) observed a positive correlation between salinity and pH in the estuarine water. Moreover high  $\text{SO}_4^{2-}$  reduction in coastal sediments decrease the abundance of Fe-oxides (Carignan & Tessier, 1988) as pyrite ( $\text{FeS}_2$ ) formation becomes dominant thereby decreasing P-sorption (Schindler, 1985; Caraco *et al.*, 1989) to the sediment. Since the oxygen of overlying water did not become anoxic ( $\text{DO}>0.3\text{ml/L}$ ) during the incubation, release of extra phosphate from surficial sediment due to reductive dissolution of ferric oxyhydroxide (Krom & Berner, 1981, Sundby *et al.*, 1992) may be ruled out. Thus  $\text{PO}_4^{3-}$  efflux seems to

be facilitated by higher saline condition. This explains the higher degree of positive correlation of benthic P release with salinity. However since P-efflux also shows negative relation with overlying  $\text{PO}_4^{3-}$  concentration (Fig. 4.15h & 4.9d), the net effect on  $\text{PO}_4^{3-}$  release seems to be an interplay between its inverse relation with overlying  $\text{PO}_4^{3-}$  concentration and positive correlation with salinity of the overlying water. The former effect outplays the latter in case of benthic chamber experiment, since overlying  $\text{PO}_4^{3-}$  decreased from 1.19  $\mu\text{M}$  in April to 0.35  $\mu\text{M}$  in August. However in this core incubation experiment the change was much smaller *i.e.* 0.47  $\mu\text{M}$ . Thus, the positive effect of salinity on benthic P release was dominant in the core incubation experiment as  $\text{PO}_4^{3-}$  efflux nearly doubled from 0.04 to 0.075  $\text{mmol m}^{-2} \text{d}^{-1}$  while salinity changed from 0 to 33 (Fig. 4.15g).

#### *Nitrate flux*

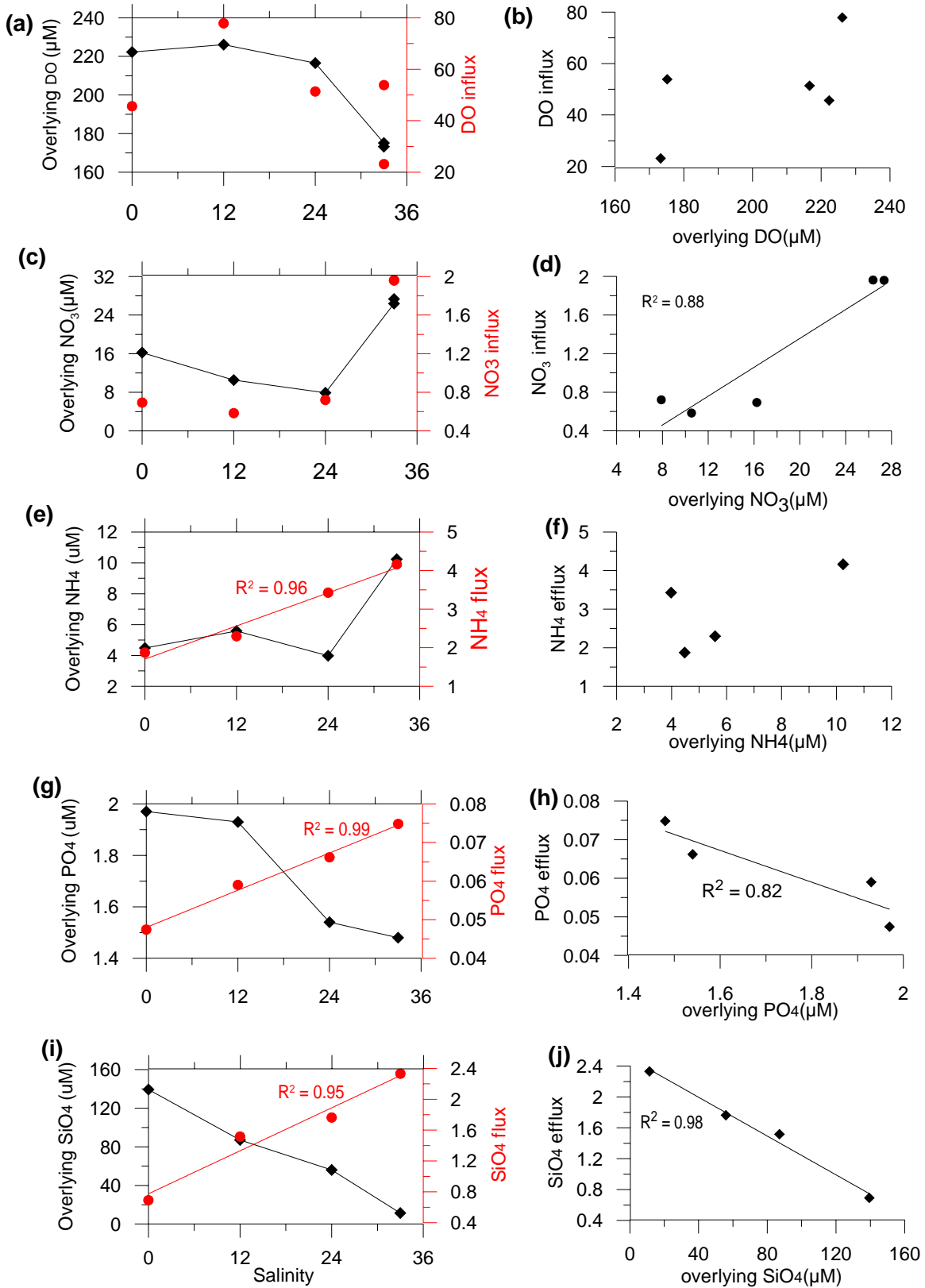
No relation was found between nitrate influx and salinity (Fig. 4.15c) but a strong correlation ( $r^2=0.88$ ) was evident between  $\text{NO}_3^-$  influx and water column  $\text{NO}_3^-$  concentration (Fig. 4.15d). Several authors mentioned that increasing water column  $\text{NO}_3^-$  fuelled higher rate of benthic denitrification resulting in higher  $\text{NO}_3^-$  uptake by sediment (Boynton & Kemp, 1985; Ogilvie *et al.* 1997; Asmus *et al.* 1998). Sorensen (1984), Jorgensen & Sorensen (1985), Trimmer *et al.* (1999) also found sedimentary denitrification to be largely controlled by  $\text{NO}_3^-$  availability in overlying water column and in turn in pore water. However decrease in  $\text{NO}_3^-$  uptake with salinity (from premonsoon to monsoon, Fig. 4.8b) in case of chamber experiment, may be because of the fact that high river flow in monsoon significantly decreases salinity and increases  $\text{NO}_3^-$  concentration in the estuary.  $\text{NO}_3^-$  influx in the estuary considerably increased to 1.23  $\text{mmol m}^{-2} \text{d}^{-1}$  following  $\text{NO}_3^-$  enrichment (7.1  $\mu\text{M}$ ) of estuarine water in August when salinity was low. But in the core incubation experiment highest  $\text{NO}_3^-$  uptake (1.96  $\text{mmol m}^{-2} \text{d}^{-1}$ ) was observed when overlying  $\text{NO}_3^-$  was 26 $\mu\text{M}$  and salinity was 33 psu. This obviously rules out any direct effect of water column salinity on benthic  $\text{NO}_3^-$  influx.

#### **4.4.1.7.3. Benthic respiration rate**

Sedimentary oxygen consumption rate did not show any correlation with salinity (Fig.

4.15a) and dissolved oxygen concentration of overlying water (Fig. 4.15b). However DO exhibited a negative correlation with salinity (Fig. 4.15a) in overlying water since oxygen solubility increases with decreasing salinity. But this did not seem to affect oxic decomposition of organic matter in the estuarine sediment. Benthic respiration rate is in fact controlled by temperature and fresh labile organic matter loading (Banta *et al.*, 1995). Nixon *et al.* (1976) also found a strong dependence of organic matter decomposition on temperature which indicates higher sedimentary oxygen uptake with increasing temperature (Officer *et al.*, 1984). Benthic macrofauna can also influence both the magnitude and timing of decomposition (Rhoads, 1974; Aller, 1980, 1982; Rudnick & Oviatt, 1986). Organic matter decomposition in sediment is controlled by organic matter supply to the sediment which in turn depends on water depth and rate of primary production (Hargrave, 1973; Suess, 1980).

In the *in-situ* measurement highest sedimentary oxygen demand (SOD) ( $98 \text{ mmol m}^{-2} \text{ d}^{-1}$ ) in April may be due to greater fresh organic loading following the spring diatom bloom accompanied by high temperature ( $31^\circ\text{C}$ ). Though heavy river runoff in August decreased salinity and in turn increased oxygen saturation level as well as brought a large amount of terrigenous organic matter to the estuary, low temperature seems to have overall dominance in decreasing SOD ( $35 \text{ mmol m}^{-2} \text{ d}^{-1}$ ). Benthic oxygen uptake did not appear to be controlled by salinity of water column.

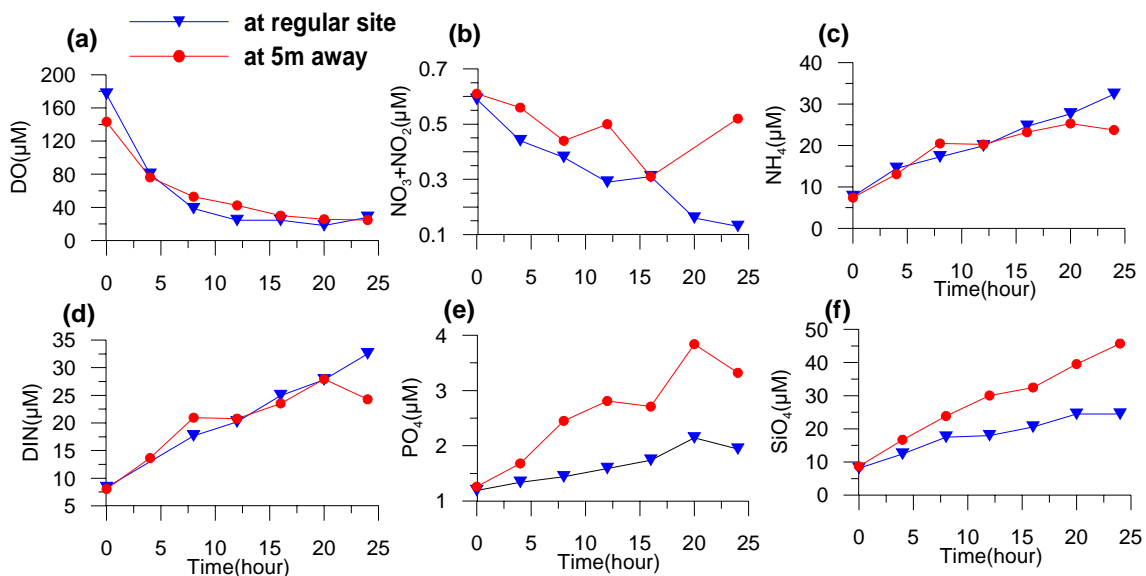


**Fig.4.15:** Correlation between concentration of oxygen and nutrients in the overlying water and their fluxes with salinity.

#### 4.4.1.8. Spatial variability of benthic fluxes in the estuary:

In April another *in-situ* flux measurement was carried out by deploying benthic chamber ~5 m away from the regular site of deployment (away from coast) to see the spatial variability of benthic exchange of biogenic elements (Fig. 4.16). Spatial variation in benthic exchange rates were observed by Berelson *et al.* (1998), Banta *et al.*, (1995), Forja *et al.* (1994) and Hopkinson Jr *et al.* (2001) which exists due to spatial heterogeneity of porosity, organic matter content and pore water concentrations of oxygen, nutrients and abundance of macrobenthos in sediments.

Variation in flux rates was found to be insignificant (One-way ANOVA,  $p = 0.7$ ). On an average 41% variation in the flux rate occurred between the two locations. Hammond (1985) observed a spatial variability of 20-40% in benthic fluxes of nutrients over a few meters due to difference in macrofaunal abundance. As discussed above high macrofaunal abundance during the premonsoon season in the estuarine sediment and their spatial variation (Ansari & Parulekar, 1993) may dominantly control the observed the spatial variation in benthic fluxes in the estuary.



**Fig.4.16:** Comparative benthic exchange of oxygen and nutrients at two sites 5meters apart in Mandovi estuary.

**Table 4.4:** Spatial variation of benthic fluxes in Mandovi estuary.

Parameter	Flux ( $\text{mmol m}^{-2}\text{d}^{-1}$ ) at regular site (site-I)	Flux ( $\text{mmol m}^{-2}\text{d}^{-1}$ ) ~5m away from the regular site (site-II)	Spatial variation
DO	-98.913	-65.373	33.9%
$\text{NO}_3^- + \text{NO}_2^-$	-0.121	-0.068	43.8%
$\text{NH}_4^+$	4.002	3.093	22.7%
DIN	3.927	2.48	36.8%
$\text{PO}_4^{3-}$	0.127	0.454	72%
$\text{SiO}_4^{4-}$	3.116	5.145	39%

#### 4.4.1.9. Inter-annual variation of benthic fluxes

To study the inter-annual variability of benthic exchange rates, sediment cores were collected in May 2005 and May 2006 to carry out flux studies by core incubation method in the laboratory at nearly *in-situ* temperatures. The results are presented in the Table 4.5. No significant variation was observed between fluxes observed in 2005 and 2006 taking all parameters into consideration (1-way ANOVA,  $p = 0.99$ ). Thus benthic fluxes observed in a particular month undergo very negligible variation ( $p > 0.05$ ) from year to year as no apparent change in solar radiation, fresh water load and temperature takes place in the estuary. But within a year flux shows significant variations particularly between premonsoon and monsoon season owing to significant change in river run off, organic matter and nutrient loading and solar radiation and primary productivity.

**Table 4.5:** Inter-annual variation of fluxes in Mandovi estuary.

Parameter	Benthic fluxes ( $\text{mmol m}^{-2} \text{d}^{-1}$ )	
	May 2005	May 2006
DO	-16.195	-16.119
$\text{NO}_3^- + \text{NO}_2^-$	-0.118	-0.737
$\text{NH}_4^+$	1.74	1.829
DIN	1.62	1.905
$\text{PO}_4^{3-}$	0.023	0.08
$\text{SiO}_4^{4-}$	2.434	2.33

**4.4.1.10. Benthic turnover time**

The turnover time is the time required in days for benthic fluxes to replenish water column concentration of a nutrient and is calculated by dividing water column inventory of a nutrient by benthic flux of that nutrient.

Turn over time (t) = nutrient concentration integrated over the depth / benthic flux.

**Table 4.6:** Benthic turn over time of nutrients in Mandovi estuary in different seasons.

Month	Benthic turnover time (day)			
	$\text{NH}_4^+$	DIN	$\text{PO}_4^{3-}$	$\text{SiO}_4^{4-}$
Feb	5.4	5.7	20.8	16.7
Mar	3.6	4.2	15.7	10.1
Apr	7.7	8.4	37.6	10.4
Aug	13.1	---	5.9	864.4

Average turnover time of DIN in premonsoon period was calculated to be 6.3 days (Table 4.6) which means that the benthic flux can replenish the whole pelagic DIN inventory in

~6 days. But since the net DIN flux during the monsoon season is directed to the sediment it could not be calculated for DIN as a whole. However if only  $\text{NH}_4^+$  efflux is taken into consideration without considering highly negative flux of  $\text{NO}_3^- + \text{NO}_2^-$  during the monsoon, it can replace the water column N stock in ~13 days. Since  $\text{NH}_4^+$  comprises a dominant fraction (89-100%) of net DIN efflux in premonsoon with an average turn over time 5.6 days, it has a high potential to supply a major part of N required by phytoplankton in that period. Similarly, the turnover time for  $\text{PO}_4^{3-}$  and  $\text{SiO}_4^{4-}$  underwent considerable change from an average 26.6 and 10.2 days in premonsoon to ~6 and 864 days in the monsoon season respectively. The long turnover time of  $\text{SiO}_4^{4-}$  in monsoon is because of higher silicate concentration in the water column supplied through riverine flow and consequent low benthic  $\text{SiO}_4^{4-}$  release. However since high riverine input in monsoon remains the main nutrient source to the estuary, and increased turbidity and cloud cover diminishes algal productivity in the estuary until September (Devassy & Goes, 1988), benthic flux of nutrients does not play an important role in meeting the nutrient demand of the estuarine phytoplankton, although it enriches the pelagic nutrient inventories of the estuary. It is however possible that for the monsoon period, there exist interannual changes as well, that could not be investigated in the present study.

#### **4.4.1.11. Benthic fluxes and nutrient demand in the estuary**

The Mandovi estuary has been found to be net autotrophic in premonsoon and post monsoon season and net heterotrophic in monsoon season (Pradeep Ram *et al.*, 2003). Excessive loading of allochthonous organic matter entering in the estuary through heavy land and river runoff and significant drop in primary production because of high turbidity and high cloud cover during monsoon period, cause community respiration to exceed gross primary production. Net ecosystem production (NEP) in the estuary by phytoplankton is 54, -34 and 47  $\text{mmol C m}^{-2} \text{d}^{-1}$  in the premonsoon, monsoon and post monsoon season respectively (Pradeep Ram *et al.*, 2003). Diatoms fix C, N, P and Si in proportions of 106:16:1:16 for photosynthesis (Redfield *et al.*, 1963). Assuming overall dominance of diatoms in the system and using these ratios, calculated DIN,  $\text{PO}_4^{3-}$  and  $\text{SiO}_4^{4-}$  demand during the premonsoon was found to be 8, 0.5 and 8  $\text{mmol m}^{-2} \text{d}^{-1}$  respectively.



For example, DIN demand =  $(16/106) * 54 \text{ mmol m}^{-2}\text{d}^{-1}$

where N:C =16:106 and NEP is  $54 \text{ mmol C m}^{-2} \text{ d}^{-1}$

Taking average benthic fluxes for the premonsoon, the contribution of benthic fluxes to primary production was calculated and are presented in the table.4.8.

Similarly nutrient demand in gross primary productivity (GPP) and contribution of benthic fluxes in premonsoon and monsoon are presented in the Table 4.7.

During the premonsoon period, benthic efflux of DIN,  $\text{PO}_4^{3-}$  and  $\text{SiO}_4^{4-}$  appear to meet 49%, 25% and 55% respectively of the N, P and Si demands of algal community in the estuary. However since the gross primary production (GPP) is  $112.4 \text{ mmol m}^{-2} \text{ d}^{-1}$  in premonsoon (Pradeep Ram *et al.*, 2003), the contributions of DIN,  $\text{PO}_4^{3-}$  and  $\text{SiO}_4^{4-}$  fluxes were found to be 23%, 12% and 26% respectively. Callender & Hammond (1982) found that benthic  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  supply can support 35% and 27% of the gross primary production in the Potomac estuary. Billen (1978) reported that benthic N release could meet 75% of phytoplankton nitrogen demand in North Sea.

In the Narragansett Bay benthic  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  efflux contributed 25% and 50% of N and P requirements for primary production (Nixon, 1981). Similarly Boynton *et al.* (1980a) concluded that benthic flux of  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  could supply between 0-190% and 52-330% of the estimated daily algal N and P demands in the Patuxent estuary. However since in the monsoon season, there is net respiration (Pradeep Ram *et al.*, 2003), net DIN flux becomes negative (taken up by sediment) and  $\text{SiO}_4^{4-}$  flux is suppressed considerably ( $0.41 \text{ mmol m}^{-2}\text{d}^{-1}$ ) because of high riverine  $\text{SiO}_4^{4-}$  input and only  $\text{PO}_4^{3-}$  flux ( $0.41 \text{ mmol m}^{-2}\text{d}^{-1}$ ) virtually contributes to the negligible low pelagic productivity in the estuary. Moreover, though river runoff becomes a dominant source of nutrients in the estuary, significant decrease in transparency and solar radiation reduce nutrient utilization by phytoplankton. Thus a comparatively insignificant benthic flux of  $\text{NH}_4^+$  ( $0.834 \text{ mmol m}^{-2}\text{d}^{-1}$ ) accompanied by DIP flux ( $0.234 \text{ mmol m}^{-2}\text{d}^{-1}$ ) only contribute little to the water column nutrient inventories during the monsoon.

**Table 4.7:** Percent contribution of benthic flux to primary production in Mandovi estuary in different seasons. \*NH<sub>4</sub><sup>+</sup> flux has been considered since net DIN flux was negative.

Month	Integrated PP (mmol C m <sup>-2</sup> d <sup>-1</sup> )	Nutrient demand (mmol m <sup>-2</sup> d <sup>-1</sup> )			Benthic flux (mmol m <sup>-2</sup> d <sup>-1</sup> )			% contribution of Benthic flux		
		DIN	DIP	SiO <sub>4</sub> <sup>4-</sup>	DIN	DIP	SiO <sub>4</sub> <sup>4-</sup>	DIN	DIP	SiO <sub>4</sub> <sup>4-</sup>
Feb	75.0	11.32	0.71	11.32	3.09	0.13	4.61	27.26	18.15	40.68
Mar	188.2	28.41	1.78	28.41	5.10	0.13	5.78	17.94	7.30	20.35
Apr	99.0	14.94	0.93	14.94	3.93	0.13	3.12	26.28	13.55	20.85
Aug	31.0	4.68	0.29	4.68	0.84*	0.24	0.42	17.95	81.19	8.88

**Table 4.8:** Percent contribution of average premonsoon benthic flux to Gross Primary Productivity (GPP) and Net Ecosystem Productivity (NEP) in the Mandovi Estuary.

Nutrients	Average flux In premonsoon (mmol m <sup>-2</sup> d <sup>-1</sup> )	Demand in Premonsoon for NEP (mmol m <sup>-2</sup> d <sup>-1</sup> )	Contribution of Benthic flux to NEP (%)	Demand in Premonsoon for GPP (mmol m <sup>-2</sup> d <sup>-1</sup> )	Contribution of Benthic flux to GPP (%)
DIN	4.036	8.15	49.52	16.96	23.7
PO <sub>4</sub> <sup>3-</sup>	0.128	0.50	25.16	1.06	12.0
SiO <sub>4</sub> <sup>4-</sup>	4.50	8.15	55.21	16.96	26.5

#### 4.4.2. Benthic fluxes over the inner shelf

##### 4.4.2.1. Sampling & experimental set up

Water samples were collected each month for dissolved oxygen, nutrients, nitrous oxide, phytoplankton and chlorophyll, temperature and salinity. Because of logistic reasons *in-situ* measurement of benthic flux was not possible. Nevertheless, a sediment core was collected in April on board CRV *Sagar Sukti* by SCUBA divers with minimal disturbance. It was stored immediately in a tub containing bottom water collected from

same location to minimize temperature change. The liner above the sediment was slowly and carefully filled with freshly bottom water from the same location and the core was kept in dark to stop photosynthetic activity. Overlying water was stirred by a magnetically driven *Teflon* coated stirrer with 60 rpm which was sufficient to cause effective mixing without disturbing surficial sediment. The overlying water was allowed to pick up oxygen through out the experiment by keeping the valves attached to the top cap open. Incubation was done in dark and at close to *in-situ* temperature. After 48 hours of incubation, the overlying water was siphoned off and replaced by fresh bottom water and again incubated in airtight condition. Samples were collected every 6-12 hours for oxygen, nitrous oxide and nutrients and the water withdrawn was replaced by helium through a tubing connected to the top lid.

#### 4.4.2.2. Results & Discussion

One way ANOVA was performed between regeneration patterns of nutrients obtained in aerated and airtight cores. Overall nutrient release pattern except  $\text{NO}_3^- + \text{NO}_2^-$  between two cores did not show any significant variance ( $p = 0.61$ ). Results are presented in the Fig. 4.17 and Table 4.9.

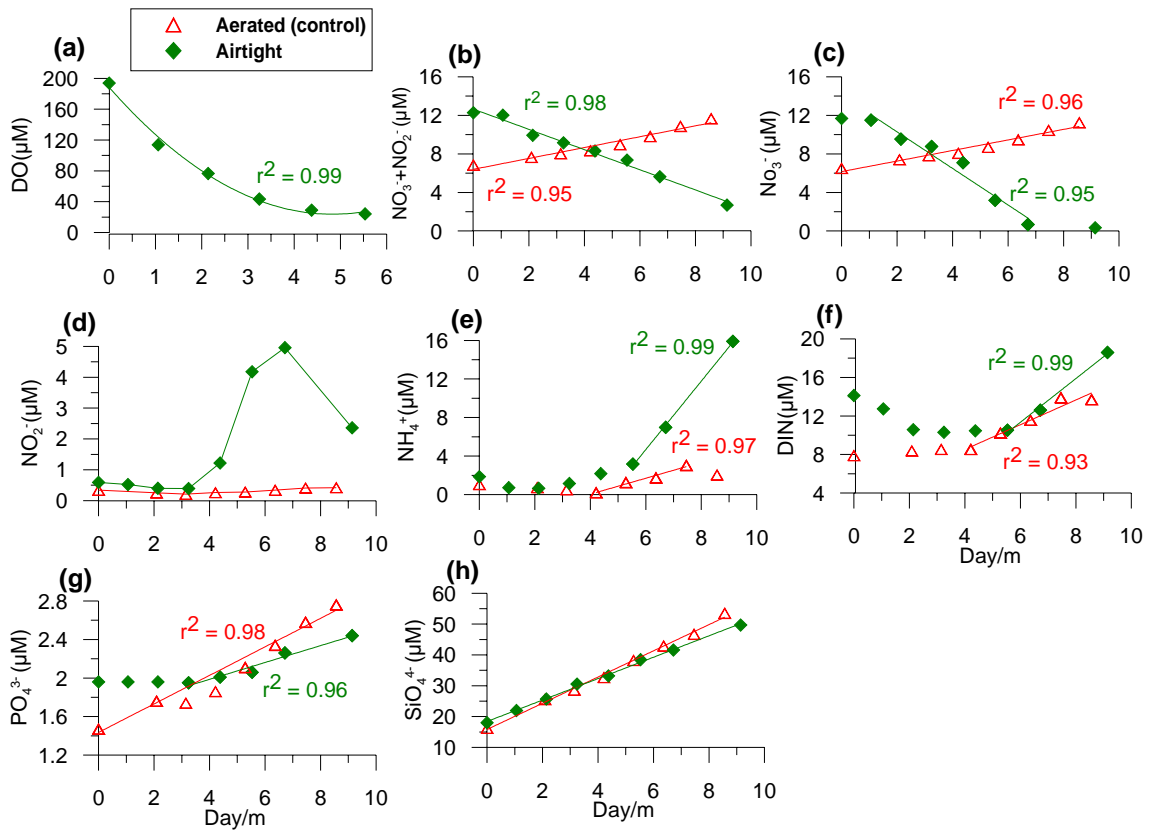
##### 4.4.2.2.1. Sedimentary oxygen consumption

Benthic oxygen uptake is enhanced by temperature, organic load and organic matter content of the sediment. Tidal and wind induced mixing from November to January distributes the regenerated nutrients throughout the water column. High incident solar radiation and low turbidity supported by benthic nutrient supply favor the growth of phytoplankton during winter. During the premonsoon season, coastal waters off Goa also experience fairly wide spread blooms of  $\text{N}_2$  fixing *Trichodesmium*. In fact a big patch of *Trichodesmium* was observed. In fact, a big patch of trichodesmium was observed few tens of meters away from the station in March. However apart from *Trichodesmium*, primary production by other species of phytoplankton like diatoms and dinoflagellates also increases during premonsoon season in the coastal waters off Goa. Surficial sediment was found to be rich in organic carbon (3.3%) (Fig. 4.19g). As there is no river influence in this region, a major part of the organic carbon could be labile. Thus the observed high oxygen uptake may be the result of high rate of benthic decomposition following sinking of algal detritus and accelerated by elevated bottom water temperature

(29°C).

#### 4.4.2.2.2. *Net benthic DIN exchange*

The nitrogenous species exhibited different exchange behaviors under aerobic and airtight conditions.  $\text{NH}_4^+$  efflux substantially increased from  $0.82 \text{ mmol m}^{-2}\text{d}^{-1}$  to  $3.55 \text{ mmol m}^{-2}\text{d}^{-1}$  from the aerated condition to the airtight condition (Fig. 14e) which indicates higher rate of benthic nitrification. This is also reflected in positive flux of  $\text{NO}_3^-$  *i.e.* flux of  $\text{NO}_3^-$  from sediment to water column indicating benthic nitrification at a rate of  $179 \text{ } \mu\text{mol m}^{-2}\text{d}^{-1}$ . In contrast  $\text{NO}_3^-$  was taken up by sediment under the airtight condition. In the aerated core the oxic-anoxic interface must have shifted down and most of organic matter must have undergone aerobic decomposition in the top oxic layer, thus the remineralized  $\text{NH}_4^+$  from organic matter might have been quickly nitrified to  $\text{NO}_3^-$  which ultimately results in efflux of  $\text{NO}_3^-$  to the overlying water. By contrast when oxygen in the overlying water was allowed to be consumed in the airtight system, the oxic-anoxic interface moved upward over time making the nitrification-denitrification coupling in the upper sediment layer, which resulted in a net uptake of  $\text{NO}_3^-$  from the water column. The consumption of  $\text{NO}_3^-$  by benthic denitrification resulted in the accumulation of  $4.9 \text{ } \mu\text{M}$  of  $\text{NO}_2^-$  in the overlying water after 36 hours of incubation. However its subsequent decrease indicates its further diffusion to the sediment and subsequent consumption in sedimentary denitrification. Irrespective of oxic state of the overlying water, sediment behaved as a source of combined N to the water column since DIN flux was positive in both aerated and airtight core. On an average, the sediment supplied  $1.93 \text{ mmole}$  of DIN to the water column per square meter in a day.  $\text{NH}_4^+$  was the major form of released N, comprising 51-100% of DIN efflux.  $\text{NO}_3^- + \text{NO}_2^-$  efflux constituted only 11% of the released DIN.



**Fig.4.17:** Benthic oxygen uptake and benthic nutrient exchange at the coastal location (G5).

**Table 4.9:** Comparative benthic exchange rate when the overlying water was aerated and kept air-tight.

Parameter	Flux ( mmol m <sup>-2</sup> d <sup>-1</sup> ) In aerated condition	Flux (mmol m <sup>-2</sup> d <sup>-1</sup> ) in air-tight condition
DO	-----	-68.219
NO <sub>3</sub> <sup>-</sup> + NO <sub>2</sub> <sup>-</sup>	0.179	-1.047
NH <sub>4</sub> <sup>+</sup>	0.827	3.552
DIN	1.605	2.269
PO <sub>4</sub> <sup>3-</sup>	0.148	0.087
SiO <sub>4</sub> <sup>4-</sup>	4.253	3.474

#### 4.4.2.2.3. Nutrient fluxes

##### *Phosphate flux*

As discussed earlier  $\text{PO}_4^{3-}$  efflux is controlled by its concentration gradient between the pore water and overlying water and its adsorption to ferric oxides and co precipitation with  $\text{FeOOH}$  within the oxic sediment layer and release from these minerals in anoxic condition. Since overlying  $\text{PO}_4^{3-}$  concentration in aerated core was less than that in the airtight core at the beginning of the experiment and since the oxygen in overlying water of the air-tight core was above anoxic level ( $20 \mu\text{M}$ ) during the incubation  $\text{PO}_4^{3-}$  mobilization from sediment did not occur. Thus the variation in  $\text{PO}_4^{3-}$  release pattern in aerated and airtight cores was not significant ( $p = 0.9$ ). The net effect was smaller  $\text{PO}_4^{3-}$  efflux in the airtight core as compared to the aerated core. Thus the  $\text{PO}_4^{3-}$  efflux did not seem to be altered by the oxygen level in the overlying water when oxygen was above suboxic level. The average benthic release of  $\text{PO}_4^{3-}$  to the overlying water was  $0.11 \text{ mmol m}^{-2}\text{d}^{-1}$ .

##### *Silicate flux*

No significant variance was observed in  $\text{SiO}_4^{4-}$  release patterns for the aerated and air-tight cores ( $p = 0.5$ ) and the similar flux rates suggest that silicate flux is not affected by oxic regime of the overlying water. The average efflux was observed to be  $3.86 \text{ mmol m}^{-2} \text{ d}^{-1}$ . This high silicate efflux may be because of abundant diatom tests in the sediment since diatom remains the dominant phytoplankton species in the coastal waters off Goa during most of the time of the year. High silicate concentration ( $369 \mu\text{M}$ ) of porewater within the uppermost (0-1 cm) sedimentary layer (Fig. 4.19d) indicates high dissolution rate of diatom tests and a sharp concentration gradient at sediment-water interface, which drives such a high silicate efflux.

#### 4.4.2.2.4. Stoichiometry of Benthic release

Since  $\text{NH}_4^+$  was subjected to substantial nitrification in aerated core benthic release ratio  $\text{NH}_4^+ : \text{PO}_4^{3-}$  decreased to 5.5 from the expected Redfield ratio ( $\text{NH}_4^+ : \text{PO}_4^{3-} = 16:1$ ), but the ratio of DIN to  $\text{PO}_4^{3-}$  (10.8) is close to the expected value (as calculated from Table.4.9). DIN: DIP in the airtight core (25.93) deviated even more from the Redfield value since  $\text{NO}_3^-$  was taken up by sediment and  $\text{PO}_4^{3-}$  release was lower.  $\text{NH}_4^+ : \text{PO}_4^{3-}$  flux

ratio was very high (40.5) in the airtight core from the expected value which may be because of greater  $\text{NH}_4^+$  efflux as compared to that for the aerated core.

Similar preferential release of  $\text{NH}_4^+$  to  $\text{PO}_4^{3-}$  was also observed by Falcao and Vale (1998) in sediments. The O: $\text{NH}_4^+$  ratio in the airtight core was 19.2 which was slightly higher than the Redfield value (13.25) but this deviation may be because of adsorption of  $\text{NH}_4^+$  onto sedimentary clay minerals (Rosenfeld, 1979) and nitrification in the upper oxic layer to some extent. Close coupling of nitrification and denitrification in nearshore sediments (Jenkins & Kemp, 1984) acts as a sink for nitrified  $\text{NH}_4^+$  and  $\text{NO}_3^-$  in the overlying water since these authors observed that 99% of the  $\text{NO}_3^-$  produced by nitrification was lost through coupled benthic denitrification. This loss of combined N in the sediment causes deviations from the Redfield stoichiometry. The closeness of flux ratio of DIN to  $\text{SiO}_4^{4-}$  (1.02) in the airtight core to the expected ratio (N:P in diatom=1:1) presumably because  $\text{NH}_4^+$  was the major form of released N and did not undergo substantial nitrification because of the lower oxygen level. In the aerated core, on the other hand loss of  $\text{NH}_4^+$  in the nitrification-denitrification coupling reduced the DIN: $\text{SiO}_4^{4-}$  ratio to 0.37. The results are consistent with the fact that diatoms comprising more than 95% of the algal community in the shelf regions off Goa.

#### **4.4.2.2.5. Pore water nutrients**

Sediment pore water was found to be highly enriched with  $\text{NH}_4^+$ ,  $\text{PO}_4^{3-}$ ,  $\text{SiO}_4^{4-}$  and organic carbon but depleted in  $\text{NO}_3^-$  and  $\text{NO}_2^-$  (Fig. 4.19). This loss of  $\text{NO}_3^-$  and  $\text{NO}_2^-$  from pore water is due to high rate of benthic denitrification. In addition to this high  $\text{NO}_3^-$  level in the bottom water (13.8  $\mu\text{M}$ ) led to steep concentration gradient across the sediment-water interface resulting in  $\text{NO}_3^-$  diffusion to the sediment and its subsequent loss in the benthic denitrification.

High concentrations of  $\text{PO}_4^{3-}$  (39.5  $\mu\text{M}$ ),  $\text{NH}_4^+$  (710  $\mu\text{M}$ ) and  $\text{SiO}_4^{4-}$  (369  $\mu\text{M}$ ) in the pore water close to the sediment-water interface and the low concentrations of  $\text{PO}_4^{3-}$  (1.89  $\mu\text{M}$ ),  $\text{SiO}_4^{4-}$  (17.2  $\mu\text{M}$ ) and  $\text{NH}_4^+$  (14.4) in the overlying water would drive high rate of diffusive flux of these nutrients to the water column. High amount of sedimentary organic carbon (3.33%) partly explains the high oxygen uptake observed in the incubation

experiment. DIN:DIP in pore water remains close to the Redfield ratio in the top 3-4 cm of the sediment but below this it increases (Fig. 4.19e) presumably because of preferential regeneration of  $\text{NH}_4^+$  (Falcao & Vale, 1998).

#### 4.4.2.2.6. Comparison between diffusive fluxes and measured fluxes

Diffusive fluxes were calculated from pore water concentration gradients following Fick's law as already described before and were compared with measured fluxes by the core incubation method. In case of core incubation experiment the activities of benthic organisms are suppressed which may be the reason for the observed lower fluxes as compared to calculated diffusive fluxes.

As described earlier *in-situ* measured fluxes remain much higher than diffusive fluxes in the estuary since benthic chamber does not affect benthic activity to a large extent. Lower rate of benthic release in incubated cores as compared to that in *in-situ* benthic chambers has also been observed by Fisher *et al.* (1982), Berelson *et al.* (1998), Eyre & Ferguson (2002). Fluxes measured by these two methods differ because of (1) heterogeneous benthic environment in aquatic systems and (2) quite different resolution and time scales that various methods operate on.

**Table 4.10:** Comparison between calculated diffusive flux and *in-situ* measured benthic flux at the coastal location.

Nutrient	Calculated Diffusive flux ( $\text{mmol m}^{-2}\text{d}^{-1}$ )	Measured benthic flux ( $\text{mmol m}^{-2}\text{d}^{-1}$ )
$\text{NO}_3^-$	-0.168	-1.288
$\text{NH}_4^+$	3.918	3.552
$\text{PO}_4^{3-}$	0.578	0.088
$\text{SiO}_4^{4-}$	1.007	3.474



#### 4.4.2.2.7. Benthic turnover time and nutrient demand

Turnover time was calculated by dividing water column nutrient concentration integrated over depth with benthic fluxes and nutrient demand was calculated as described earlier in case of the Mandovi estuary. Longer turnover times at the coastal station are due to greater depth (27m) than the estuarine site (4m). Average integrated gross primary productivity (GPP) in the coastal waters was  $90.3 \text{ mmol C m}^{-2} \text{ d}^{-1}$  (Pradeep ram *et al.*, 2003) from which nutrient requirements of coastal phytoplankton were calculated (Table 4.11).

**Table 4.11:** Percent contribution of benthic flux to the Gross primary productivity at the coastal location.

Nutrient	Benthic Turnover time (Days)	Nutrient demand for for GPP ( $\text{mmol m}^{-2} \text{d}^{-1}$ )	Contribution of Benthic flux (%)
$\text{NH}_4^+$	10	13.63	26.06
DIN	59	13.63	16.65
$\text{PO}_4^{3-}$	423	0.85	10.33
$\text{SiO}_4^{4-}$	93.2	13.63	25.48

#### 4.4.3. Comparison between benthic exchanges in the estuary and in the Shelf.

The purpose of the flux studies carried out in the Mandovi estuary **and at the coastal station** off Goa (G5) was to find out the factors responsible for the differences in benthic exchange rates between the estuarine and the shelf region. As discussed previously Mandovi estuary remains a tidal dominated system in premonsoon (February-May) and post monsoon season (October-January). But in monsoon heavy river influence has a considerable impact on its benthic biogeochemistry. The coastal station off Goa (G5) remains nutrient poor in non-monsoon period instead. This station is highly influenced by upwelling induced by southwest monsoon which causes nutrient enrichment in the water column. Flux measurements carried out in May 2006 by incubating sediment cores from

both the estuary and G5.

#### 4.4.3.1. Benthic fluxes and benthic denitrification

Since this comparative study was carried out in the same month during premonsoon season, variation in flux rates due to seasonal effect and riverine flow are ruled out. The observed differences in oxygen consumption rate may be because of comparatively higher labile organic matter availability at the coastal sediment. Since G5 has been found to more productive in premonsoon period, the source of organic matter could be pelagic primary production. Higher  $\text{NO}_3^- + \text{NO}_2^-$  uptake can be attributed to higher  $\text{NO}_3^- + \text{NO}_2^-$  ( $8.6\mu\text{M}$ ) in the bottom water of the coastal station as compared to the estuary ( $2.24\mu\text{M}$ ) (Table 4.13) as increased water column  $\text{NO}_3^-$  have been observed to enhance benthic denitrification rate.

Thus benthic denitrification rate in coastal sediment should be  $\sim 2$  times that in the estuarine sediment during the peak premonsoon season as N loss at G5 was  $1.048\text{ mmol N m}^{-2}\text{ d}^{-1}$  as compared to  $0.538\text{ mmol N m}^{-2}\text{ d}^{-1}$  in the estuary.  $\text{NH}_4^+$  flux represents 96% of total DIN flux in the estuary whereas it comprised 100% of the DIN released from coastal sediment.

Comparatively higher fluxes of  $\text{NH}_4^+$  and  $\text{SiO}_4^{4-}$  at G5 can be attributed to the higher porosity and higher pore water concentration of coastal sediment compared with the estuarine site. However  $\text{PO}_4^{3-}$  effluxes at both the sites were similar. Lower  $\text{PO}_4^{3-}$  flux at G5 than the expected value may be due to presence of a thicker oxidized surficial sediment layer which acts as trap for mobilized  $\text{PO}_4^{3-}$  that moves upward along the concentration gradient. Ferric oxides, Mn-oxides and ferric oxyhydroxides present in the sediment, have been known to be very effective scavenger of dissolved inorganic phosphate under oxic condition as  $\text{PO}_4^{3-}$  remains adsorbed to/ co precipitated with these minerals in oxic sediments (Krom & Berner, 1981).

**Table 4.12:** Comparison between premonsoon fluxes in the estuarine and at the shelf site of Goa. Fluxes are in  $\text{mmol m}^{-2} \text{d}^{-1}$ .

	<b>Mandovi Estuary</b>	<b>Off Goa (G5)</b>
DO flux	-23.151	-68.219
$\text{NO}_3^- + \text{NO}_2^-$ flux	-0.538	-1.048
$\text{NH}_4^+$ flux	1.830	3.552
DIN flux	1.701	2.270
$\text{PO}_4^{3-}$ flux	0.080	0.088
$\text{SiO}_4^{4-}$ flux	2.331	3.474

**Table 4.13:** Comparison in nutrient content of in the Mandovi estuary and at the coastal location in premonsoon season.

<b>Nutrient</b>	<b>Estuarine bottom water</b>	<b>Coastal bottom water</b>
$\text{NO}_3^- + \text{NO}_2^-$	2.24 $\mu\text{M}$	8.61 $\mu\text{M}$
$\text{NH}_4^+$	4.24 $\mu\text{M}$	0.23 $\mu\text{M}$
DIN	7.23 $\mu\text{M}$	8.84 $\mu\text{M}$
$\text{PO}_4^{3-}$	0.74 $\mu\text{M}$	1.45 $\mu\text{M}$
$\text{SiO}_4^{4-}$	11.36 $\mu\text{M}$	13.64 $\mu\text{M}$

#### 4.4.3.2. Stoichiometry of benthic release

Closeness of O: DIN ratio in estuary (Table 4.14) to the expected value (13.25) (Redfield *et al.*, 1963; Alvarez-Borrego *et al.*, 1975) further indicates that the  $\text{NH}_4^+$  is the end product of benthic mineralization without substantial subsequent nitrification to  $\text{NO}_3^-$ . But departure of O:DIN at the coastal station from the expected Redfield value implies significant nitrification of remineralized  $\text{NH}_4^+$  to  $\text{NO}_3^-$  and subsequent  $\text{NO}_3^-$  diffusion to underlying suboxic layer and its loss in benthic denitrification in a tightly coupled nitrification-denitrification system. Closeness of O:  $\text{NH}_4^+$  in the coastal system to the expected value (17.25, when the end product is  $\text{NO}_3^-$ ) further proves that benthic nitrification is very significant in the coastal environment.

Loss of  $\text{PO}_4^{3-}$  through adsorption and co precipitation with ferric minerals possibly caused  $\text{NH}_4^+ : \text{PO}_4^{3-}$  and DIN: DIP ratio to deviate from usual Redfield ratio of 16:1 in both estuary and coastal station. But these ratios in estuary are more close to Redfield ratio than that in coastal station which indicates that geochemical scavenging of DIP is more in shelf sediments.

Near unity  $\text{NH}_4^+ : \text{SiO}_4^{4-}$  ratio at G5 suggests that most of the organic debris is derived from diatoms which in turn suggest the phytoplankton community to be dominated by this group.

**Table 4.14:** Comparison between benthic flux ratios in Mandovi estuary and at the coastal location off Goa

Flux ratio	Estuarine	Coastal
O:DIN	13.6	31
O: $\text{NH}_4^+$	12.65	19.2
$\text{NH}_4^+ : \text{PO}_4^{3-}$	22.87	40.36
DIN:DIP	21.26	25.79
$\text{NH}_4^+ : \text{SiO}_4^{4-}$	0.772	1.02

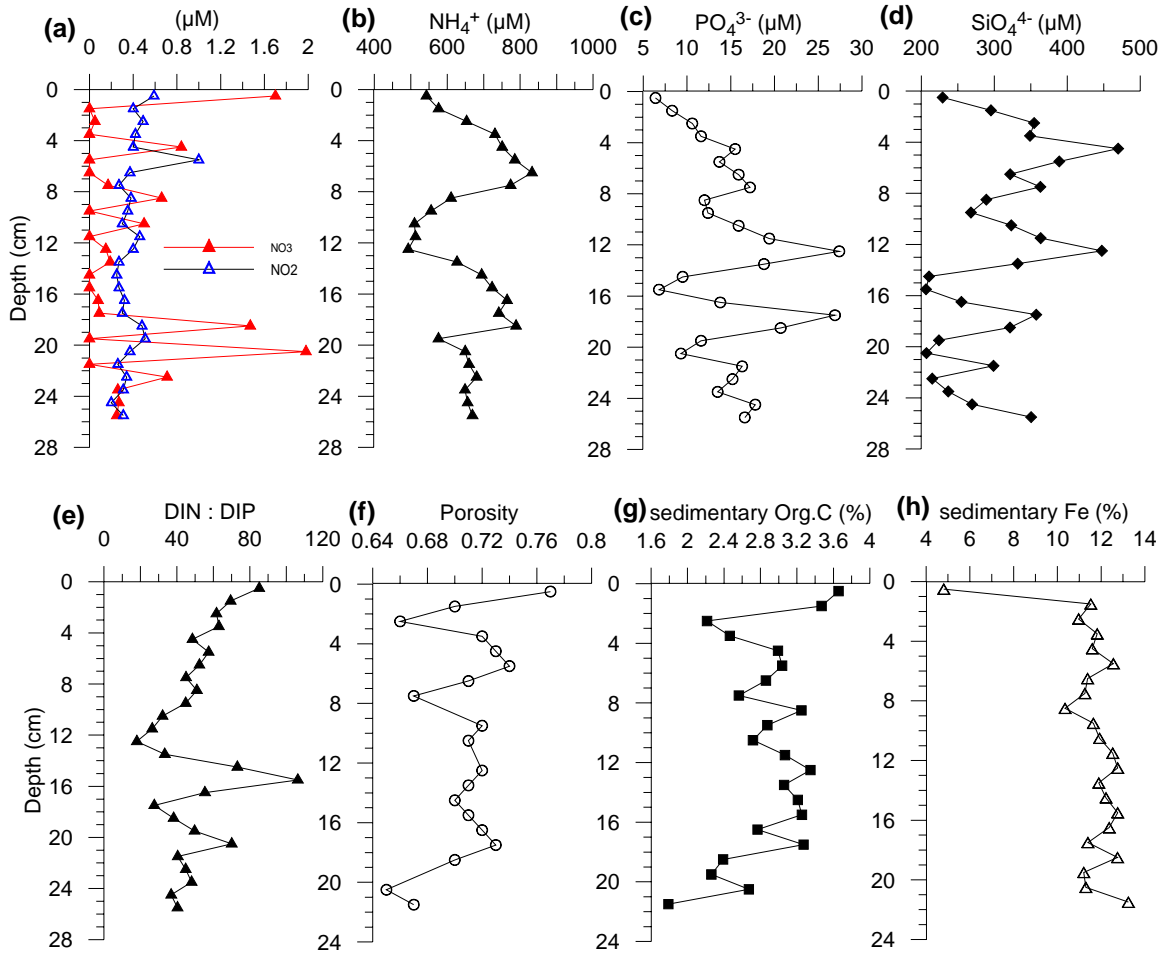
#### 4.4.3.3. Pore water nutrients

Pore water in both estuarine and coastal sediments was found to be depleted of  $\text{NO}_3^-$  and  $\text{NO}_2^-$  because of high denitrification rate (Seitzinger, 1988; Nixon *et al*, 1980). Pore water DIN: DIP ratio in sediment of the Mandovi estuary (85.2) was found to be ~5 times higher than that in coastal sediment (17.9) (Fig. 4.18e & 4.19e) which could be due to presence of higher amount of Fe minerals in the estuarine sediment (Fig. 4.18h & 4.19h) and consequent immobilization of  $\text{PO}_4^{3-}$ . Closeness of Redfield ratio in the coastal sediment to the expected value (16:1) implies that phytoplankton detritus is the dominant source of sedimentary organic matter. Again higher pore water  $\text{SiO}_4^{4-}$  in the surficial coastal sediment compared to that in estuarine sediment shows that diatom are the major algal group at G5 in premonsoon period though episodic *Trichodesmium* blooms have

been observed between February to May. Higher percentage of sedimentary Fe in estuarine sediment indicates greater immobilization of  $\text{PO}_4^{3-}$  as compared to that in coastal sediment but still  $\text{PO}_4^{3-}$  fluxes at both stations are close to each other which could be because of a thicker oxic surface layer in the coastal sediment. Higher level of labile organic matter and consequently higher accumulation of pore water  $\text{NH}_4^+$  in coastal sediment probably results in ~2 times higher  $\text{NH}_4^+$  flux compared to that in the estuary, ultimately raising DIN:DIP flux ratio.

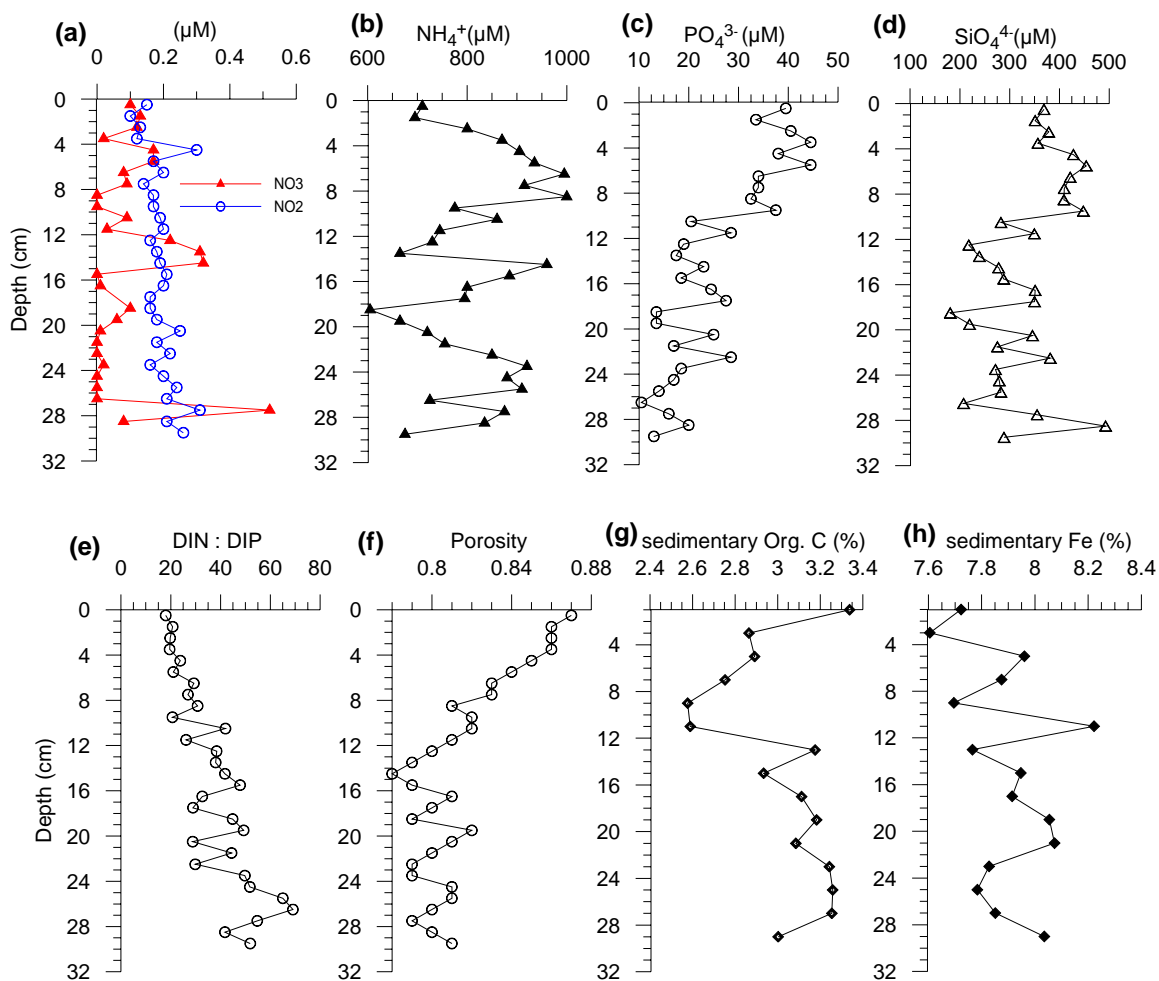
#### **4.4.3.4. Benthic turnover time and nutrient demand**

Though the flux measurement was also carried out in the Mandovi estuary by benthic chamber deployment in premonsoon months, but while comparing fluxes, turnover time, and contribution to primary productivity etc, with those at the coastal location the data obtained from core incubation was used for this purpose as the discrepancy exists between *in-situ* and core incubation method. As discussed before to the observation of many authors, flux data obtained by *in-situ* measurement and core incubation method does not agree in some estuaries and coastal systems. There are two reasons for considering the estuarine flux data obtained only by core incubation method (1) it was measured in the same month when core from G5 was incubated so that effect of physical factors causing seasonality would be minimized (2) flux data at G5 was obtained only from the core incubation method. Thus while comparing flux related parameters, by using laboratory incubation data in case of estuary, the inherent difference in fluxes between *in-situ* method and core incubation method would be minimized.



**Fig.4.18:** Profiles of porewater nutrients and porosity, sedimentary organic carbon and sedimentary iron in Mandovi estuary during May.

Though the nutrient levels in the coastal water were higher than those in the estuarine water, comparatively much shallower depth in the estuary leads to shorter turnover time of nutrients through benthic supply as compared to the coastal station (Fig. 4.15). Nevertheless because of higher benthic fluxes and lower gross primary production ( $90.3 \text{ mmol C m}^{-2} \text{ d}^{-1}$ ) consequently lower nutrient demand, observed at G5, a greater percentage of nutrient requirement by phytoplankton is expected to be met at the coastal station, as compared to the estuary which was more productive ( $\text{GPP} = 112.4 \text{ mmol m}^{-2} \text{ d}^{-1}$ ) in the studied period.



**Fig.4.19:** Profile of porewater nutrients, porosity, organic carbon and Iron of the coastal sediment at G5 in May.

**Table 4.15:** Comparison between contributions of benthic fluxes to the Gross primary productivity (GPP) in Mandovi estuary and Shelf region off Goa.

Nutrient	Mandovi Estuary (May)			Coastal station (May)		
	Turnover time (day)	Demand in GPP (mmolm <sup>-2</sup> d <sup>-1</sup> )	Contribution of flux to GPP (%)	Turnover time (day)	Demand in GPP (mmolm <sup>-2</sup> d <sup>-1</sup> )	Contribution of flux to GPP (%)
NH <sub>4</sub> <sup>+</sup>	5.4	16.966	10.786	10.4	13.630	26.06
DIN	8.5	16.966	10.026	59.9	13.630	16.65
PO <sub>4</sub> <sup>3-</sup>	18.5	1.060	7.544	423.7	0.852	10.33
SiO <sub>4</sub> <sup>4-</sup>	9.7	16.966	13.739	93.3	13.630	25.48