CHAPTER 4

DISCUSSION
AND
CONCLUSION
Though mangroves are generally regarded as productive coastal marine ecosystems in the tropics (Qasim and Wafar, 1990) measurements of concentrations of nutrients, especially of nitrogen, that sustain this production have been few and far between. Several cover only part of the annual cycle and only a few such as those in the mangroves of Australia (Boto and Wellington 1988; Trott and Alongi 1999) Pakistan (Harrison et al., 1997) Mexico (Rivera-Monroy et al., 1995) and India (Krishnamurthy et al., 1975) present seasonal cycles. None of these studies included all assimilable forms of nitrogen, and the seasonality of phosphorous and silicate. Nutrient cycling in mangrove ecosystem was studied at Achara estuary examining the distribution and fluxes of various nitrogenous nutrients and that of phosphorous and silicate in water column and sediment.

Variation in concentrations of nutrients among estuaries and mangrove waterways can be ascribed to differences in the extent of freshwater and ground water input, degree of solar insolation, oxygen availability, standing stocks and productivity of phytoplankton and bacterioplankton. Dissolved nitrogen concentrations decrease with increase in salinity at the seaward end in mangrove estuaries of the wet tropics (Southeast Asia, India). Lowest concentrations are generally recorded in the premonsoon season, coincident with high rates of primary productivity (Sarala Devi, 1983). In the dry tropics, variations in estuarine nutrient concentrations are greatest over a tidal cycle with highest concentrations occurring at high tide and decreasing during ebb tide (Guerrero et al., 1988, Ovalle et al., 1990).

The composition of nutrients in water column overlying the sediment is affected by the river hydrology. Factors that affect the composition are non point source input resulting from precipitation, river runoff, algal productivity, water column turbulence caused by wind driven waves and tidal currents.
Temperature

Temperature controls the rates at which chemical reactions and biological processes (such as metabolism and growth) take place. Resistant to chemical reaction is lowered by increase in temperature; hence a rise in temperature speeds up reactions. Temperature and salinity variations combine to determine the density of seawater, which in turn greatly influences vertical water movements with consequent changes in chemical and biological events within the water column. Water temperature partly determines the concentrations of dissolved gases in seawater these include dissolved oxygen and carbon dioxide, which are profoundly linked with biological processes. In the present study the maximum temperature was recorded during the premonsoon season due to high solar radiations there by increasing the temperatures and low temperatures during the monsoon months due to dilution by precipitation and freshwater flow.

pH

pH affects the precipitation of colloids and metals. Studies by Thomas and Ragethaman, (1987) have recorded the tendency of slight decrease in pH in the estuary of Hazara coast due to river water incursion and excessive land drainage while Kannan and Kannan (1996) reported that high pH recorded could be due to the removal of CO$_2$ by photosynthesis. Studies by Zingde and Desai, (1987) suggested the temporal variations in pH as presumably due to the change in primary production, respiration by organisms, mineralization as well as decomposition of organic matter in sediments. The increasing pH has direct bearing with high phytoplankton productivity to a certain extent. pH values can reach upto 7.5 in waters of reduced salinity or in anaerobic (anoxic ) condition where bacteria using reduction of sulphate as a source of oxygen for the decomposition of organic matter release H$_2$S in solution. However when the sulphate has been used up decomposition of organic matter under anaerobic conditions involves the reduction of carbon dioxide itself and leads to the formation of hydrocarbons such as methane. Under these conditions, the pH may rise to values as high as 12.
The pH in the present study ranged up to 9.9 and was alkaline during the non-monsoon season due to non-interference of freshwater in these months and the pH decreased in the monsoon due to influx of freshwater and dilutions by the rainwater.

**Salinity**
The salinity is an important ecological parameter; wherein slight variations result in physical as well as physiological changes. A repeated fluctuation in salinity is the general fact observed in the mangrove environment. It is well known that estuaries and adjoining marine realms in general are subjected to wide variations in salinity due to the impact of tidal and seasonal changes. Lower salinities were observed due to dilution by rainwater and freshwater runoff in the monsoon season and higher salinities were recorded in the non-monsoon season due to no freshwater dilution.

**Dissolved Oxygen**
DO is the most significant ecological parameter, used as index to assess the water quality, primary productivity and status of pollution. Oxygen is produced as a byproduct of photosynthesis and consumed by respiration. In aquatic environments, oxygen concentrations usually exhibit a characteristic diurnal pattern, with concentrations increasing from morning to mid-afternoon as photosynthesis exceeds respiration. Declining oxygen concentrations occur during the late afternoon or evening in response to decreasing photosynthetic rates and continue to decrease throughout the night when photosynthesis does not occur. In addition to these biological processes, physical processes can also affect oxygen concentrations. Diffusion of oxygen across the air-water interface can increase or decrease water column concentrations, with diffusion from the air into the water occurring when the water is undersaturated and vice versa when the water is supersaturated. The key factors influencing dissolved oxygen concentrations include excess nutrients, phytoplankton growth, death and decomposition, freshwater and salt water inflow. Excess nutrients cause rapid growth of phytoplankton creating dense populations of algal blooms. These blooms may become so dense that they reduce the amount of sunlight available...
to other plants. Without sufficient light the plants die off and settle to the bottom and decay. The decomposition process results in utilization of oxygen and thereby decreasing its concentrations. Temperature plays a critical role in determining the amount of dissolved oxygen in water. The colder the water the more oxygen it can hold.

The solubility of gases generally decreases with increasing temperature and salinity and increases with increasing pressure. Surface waters are usually supersaturated with oxygen partly due to liberation of oxygen during photosynthesis but mainly as the result of air bubbles formed at the crests of waves being forced down into the water column where part of the gas they contain is driven into solution by the increased hydrostatic pressure.

Waters temperature was minimum during the monsoon and the beginning of postmonsoon. This led to increase in concentrations of dissolved oxygen during the monsoon season and post monsoon season. The high amount of litterfall in the premonsoon (Wafar, S et al., 1997) and its subsequent decomposition during the postmonsoon season may have led to utilization of dissolved oxygen. The concentrations of DO decreased in late post monsoon and reached peak values in pre monsoon and early monsoon seasons. Higher concentrations in the premonsoon season were due to favorable light conditions resulting in increase in photosynthesis. Depletion of oxygen may result in changes in biochemical cycling (Naqvi et al., 2000). The increasing occurrence of hypoxia in estuaries is believed to be related to increase in the nutrient loadings in rivers (Cloern, 2001).
Chlorophyll

Phytoplankton abundance in estuaries is known to depend on factors such as light (Cloern, 1987), nutrients (D'Elia et al., 1986) and zooplankton grazing (Verity, 1986). In portions of some system a single factor such as turbidity (Cloern, 1987) or nitrogen (Rudek et al., 1991; Mallin et al., 1993) may regulate phytoplankton production year round with changes in, e.g., river flow (Fisher et al. 1992) or physical factors (temperature and incident irradiance). Higher concentrations of chlorophyll a in the premonsoon may be ascribed due to increase in amount of available light, nutrients and decrease turbidity.

Chlorophyll a concentrations were high during the premonsoon season and low in monsoon and postmonsoon. At high tide, the differences between the stations are low, indicating the dominance of marine conditions. At low tide, the differences become prominent, with lower concentrations in the upstream stations than downstream.

Nitrite

A pattern of monsoonal rise and summer depletion in nitrite is a typical trend of estuaries. Similar observation was noticed by Nair et al., (1984) owing to its position in the nitrification – denitrification process. Similarly higher values were also recorded by De Souza et al., (1981) in Zuari during monsoon months and were related to the terrigenous input by river flow. It is interesting to note that, though the monsoon conditions prevailed in the investigation from June to August, the higher values of nitrite – nitrogen were recorded during the onset of monsoon. The observed nitrite peak in the post monsoon season was due to high concentrations of ammonium during the monsoon at the mangrove-dominated stations.
Nitrate

Nitrate has often been attributed an important status as a nitrogen source for marine phytoplankton for two reasons. The first one is that it is the most abundant form of nitrogen in the dissolved state next to nitrogen and the second is that it is the most abundant one among the biologically assimilable forms. Hence the availability of nitrate has often been associated with primary production where its low concentrations limit primary productivity.

The supply of nitrate is mostly based on physical processes such as riverine input (Edmond, 1981) upwelling (Dugdale & Goering, 1967) and atmospheric washouts (Soderlund and Svennsson, 1976). The biological processes through which nitrate is added is by nitrification. Sharp (1983) presented a review of studies on oceanic nitrate distribution.

Generally, the higher values were recorded during monsoon and early post monsoon months both at high and low tides of mangrove areas. Similar observations were made by Nair et al., (1984) in Ashtamudi estuary and Ayakkannu (1989) in Kolli dam estuary and Dham et al., (2002) in the Achara estuary. The higher values during monsoon season are attributed to the terrestrial input through riverine discharge, high freshwater inflow, from the mineralization of organic material through bacterial and chemical decomposition. Nitrate concentrations were modulated by monsoonal addition, productivity – utilization and fixation by bacteria.

The smaller peaks noticed during post monsoon season are believed to be related to both reduced river transport and utilization. Low concentration of nitrate is due to high uptake (Dham et al., 2002) (average 65% and range 56-82 %) since nitrate was the major N source immediately after the monsoons. Uptake rates were lower during the monsoons for all the four nutrients viz nitrite, nitrate, ammonium and urea in the Achara estuary (Dham et al., 2002). Lower concentrations may also be due to denitrifying bacteria, which are commonly present in these shallow environments, utilizing the inorganic nitrates for their energy requirements.
The concentrations of nitrate ranged from 0.15 to 52.6 µg at N l⁻¹ (average 5.53 µg at N l⁻¹) in the present study. Studies by Dham et al., (2002) reported concentrations of nitrate for three stations and ranged from (0.4 – 19.6 µg at N l⁻¹, average 4.5 µg at N l⁻¹) and are closer with the values reported in the present study for the three stations (0.15 - 18.07 µg at N l⁻¹; average 3.6 µg at N l⁻¹).

Highest concentrations were recorded at station 5 where the salinity was almost nil during the monsoon. High concentrations of nitrate during monsoon (Figure. 19) suggest that the major input of nitrate to the estuary is from the freshwater sources through precipitation and river flow. Though the non-monsoon concentrations were several times lower than in monsoon, a pattern of increase from post-monsoon to pre-monsoon can be seen. This is more evident at the downstream stations (1-3). As fresh water supply to these stations is practically nil during pre-monsoon, the increase in nitrate concentrations is mainly due to in situ nitrification.

Sharp (1983) reported nitrate values in the fresh water end to range from 10-40 µg, at N L⁻¹ and decrease linearly to near zero at the high salinity end. Also studies conducted by (Yin et al., 2000) at Pearl River estuary high nitrate concentrations were recorded at the upstream end during the high river discharge.

Nitrate transport is very much evident in monsoon season as seen by the very high concentrations in these months. There is maximum river flow, high precipitation and land run off during these months due to which the salinity is decreased to almost zero. The nitrate is being transported by these processes resulting in an increase in concentrations of nitrate in the estuary. Also there was high biological productivity during the monsoon wherein chl a values were high with high nitrate concentrations at station 1, 2, and 3.
Ammonium

Ammonia occurs in solution in seawater chiefly as ammonium ion. It is eventually oxidized to nitrate but it can also be used as a nutrient by phytoplankton (and it is the only source of nitrogen for many free living bacteria). Biological production of ammonium can only be sustained if nitrate continues to be supplied to surface waters by rivers, atmospheric fallouts or upwelling from below the nutricline. Ammonia is added to seawater through ammonification, excretion by microorganisms particularly by zooplankton, river run off and rainfall. Removal of ammonia can occur through assimilation by phytoplankton (MacIsaac and Dugdale, 1972) and by nitrification. McCarthy et al., (1977) reported that the order of nitrogen preference for Chesapeake bay phytoplankton as measured by uptake relative to availability was ammonium > urea > nitrate > nitrite and therefore the significance of ammonium was recognized. It includes the most preferred form of dissolved inorganic nitrogen by phytoplankton (Eppley, 1979) and a major form of biogenic input to the ocean (Sharp, 1983). This is oxidized microbially (nitrification). Nitrite and ammonium are generally considered as intermediates in the nitrogen cycle. As labile compounds they are usually in low concentrations and often show discrete maxima near the photic zone. Ammonium maximum is found near the bottom of the photic zone. It is a central component in the regeneration pathway. The regeneration of nitrogenous nutrients is well known to be a major source of nitrogen for oceanic primary producers (McCarthy 1972; Eppley et al., 1973; McCarthy et al., 1977; Harrison 1978; Gilbert 1982). Annual cycles of ammonium in most coastal and estuarine waters are controlled by terrigenous input. Sharp (1983) observed that terrigenous input often from sewage can affect ammonium concentrations and values can reach 20-25 µg at N L⁻¹ in open coastal waters (Thomas and Carsola, 1980) and mangrove ecosystems often receive such inputs from external sources.
Almost all the measurements of ammonium in mangroves show that the concentrations are very low and lie in narrow range from 0.1 to 7 µM. Studies on seasonal changes of ammonium concentrations by Dham et al., (2002) in the Achara estuary ranged from 0.1 to 1.5 µg at N l⁻¹ with an average value of 0.5 µg at N l⁻¹. Higher values in the premonsoon and a decrease through monsoon and post monsoon seasons was noted.

Lerat et al., (1990) observed that seasonal cycles in water column ammonium concentration were associated with phytoplankton development. A comparative plot of ammonium concentrations against chlorophyll a reveals a good correlation wherein increase in chlorophyll concentration were found with the increase in ammonium concentrations. The inference is that phytoplanktons are dependent on the availability of ammonium during the post monsoon season and they utilize it efficiently during this season. This is also evident from increase in concentrations of nitrate with the increase in ammonium concentrations through nitrification. Phytoplankton abundance, assimilation and nitrification result in the utilization of ammonium thereby decreasing in the concentrations of ammonium and enhancing the rates of these processes.

Lerat et al., (1990) reported the oxidation of soluble organic nitrogen as a major source of ammonium accumulation in the sediment pore water. This is effluxed back into the water column resulting in high concentration. Enhancement of ammonium levels is also attributed to the increase in organic matter in the non monsoon months leading to the ammonia production (ammonification) through degradation and also through remineralization.

The subsequent decrease would be due to its consumption by autotrophic and heterotrophic processes, since nitrate becomes less and less important as N source for phytoplankton in pre-monsoon and nitrification becomes progressively intense (Dham et al., 2002). Ammonium uptake rates were higher in the premonsoon season and were concentration dependent and were also related to chl a concentrations (Dham et al., 2002).
Urea

The importance of urea as a nitrogen source in the marine and freshwater environment after ammonium was demonstrated by McCarthy et al., (1977) for phytoplankton nutrition. Since then a large number of studies have also shown urea to be an important source of available nitrogen for phytoplankton in coastal and offshore waters especially during the periods of decreased nitrate levels. Microbial degradation of organic N compounds is a major source of urea in marine waters. The decomposition of organic matter is another factor that contributes significantly to the urea production from the sediments (Pedersen et al., 1993 a and b).

Heterogenous distribution of urea is seen in the present study and accounted for 19% of total nitrogen. Eppley et al., (1973) demonstrated that urea was as important as ammonium nitrogen source for assimilation by phytoplankton and excretion through zooplankton. Another important reason is due to its rapid turnover cycle 36 – 133 min (Therkildsen and Lomstein, 1994). Sources of urea include bacterial decomposition of organic matter. Another important source is excretion by organisms, terrestrial output from sewage outlets and freshwater discharge. In monsoon months all these process are at a low pace leading to decrease in urea concentrations. Also the monsoonal influence did not show very high concentration of urea leading to decrease in urea concentrations. The present observations therefore suggest that the regeneration play an important role in the fluxes of urea than input derived from external sources.

In mangroves, the supply of organic matter can come from varied sources – decomposing litter, wastes from organisms, high macrofaunal biomass, terrestrial inputs, and agricultural sources. Enhanced organic matter in the non monsoon months followed by increase in biological productivity and concomitant increase in biomass could have contributed a significant source of urea in the non monsoon months. Studies by Dham et al., (2002) in the same estuary reported urea concentration to range from 0.05-0.35 µg at N l⁻¹ and was similar to that of ammonium except the peak was in June instead of May.
The prominent feature in this study is the low concentrations of urea in the monsoon months and almost similar values in the non-monsoon months. Most of the urea production in the marine environment can be attributed to zooplankton excretion in the water column (Bidigere, 1983) or to macrofauna in both sediment and water column and flux of terrestrial origin (Remsen, 1971).

DON

In the present study, DON pool comprised of 30-32 % of water column TDN while river dominated estuaries often have substantial allochthonous inputs of DON (Meybeck 1982; Hopkinson 1998) the DON in this system appears to come from riverine input or allochthonous sources. The proportion of DON, DIN and urea remain relatively constant between sites, suggesting that the estuary is very well mixed. The input of DON to the water column from decomposing organic matter in the sediments and from living macroalgae on the sediment surface has important consequences for the metabolism of heterotrophs and autotrophs capable of DON uptake. Dissolved organic nitrogen makes up a large fraction of the total nitrogen in marine system (Sharp, 1983). Coastal systems receive inputs of DON from allochthonous sources (Meybeck 1982; Hopkinson 1998) including atmospheric deposition (Pearl 1995; Pearl 1990; Cornell 1995) and autochthonous production.

Some studies have shown DON to be an important component of the overall N flux (Lomstein et al., 1989; Enoksson 1993; Blackburn et al., 1996; Cowan & Boynton 1996) while others have shown that DON fluxes were either insignificant (Nixon 1981; Burdige & Zheng 1998) or only seasonally important (Boynton et al., 1980).

Billen (1984) reported three main sources of DON production in the sea 1) Due to extracellular release of dissolved organic matter by phytoplankton 2) Spontaneous lysis or spillage during zooplankton feeding 3) Excretion by zooplankton. Cornell (1995) reported that atmospheric input of DON is another factor, which contributes to the oceanic nitrogen input and forms a significant component of precipitation.
The concentrations of DON in the marine environment vary widely between surface, deep, coastal, oceanic and estuarine waters. DON concentrations in marine systems were measured earlier by Sharp (1983) and Antia (1991). Sharp (1983) listed values ranging from 3-7 µg at N l⁻¹ in oceanic waters to the very high values usually observed in coastal (3-20 µg at N l⁻¹) and estuarine (5-130 µg at N l⁻¹). Billen (1984) reported highest DON concentrations (105-200 µg at N l⁻¹) in the estuaries and constituted about 25-80% of total nitrogen as a function of season and represents both nitrogen and an energy source for heterotrophic microorganisms in the sea. DON values are correlated with the fluctuations of several biological processes that occur diurnally or seasonally due to close interdependence of micro and macro organisms (flora and fauna) in a system which either produce or utilize the compounds at various rates and at different molecular levels.

**Phosphate**

In the present study maximum phosphate concentrations occurred towards the mouth of the estuary and on seasonal basis in the monsoon period. Vertical gradient in phosphate showed temporal shifts. Suspended sediments in floods harbour phosphate and in summer, bacterial mineralization from sediments lead to release of phosphate into the overlying water. The mangrove sediments are reported to contain large amount of organic phosphorus. Hesse (1963) reported that organic phosphorus accounted for 75 – 80% of total phosphorus as complexes with humic acid and inorganic phosphorus is incorporated with hydrated iron. Sarala Devi et al., (1983) noticed 80-90% of phosphorus being trapped in sediment of estuaries. It is also known that the concentration of phosphate in polluted water was higher than the unpolluted.
Silicate

Silicate is used to build the skeletons of planktonic plants (diatoms) and animals (radiolarians). The silica secreted by organisms is an amorphous form and it is hydrated. After the organisms die or are consumed the skeletal debris sinks through the water column and slowly dissolves in deep waters giving concentrations profiles.

Silicate – silicon concentration exhibited bimodal oscillations, both peaks were encountered corresponding to monsoon and post monsoon seasons. Gradual seaward decrease coupled with higher monsoonal concentrations indicate that intrusion of silicate into the estuary mainly takes place through surface run off. Lowest silicate concentrations during premonsoon season suggest that biological utilization act as an important factor associated with removal of silicate from the medium. Similar instances of silicate depletion during premonsoon had also been reported from Vellar estuary and Cochin backwater. Silicate concentration showed marked seasonal patterns highest concentrations were accomplished by monsoonal drainage and lower levels coincided with the late pre-monsoon. A linear inverse relationship between salinity and silicate was apparent in the spatial distribution. Salinity stratification inversely influenced silicate distribution in the water column. Diatoms and silicoflagellates require it for the purpose of growth. During intense growth of diatoms, there is appreciable decline in the silicate content of water. Studies by (Heredia, 2000) revealed that diatoms constituted the major group of phytoplankton in the Achara estuary. The occurrence of Trichodesmium blooms appeared to be a recurring phenomenon in the month of May and may significantly increased the total phytoplankton cell counts. This resulted in the decrease in silicate concentrations in the pre monsoon season due to its utilization by the diatoms. The seasonal changes showed high cell counts in the pre and post monsoon seasons and lowest densities during the monsoon season. Highest concentrations were recorded at the mangrove station.
PON

PON is produced by phytoplankton in surface waters. It sinks out of the euphotic zone or usually enters marine food chain through zooplankton grazing. Heterotrophs convert the organic nitrogen from the fecal pellets and particles of dead plankton into inorganic nitrogen. This inorganic nitrogen can then serve once more as a nutrient for phytoplankton. Estuarine PON values have been reported to lie in range of 5-100 μg at N L⁻¹ (Haines, 1979). Morrel and Corredor (1993) calculated the overall mean fluxes through particulate organic matter input to the sedimentary environment as 789 μmol m⁻² h⁻¹.

Studies by Dham et al., found PON concentrations to be substantially higher in the monsoon (average 121.9 μmol N L⁻¹) than in the dry season (average 48.9 and 44.2 μmol N L⁻¹ respectively in the premonsoon and post monsoon months. Spatial gradient was highest at station 1 (in vicinity of mangrove vegetation) and decreased towards the seaward end. These results are in consistence with the results obtained here.
Sediment exchanges

The movement of solutes in sediment has been attributed to a vertical diffusion phenomenon (Blackburn et al., 1994; Glud et al., 1994; Thamdrup et al., 1994b; Rysgaard and Berg 1996). Vertical diffusion can be separated into two contributions: molecular diffusion and bioturbation (that is diffusion like transport caused by random movements of meiofauna). Other studies have shown that irrigation (that is the pumping activity of tube dwelling animals) can significantly influence the transport of solutes in sediments (Aller 1983; Pelegri et al., 1994; Wand and Van Cappellen 1996). The source of nutrients for primary production in the estuarine water column is often strongly linked to the sediments (Nixon 1981; Caffrey 1995; Cloern 1996) For example, in the Potomac River estuary and Naragansett, Chesapeake and Port Phillip Bays, benthic fluxes of ammonium can provide a large part of the phytoplankton N requirements. (Callender and Hammond 1982; Kemp et al., 1982). Studies by Welsh et al., (2000) in Zostera noltii meadow have found that though the water column DIN concentrations were low fluxes of DIN, nitrate and ammonium were large and always directed into the sediment compartment throughout the year.

The release of nutrients from sediments is affected by several factors, including oxygen condition, bioturbation, temperature and pH (Bostrom et al., 1988).

Macrofauna probably contributed to nutrient release in the present study. In the present study oxygen depletion was probably unimportant for nutrient mobilization, since the water column was always oxic.

A high temperature promotes nutrient release from sediment (Aller and Benninger 1981; Jensen and Andersen 1992) primarily due to its intensifying effects on chemical reactions and biological activity.
Oxygen production by benthic microalgae may increase the oxygen penetration into the sediment by several mm (Revsbech and Robinson, 1983) and thereby influence sediment metabolism as well as the turnover and flux of nutrients on both diurnal and seasonal basis (Sundback 1986; Sundback and Graneli 1988; Risgaard and Petersen et al., 1994).

Denitrification is the predominant microbial degradation process occurring in sediment and generally occurs within the top 2 cm (Mortimer 1998). Nitrification is also significant process taking place at the sediment water interface. High rates of nitrification associated with the suspended particles in the high turbidity zone (Barnes and Owens, 1998) produce the high concentration of nitrate, which in turn sustain high rates of denitrification.

Nutrient fluxes are strongly influenced by the dynamic nature of the estuary. Sediment mixing and resuspension processes are key controls on fluxes together with an enhancement of bioirrigation by macrofauna during periods of mudflat stability.

Calculations by Mortimer (1998) suggest that sediment water exchange is an important process for nitrate and ammonia with the sediments acting as a sink for nitrate, a source of ammonia and hence an overall sink of DIN. However this calculation is at odds with calculation of Sanders et al., (1997) who suggest that the estuary is large sink of ammonia and minor source of nitrate and hence a minor sink of DIN.

**pH**

Differences in the pH between different depths did not reveal much variation that reflects the presence of organic matter and its decomposition products at a given depth. Low pH was recorded in the monsoon and premonsoon and high in the postmonsoon season.
Chlorophyll a

Spatial and temporal variations of the concentrations of phytoplankton pigments followed the patterns found in the water column. The concentrations of all pigments were highest at station 3 due to the presence of the dense mangrove vegetation at this station, high nutrient and favorable light conditions. High values were observed during the non monsoon months (postmonsoon) and low values in the monsoon season. High nutrient concentrations (nitrate and silicate) in the monsoon led to an increase in chlorophyll concentrations in the subsequent season (postmonsoon months). The presence of this station at upstream end and low salinity could have led to decrease in turbidity and high light penetrations and also the chlorophyll derived from terrestrial vegetation (leaves) may have led to increase in the chlorophyll concentrations.

Nitrite

Highest concentrations of nitrite were found at station 3 (upstream end). Concentrations were high mainly due to allochthonous sources in the monsoon months and in situ regenerations in the non monsoon months. Measured nitrite fluxes were highly variable and larger than recorded at other sites (Mortimer, 1998). Nitrite is an intermediate in both nitrification and denitrification and therefore fluxes are difficult to interpret, particularly since these processes are closely coupled in marine sediments (Jenkins and Kemp, 1984). High nitrite influxes associated with high nitrate effluxes are indicative of net nitrite consumption by nitrification whereas high nitrite influx associated with high nitrate efflux reflects net nitrite consumption by denitrification (Hall et al., 1996). Both of these processes are seen in Humber estuary.
Nitrate

The initial high nitrate concentration increase in premonsoon accompanied by an increase in phytoplankton biomass as indicated by chlorophyll a concentrations of April and May revealed that favourable conditions such as high nutrient concentrations led to an increase in the phytoplankton biomass and in turn productivity of the system.

Seasonal changes showed relatively higher concentrations during premonsoon. This could be due to in situ nitrification. The high temperature prevailing at this time are conducive for an increased diffusion of oxygen into sediments that, along with a high availability of ammonium as substrate (Figure.20) in the preceding months, could have strongly favoured nitrification. Earlier studies using stable isotopes (Dham, 2000) on the nitrification in sediments at the present study site showed that nitrification increases steadily in postmonsoon to a seasonal maximum in premonsoon. The high concentrations during monsoon would have been caused by percolation of overlying water into the sediments, thereby increasing the concentrations in sediments. At this time of the year, river transport, rather than in situ nitrification, is responsible for changes of nitrate in the sediments. There was no difference in nitrate concentrations with depth (Rivera Monroy, 1995). Similar observations were recorded here in the present study.

Nitrate profile show elevated concentrations at or just below the sediment water interface indicative of nitrification (Kemp et al., 1990). There is depletion in the lower layers of the sediment as nitrate is removed by denitrification. There were no differences in nitrate concentration with depth and did not show any pattern. Similar observations were recorded by Kemp et al., (1990).
Ammonium

Ammonia profile in sediments showed a characteristic increase with depth this is due to build up of ammonia as a result of remineralization process (San Diego, 1995). Similar results were obtained in the present study. The regenerative release of nutrients and hydrogen sulphide in the sediments bring about an increase in their pore water concentrations. Studies have shown that the sediments can be important source of nutrients to the water column and could perhaps maintain productivity (Elder field et al., 1981; Berelson et al., 1987). Consequently concentration gradients are established in the sediment water interface leading to diffusion of these products from the sediment into the overlying water column. The flux across the sediment water interface of a constituent dissolved in sediment porewaters is primarily controlled by diffusion across the interface (Klump and Martens, 1981).

Urea

Urea was an important component of the sediment N flux comprising 36-70% in Northern Bering shelf sediment (Urea+NO_3^-+NH_4^++ NO_2 Lomstein, 1989) and approximately 30 % in the Bay of Pampoul, France (Urea+NH_4^+, Boucher & Boucher- Rodoni, 1988).

In the present study higher concentrations were recorded during premonsoon at all stations, with the peak value at station 2. The concentrations at all the stations varied within a narrow range but showed significant decrease during monsoon months. High concentrations in the premonsoon months may be due to high chlorophyll values in these months, which have led to increase in zooplankton biomass. Since urea concentrations are influenced by excretion from zooplankton the concentrations may have increased in the premonsoon season at all the stations.
DON

Few studies have examined sediment fluxes of DON. The magnitude of sediment nutrient fluxes is generally related to the magnitude of primary production in the system, as primary production is the source of organic matter to the sediments (Nixon 1981). Nutrients regenerated in the sediments and released to the water column are thought to support a significant portion of primary production in coastal ecosystems. Concentrations of DON ranged from 0.5 to 22.3 μg at N l⁻¹ (Figure 38). Highest concentrations were observed during late postmonsoon and early premonsoon at all stations due to its non-utilization and production. DON concentrations may also be influenced by the coastal processes like river run off and ground water discharge. Also due the presence of high amounts humic compounds in the mangrove areas that contribute significantly to the dissolved organic matter thereby increasing the concentrations of DON.

Phosphate

Concentration of phosphate ranged from 0 to 3.07 μg at P l⁻¹ with high concentrations in postmonsoons at station 2. Peak values occurred in the month of October (post monsoon) at station 1 and 2 and they decreased later on though pre-monsoon to monsoon. The values reached to almost trace levels in the monsoon months at all stations except for a slight increase from August to September at station 1. The concentrations at station 3 were low compared with those of stations 1 and 2. A high pH in the water column, especially a pH of 9 or more, is frequently mentioned as a factor increasing the P flux from the sediment. Such pH levels usually result from intensive photosynthesis in eutrophic conditions. With a decrease in pH and redox potential in surficial sediment relative to overlying bottom water the solubility of basic iron phosphate phases should increase. This would explain the rapid increase of interstitial orthophosphate concentrations.
In experiment with wastewater addition to mangrove sediment (Tam and Wong; 1995; 1996) found a high retention of phosphate in the sediment. They discharged sewage in a mangrove area and observed that 85% of added P was retained. Adsorption maxima in the range 250-700 µg P g⁻¹ dw of sediment was reported by Clough et al., (1983) for several mangrove sediments of Australia. The large adsorption of P may be due to the very high silt and clay content (79-91%). Alongi (1992) pointed out that clay such as kaolinite which is abundant in tropical sediments are very efficient in P adsorption. In the upper 5 cm when the conditions are oxic the phosphate is sorbed onto iron oxides and pore water concentrations are low (Mortimer 1998). Below this depth where conditions become sub oxic (- ve Eh) the iron oxides are reduced releasing phosphate into the pore water. Hence the decrease in concentrations of phosphate at stations 3 where the sediment is dominated by silt and clay (5-23 %) that result in adsorption on to the sediment. This leads to decrease in phosphate concentrations.

Phosphate is released during the decomposition of organic matter in aquatic sediments. Phosphate release from the sediments is generally controlled by sulfate reduction in marine sediments (Caroco et al 1989) as sulfide produced from sulphate respiration may reduce the iron oxides in the sediment and thus promote a release of iron bound phosphorous (Jensen et al., 1995, Howarth 1995). Low DIP concentrations may be due to a combination of low P content of detritus and high C: P and subsequently bacterial uptake during decompostion. A relatively low sulphide concentration leading to low release of iron bound phosphate due to iron sulphide formation and effective P sorption.
Studies by Doering et al., (1995) indicated that phosphorous was limiting in 0, 5, 10 ppt salinities while nitrogen was limiting at 25 ppt. This indicates that the concentrations of phosphate were high at higher salinities and that of nitrogen were high at lower salinities. The data presented here supports this concept. Howarth (1988) identified 3 major factors 1) which control whether N or P is more likely to be pellets, or adsorption of P. 2). The extent to which any relative deficit in N availability is made up through N fixation and 3) the ratio of N to P in external inputs.

**Silicate**

Seasonally the concentrations decreased through postmonsoon to lowest levels in monsoon at station 1 but increased at station 2 and 3 (upstream). The high concentrations at the upstream end in the monsoon months in the water column could have led to an increase in the silicate concentrations mainly due to percolation of silicate from the water column to the sediment.

**PON**

PON concentrations (Figure. 41) were high during monsoon with the highest concentration at station 3. The concentration of PON ranged from 0 to 2.42 mg N (g sediment)^{-1} and decreased through postmonsoon to premonsoon. High amount of litterfall and chlorophyll in the premonsoon have led to an increase in PON concentrations in the monsoon months. Besides phytoplankton production also decomposition and remineralization of DON play a major role in determining the PON pool. Phytoplankton dependent PON production was observed in the present study. To conclude PON production is solely dependent on the primary producers as shown from the seasonal study and the production of new nitrogen in the monsoon months and also on the insitu process of regeneration within the system.
Possible factors that may explain within and between variability in the marine systems Alongi (1998) proposed that

- In tropical sediments the nutrient turnover is faster.
- Many nutrients are tied up in microbial and tree biomass in mangrove forest.
- Tropical sediments are more weathered and leached with respect to nutrients than temperate marsh sediments.

The relatively high bacterial biomass and productivity in mangrove sediments (Alongi 1988) is responsible for a dynamic turnover of the limited inorganic N pool, implying a tight coupling between microbial mineralization and assimilation (Alongi 1988; 1996; Rivera Monroy, 1995; Kristensen 1998). This is evident from the low pore water concentration and the low net production rates of ammonium.
Fluxes at Mangrove – Seawater Interface

Whether or not nutrients and dissolved and particulate matter are exported from mangrove creeks has attracted strong attention but remains to be difficult question to resolve (Twilley, 1985; Boto and Wellington 1988; Wattayakorn et al., 1990; Moran et al., 1991; Simpson et al., 1997). This is often ascribed to methodological difficulties associated with flux measurements. Efforts are being made to improve the reliability (Kjerfve et al., 1981; Boto and Wellington 1988; Simpson et al., 1997). However more attention needs to be drawn towards the fact that one mangrove creek is vastly different from another in terms of hydrology, tidal range, geomorphology, soil chemistry, mangrove plant biomass and community structure and so on. Any of these characteristics probably have a certain effect on the direction and magnitude of material fluxes in mangrove creeks. This needs to be further studied for a clearer picture.

Similar studies were conducted by Simpson et al., (1997) wherein they measured current speed, temperature, salinity and concentration of nutrients at intervals of one lunar hour over 31 tidal cycles at 4 stations across the section of the lower Sungai Merbok estuary in Malaysia wherein they obtained a large variability of flux estimates. Boto and Wellington (1988) studied the seasonal variations in fluxes of nutrients and dissolved organic matter in Coral creek using the Eulerian method and concluded that the system is in a finely balanced state. They were able to detect a statistically significant difference in fluxes of nitrate, phosphate and DOC between ebb and flood periods. However, there was no consistency in direction and magnitude of fluxes of any particular property and when summed over a full year the net flux was negligible. Fluxes of nitrate and phosphate in Coral creek are within the range of flux estimates reported by Boto and Wellington (1988) —5.8 to 13 kg N d\(^{-1}\) vs —4.2 to 9.1 kg N d\(^{-1}\) and 0.3 to 2.4 kg P d\(^{-1}\) vs —3.1 to 10.2 kg P d\(^{-1}\).
Boto and Wellington (1988) and Robertson et al., (1992) suggested that the presence and absence of freshwater inputs might have a strong influence on the results of flux measurements. This study supports Boto and Wellington's view that mangrove forests in the Hinchinbrook area are inclined to conserve nitrogen and phosphorous. They have pointed out that mangrove forests in the area are limited by the availability of N and P (Boto and Wellington 1983). There is also evidence that mangrove sediments in the area are sink rather than a source of N and P (Alongi 1996). Studies by Tensh Ayukai et al., (1998) suggested that the direction and magnitude of the fluxes of nutrients and dissolved and particulate organic matter could vary considerably between samplings or over time. However, further studies are required to elucidate factors or processes causing such variability. Attempts should be made to fully resolve the variations in concentrations of nutrients along mangrove creeks.

In the present study on the fluxes between mangroves and coastal waters the net transport of nitrate was from mangroves to sea in premonsoon and monsoon seasons and from sea to mangroves during postmonsoon season. The overall dominant transport was from mangroves to sea. The main source for this transport could be attributed to the freshwater flow in monsoon months. The mangrove water and sediment are the sites of high nitrate concentrations during these months that has resulted in the transport of nitrate from mangroves to the sites where their concentrations are low (sea water). Besides these intense nitrification in premonsoon months, explains the seaward transport in premonsoon. Import of nitrate in postmonsoon might be related to the asymmetry between flood and ebb tides. Net daily fluxes of nitrate were completely ebb dominated. Highest net nitrate transport was during the monsoon months (June and July, 7300-7600 mmoles/6h) due to high fresh water flow and precipitation. The values decreased during the postmonsoon and increased again in the premonsoon period. The nitrate transported was about 23 times higher in magnitude to that of nitrite in the monsoon.
Nitrite
Net transport of nitrite was seaward during pre-monsoon months. However, import of nitrate into the mangroves in monsoon and post-monsoon months. Highest transport in the monsoon months indicates that fresh water sources and addition of rain water were the major contributors for the nitrite concentrations rather than insitu nitrification.

Ammonium
Net transport of ammonium was mainly from mangroves to the seaward end since the mangroves are the sites of intense regeneration the high concentrations in the mangrove dominated areas led to the transport of ammonium from the mangrove to the sea, Net fluxes of ammonium were ebb dominated. Since this is the first product of decomposition the export of ammonium is quite natural. Besides the presence of large amount of mangrove litter, and the concentrations of ammonium were generally higher within the mangroves due to decomposition of organic matter and production of ammonium through ammonification. Export was variable between seasons with high in the premonsoon months and decreasing from monsoon to lowest values in the postmonsoon season.

Urea
Transport of urea was seaward. Highest transport was recorded during the premonsoon season and decreased from monsoon to lowest values in the postmonsoon months. Urea transport was from mangroves to the sea in the monsoon and the post monsoon season that is it was ebb directed due to high concentration in these months. chlorophyll a concentrations were high in the premonsoon months based on the seasonal studies which may have led to increase in the zooplankton biomass in the subsequent season. Increase in zooplankton biomass may have led to increase in urea concentrations mainly due to the excretory products of these organisms. In the premonsoon months it was flood directed (February and April) while ebb directed in (March and May)
DON
Net transport of DON was highly variable it was either seawards or towards the mangroves since the concentrations of DON was high in seawater than the mangrove waters. In the early premonsoon (February- March) the fluxes were mainly flood directed and in the late premonsoon (April – May) ebb directed. Fluxes were variable in the monsoon months and in the postmonsoon fluxes were ebb directed. Highest DON transport was recorded during the monsoon period and decreasing in the post monsoon months to attain high values in the premonsoon season.

Phosphate
The import and export of phosphate from the mangrove ecosystem was balanced during the pre monsoon. During other periods, however, there was a net import into the mangrove ecosystem. Highest fluxes were recorded during the monsoon season and decreased from postmonsoon to lowest values in the monsoon months. The impact of exported P from land sources to adjacent coastal water may be reduced due to the adsorptive capabilities of the mangrove sediment. P resulted in net export during the monsoon months.

Silicate
There was a net transport of silicate to the sea in the monsoon months due to increased freshwater input and precipitation. During non monsoon the import and export remain balanced, due to the decreased influence of freshwater-advected silicate. In the pre-monsoon months (February, March and May) the mangroves imported silicate.
PON

PON was high during the flood tide and low during the ebb in the premonsoon season. In the monsoon they were high at the ebb tide indicating possible sources of PON from the terrigenous input along with the precipitation during the monsoon season resulting in increased concentrations during this season. In the post monsoon season they did not follow pattern and varied. The transport was from the mangroves to the sea.

Results on transport obtained here are consistent with the findings of Tenshi Ayukai et al., 1998 and concluded that the concentrations of silicate and DOC were consistently higher upstream than downstream. The concentrations of Nitrate and POC also decreased from upstream to downstream while that of phosphate was higher downstream than upstream. These results suggested that Silicate and DOC are usually exported to adjacent coastal waters whereas the import and export of nitrate, phosphate and POC are often finely balanced. Net fluxes were ebb directed, for most of the nutrients. Increased concentrations on ebb tides and in lower salinity waters are indicative of river input. Increased Nitrite + Nitrate during high river input has been well documented by previous investigators (Caffrey 1986; Childers and Day 1990; Day et al., 1994; Madden 1996; 1992). High river discharge led to high amounts of freshwater input to the estuary which was one of the major factor in determining high nutrient concentrations and strong ebb directed fluxes.

During flood there was a decrease in concentration of nutrients (except for phosphate) as the coastal water entered the estuary. On the other hand during the ebb tide an increase of freshwater contribution to the estuary was noted resulting in the increase in all nitrogen nutrient and silicate concentrations. The other predominant form of DIN was NH$_4$ related mainly to fluvial inflow and may be directly related to the biological activity and decomposition of organic matter.
Concentrations varied with changes in tide height and concentrations were directly proportional to the volume of water transported. The concentrations and fluxes of dissolved and particulate components is influenced by the tidal action and also effects from terrestrial run–off, ground water input and atmospheric inputs. Studies in the Humber and Thames estuaries (Sanders et al., 1997) have shown considerable seasonality in the riverine flux of water into the southern North Sea with highest water flows in winter resulting in highest nutrient fluxes. The pattern of higher DIN concentrations in estuaries with increasing freshwater input as well greater DIN concentrations in the upper estuary compared with the lower estuary is well documented. (Ven Beusekom and De Jonge, 1998) The extremely low concentrations are due to the increase in residence time of freshwater in the bay that allows greater rates of biological uptake and denitrification.

Phosphate concentrations were low and relatively constant throughout the study. Phosphate concentrations were somewhat higher during periods of strong marine influence but elevated concentrations at other times suggest benthic remineralization (Twilley et al., 1999). Phosphate sorption desorption reactions with clay and organic particles have been recognized as buffering mechanisms in estuarine environments (Lebo and Sharp 1992; Sharp et al., 1982) and are likely processes regulating the temporal stability of phosphate concentrations. Phosphate concentrations import occurred more often during April likely due to increased metabolic activity with higher water temperatures and regeneration.

There is a need to understand the factors controlling N retention because small changes in retention can lead to large changes in N export (Caraco and others 2003), potentially intensifying coastal eutrophication problems associated with N enrichment. Denitrification provides a sink in the global nitrogen budget and thereby plays an important part in controlling the degree of eutrophication in waters subjected to substantial anthropogenic input of nutrients. Denitrification in estuarine sediments thus decrease the transport of nitrogen from land to the open sea (Seitzinger 1988). The process may be supported by nitrate diffusing
from overlying water column into the sediment or nitrate being produced within
sediment by nitrification (Vanderborght & Billen 1975, Nishio et al., 1983; Jenkins
and Kemp 1984). Most of the denitrification studies have focused on direct
denitrification to understand the potential use of mangroves as a natural tertiary
treatment of wastewater (Nedwell 1975; Corredor and Morell 1994). Corredor
and Morell (1994) concluded that sediments in a fringe mangrove in Puerto Rico
receiving secondarily treated sewage effluent were capable of denitrifying up to
15 times the normal nitrate concentrations (200 to 1000 μM). Denitrification, the
dissimilatory reduction of nitrate to produce N₂O and nitrogen was considered the
process that contributed to nitrate loss in these studies. Denitrification may be
an important process that regulates nitrogen flux at the mangrove estuary
boundary. Boto and Wellington (1988) reported that nitrate was actually
exported from mangroves, indicating a source of inorganic nitrogen to coastal
waters. In particular it is not clear how coupled nitrogen transformations within
the forest influence the exchange of nitrogen at the boundary of mangrove with
coastal waters. Denitrification may be an important process that regulates
nitrogen flux at the mangrove estuary boundary (Twilley 1988) and is primarily
dependent upon anoxic conditions, the presence of energy source and
availability of nitrate substrate (Mosier and Schmiel, 1993). Depending on nitrate
source there are two types of denitrification 1) that is fueled by nitrate that
diffuses into the sediment while coupled denitrification is supported by nitrate
produced by nitrification in sediments. (Jenkins and Kemp 1984; Henriksen and
Kemp 1988). However direct denitrification rates were lower in sediment from an
unpolluted mangrove tidal channel in Australia (Lizumi, 1986) and represented
minor loss of nitrogen from the ecosystem (Alongi et al., 1992) Boto and
Wellington 1988 reported that nitrate was actually exported from this system
indicating a source of inorganic nitrogen to coastal waters.
**Fluxes at sediment water interface**

Denitrification is a significant pathway of nitrite and nitrate loss as well as uptake by phytoplankton. Smith, DeLaune and Patrick estimated that approximately 50% of annual nitrate entering the bay was lost via denitrification. They also suggested potential losses via dissimilatory reduction to ammonium since denitrification rates in the sediment did not account for all of the nitrogen lost.

Similar rates of N loss have been calculated for other estuarine systems (19% Van beusekom and De Jong, 1998) Chesapeake Bay (26% Nixon et al., 1996) Narrangsett Bay (13-27% Nixon et al., 1996) and the Potomac (16% Nixon et al., 1996).

Another potential important N loss is via burial and uptake in adjacent marshes and sedimentation on bay bottoms (De Laune 1981; Smith 1985). Several recent publications have reported that a high proportion of nitrate can be lost via denitrification when residence time are long (Nixon et al., 1996; Seitzenger 2000).

In the present study on fluxes at sediment water interface the fluxes of nitrite and nitrate were predominantly small and negative. The concentrations of these nutrients decreased as the period of incubation increased. This reflects that the decrease is mainly attributed due to denitrification that is loss of nitrogen in the gaseous form using nitrate as a substrate and anoxic conditions and temperature dependence (Hansen, 1981). There was a much larger influx of ammonia that is the fluxes were positive and the concentrations of ammonium increased initially since the mangrove sediments are the sites of intense regeneration where the ammonium concentrations are high due to ammonification. More ammonia was produced by suboxic to anoxic degradation of organic matter and effluxes are enhanced by active bioirrigation (Davey, 1994). The favorable temperature probably contributed to nutrient release in the present experiment.
A probable explanation for the decrease in ammonium after the two hour incubation was due to slow renewal from organic and inorganic sediment particles into the porewater. Contributing to the NH₄ loss may have been coupled nitrification denitrification, its role, however, is hard to evaluate, since it has been found to vary considerably in shallow-water sediments (Sundback and Miles, 2000; Risgaard-Petersen, 2003).

In earlier study on a mangrove ecosystem on the central west coast of India at the same study site Achara (Wafar et al., 1997) a model for prediction of litter fall was constructed and elemental flux as C, N and P from mangrove vegetation to the aquatic food chain was quantified. Their study also showed that most of the terrestrial production ends up in mangrove waters. While this was important for sustaining the microbial food chain and nutrient regeneration in the water column and was inadequate for the nitrogen budget of the water column. The regeneration of nitrogenous nutrients is well known to be a major source of nitrogen for oceanic primary producers to phytoplankton.

Nutrients regenerated in the sediments and released to the water column are thought to support a significant portion of primary production in coastal ecosystems (eg Nixon 1981; Fisher et al., 1982; Koop et al., 1990; Cowan & Boynton, 1996). The flux of nutrients from sediments is generally thought to be proportional to the amount of organic matter delivered to the sediment surface (Nixon 1981). Kelly and Nixon (1984) and Kelly (1985) demonstrated a positive relationship between sediment nutrient regeneration and primary production in experimental mesocosms and many others have reported increases in sediment DIN, DON and/or urea fluxes with the addition of organic material to the sediment surface both insitu (Jensen et al., 1990) and experimentally (Enoksson 1993; Sloth et al 1995; Therkildsen et al., 1996).
DOM plays a pivotal role in the ecological structure of aquatic ecosystems (Hessen and Tranvik, 1998; Findlay and Sinsabaugh 2003). The presence of DOM can influence microbial growth, light penetration, the complexation of metals and the availability of nutrients (Tranvik 1992; Scully and Lean 1994; Morris et al., 1995; Tranvik, 1998; Lu and Jaffe 2001; Qualls and Richardson 2003). Coastal marine systems may subsequently receive significant quantities of allochthonous DOM from wetlands via river discharge. (Kattner 1999; Miller 1999). Leaf litter organic matter export from mangrove forests may also greatly influence DOM cycling in estuaries (Del Castillo et al., 2000; Dittmar et al., 2001).

Accumulation of silicate in the pore water at a depth is from dissolution of siliceous material. The concentrations of silicate are low and vary little with depth (Mortimer et al., 1998). This is due to a combination of resetting of the pore water by sediment mixing and resuspension and low rates of silica dissolution due to low temperatures. Higher temperatures cause an increase in silica dissolution resulting in higher pore waters. Fluxes of silicate were normally assumed to be straightforward with release due to dissolution of siliceous material, controlled by temperature (Hammond et al., 1985) and limited uptake by phytoplankton. The rate of release was 2-5 times higher.

Resuspension of the sediment and altering the adsorption desorption state of iron oxides and clays is more likely to have played an important role. Silicate uptake by sorption onto clays has been demonstrated by Macekenzie et al., (1967) and Siever and Woodford (1973) and may be analogous to removal of Al by formation odd authigenic aluminosilicates reported by Mackin and Aller (1984). Removal of silicate by sorption onto iron oxides has been reported by several groups (Mayer et al., 1991; Michalopoulos and Aller 1995).

The flux of nitrate was generally directed into the sediment this being attributable to benthic assimilation in the surface layers and denitrification in the deeper sediment layers (Rysgaard et al., 1995) and concluded that benthic microalgae may have a strong regulating effect on the efflux of nutrients from the sediment.
surface to the overlying water in shallow estuarine waters. During summer when
the water column concentrations of nitrate and ammonium is low there is strong
competition for inorganic nitrogen between benthic microalgae, nitrifiers and
denitrifiers.

The results indicate that sediments have essential effects on nutrient dynamics
and contribute to eutrophication in shallow and littoral coastal areas, even where
the content of organic matter in the sediment is low and oxygen conditions in the
near-bottom water are good.

Lower temperatures suppress the activity of denitrifiers to a greater extent than
nitrifiers (Hansen et al., 1981) resulting in net nitrification and hence a positive
flux. Since the sediment was oxic to a greater depth it promoted nitrification and
inhibited denitrification.

The flux of nitrate was generally attributable to benthic assimilation in the surface
layers and denitrification in the deeper sediment layers. Assimilation of inorganic
nutrients by the benthic microalgae also influenced the PO₄ flux a lower flux
being observed in light than in dark incubated sediment. The phosphate flux into
the sediment during winter was most likely due to binding of phosphate to
oxidized iron which is more abundant within the sediment during the cold season.
The competition between nitrifiers and benthic microalgae for inorganic nitrogen
in the overlying water and within the sediment is of major importance when
evaluating the effect of benthic photosynthesis on nitrogen processes.

It is clear from our results that one or more processes are operating in the
Achara estuary to enhance the effect of denitrification on benthic exchange. The
largest flux enhancement was observed in the case of nitrate and may be
attributed to denitrification.
The decrease in water column concentration of nitrate at the sediment water interface may be due to either assimilatory or dissimilatory denitrification. Nitrate fluxes are generally considered to be an indication of denitrification when the direction of flux is from water column to the sediment and nitrification when the direction of flux is from sediment to water column.

The flux of nitrate exceeded the flux of ammonium by approximately one order of magnitude. On this basis it would appear that there was a net loss of inorganic nitrogen from the water column to the sediment. Denitrification was suggested an important process in these sediments.

Studies on nutrient fluxes and processes occurring at the sediment water interface in Australian estuaries and coastal waterways by Heggie et al (2002) have shown that coupled sedimentary nitrification and denitrification are important processes controlling the concentrations distributions and speciation of nitrogen in pore waters and fluxes to overlying waters. High denitrification was recorded when organic carbon loadings are below about 40 mmol m$^{-2}$ day$^{-1}$. Also oxic to suboxic conditions in near surface sediments maintain high denitrification and these conditions are effective in trapping of phosphate in interfacial sediment. Heggie et al., (2002) also suggested that bioirrigation processes in sediments rather than diffusion drive benthic nutrient fluxes. Denitrification from NO$_3$ diffusing into the sediments may act as a buffering mechanism for high NO$_3$ loading from rivers (Trimmer et al., 1998).

A mass balance approach can be used to evaluate our present understanding of the functions of mangroves in the productivity and nutrient cycling of coastal ecosystems. The coupling of mangroves to estuarine and coastal waters involves exchange across the mangrove – estuary boundary followed by transport from the estuary to coastal waters, tides and run off control the exchange of materials across the boundaries of mangrove estuarine ecosystem.
Export from mangroves may also be associated with the amount of hydrologic energy within the intertidal zone. Rate of transport was dependent on the volume of tidal water inundating the forest each month and accordingly export rates were seasonal in response to seasonal rise in mean sea level (Twilley, 1985).

Processes involving the exchange of materials from mangroves vary among tropical estuaries depending on hydrologic energy (tides and/or runoff) and geomorphology. Hydrologic energy influences the per area productivity and flux of materials in mangroves and together with geomorphology these two factors also determine the areal extent of mangroves surrounding an estuary. The importance of this total flux of detritus from mangroves to the organic matter budget of estuarine ecosystems depends on the relative size of both systems.

More studies on mangroves are needed that represent sites with different hydrologic energies and geomorphology. There are many processes that need to be studied before generalization of mangrove functions can be made. Studies on the importance of nitrogen fixation, denitrification, fertilization, sedimentation and exchange on nutrient budgets would greatly expand our understanding of nutrient dynamics in mangrove ecosystems and processes associated with these transformations may be important in understanding this function.
Conclusions

The aim of this study was to assess the relative importance and quantify the rates of nitrogen flux in space and time at Achara estuary. Fluxes at different interfaces, which include mangrove-seawater interface and sediment - water interface, were studied. The specific objectives were

1. To study the spatial and temporal variations of ambient particulate and dissolved nutrient concentrations.

2. To measure the fluxes of nutrients due to coastal waters, and

3. To measure the fluxes at water-sediment interface.

- The dissolved inorganic and organic nitrogen concentrations showed significant spatial and temporal variations among all the three seasons and between monsoonal and non monsoonal months.

- Seasonal changes of conservative nutrients (nitrite, nitrate, phosphate and silicate) reflect the hydrographic changes. During monsoon, transport of these nutrients is at the maximum, about 1 to 2 orders of magnitude higher than in non-monsoon months.

- The high concentration of nitrate in rainwater reveals that this could be an important source of new nitrogen to the ecosystem.

- Nitrate was the major form of nitrogen available in the water column at any time, followed by ammonium, urea and nitrite. (Nitrate range from 51% to 75%, Ammonium range from 17% to 29 %, Urea from 7% to 19% and Nitrite ranged from 1.5% to 5.4%)

- The waters of the study area were well oxygenated throughout the year, except for the beginning of postmonsoon, when there was a slight undersaturation at all stations. This could perhaps be explained by the transition from freshwater to marine conditions (low solubility of oxygen) and low levels of primary production (low chlorophyll-a concentrations).
In spite of the nearly uniform marine conditions in non-monsoon months, seasonal changes of nutrients were marked. This suggests that in-situ biological processes are important in controlling their dynamics.

The concentrations of phosphate are dependent on grain size indicating that the clayey sediment at station 3 resulted in the adsorption of phosphate thereby decreasing in their concentration whereas, the sandy soil at station 1 had high concentrations. Based on these studies it is concluded that the physical properties of the sediment may influence the water column concentrations besides the biological ones.

As expected with any productive ecosystem, concentrations of DON were high, up to 45 μmol l\(^{-1}\). Even though fluctuations in its concentrations were high within the seasonal cycle, some patterns could still be recognized. Higher concentrations at the beginning of the monsoon could be related to washing off of organic nitrogen from the drainage basin by the first rains and their transport into the estuary. The second instance of high concentrations at the end of the post-monsoon follows chlorophyll a peaks at the beginning of the post-monsoon and suggests that high DON concentration may owe the origin to decomposition of POM; time intervals of several weeks between the decline of chlorophyll and increase in DON have also been reported.

While river transport is a major source of nitrate to these waters in monsoon, in situ nitrification is important in non-monsoon months. This is evident from the successive high concentrations of DON in December - January, ammonium in January - February and nitrate in March - April. Accumulation of nitrate was not well marked, possibly because oxidation of ammonia and nitrate remained in balance.

Changes of the concentrations of silicate showed a monsoon high, especially at stations 2 and 3, suggesting that percolation of silicate-rich freshwater into the sediments increases silicate concentrations in the pore waters.
Unlike with other conservative nutrients, concentrations of phosphate in the interstitial water in the monsoon were low, possibly because of desorption from the sediments.

The similarity in the changes of the concentrations of DON and ammonium suggest that remineralization of DON in premonsoon and postmonsoon is a major source of ammonium to these waters.

Presence of all nitrogenous nutrients in measurable concentrations at anytime suggests that the ecosystem processes are not nitrogen-controlled. High concentrations of nitrate in the monsoon and those of ammonium in the post and premonsoon seasons represent a continuous supply of N to the estuary making it highly productive.

Fluxes between water and sediment were found to exchange nitrate and nitrite from water column to sediment. While the exchange of ammonium was from sediment to water column in the post monsoon period and water column to sediment in the monsoon and the pre monsoon season.

Studies on fluxes at water sediment interface reveal the study site to be a sink for nitrate, nitrite and a source of ammonium. As sediments in general are sites of nitrogen regeneration and have expected to flux nitrate, into the water column, the decrease in nitrate could be due to denitrification. Nitrate flux was negative for sediment dominated by silts and clays (that is into the sediment). These sediments are the best sites for the loss of nitrogen through denitrification. This could be useful in removal of excess nitrogen thereby preventing eutrophication.

The rate of loss of nitrite was from an initial concentration of 0.3 to 0.06 at the end of the 6h incubation period.

Ammonium concentrations increased indicating that mangrove sediments were a source of ammonium.
Net transport of nitrate was from mangroves to sea in premonsoon and monsoon seasons whereas it was from sea to mangroves during postmonsoon season. The overall dominant transport was from mangroves to sea. Freshwater flow would have been responsible for the seaward transport in monsoon months. The mangrove water and sediment are also zones of intense nitrification in premonsoon months, which could explain the seaward transport in premonsoon.

Net transport of nitrite was seaward during premonsoon months. Highest transport was recorded in the month of July in the monsoon months indicating fresh water supply as the major contributor for the nitrite concentrations rather than insitu nitrification.

Net transport of ammonium was mainly seaward, Net fluxes of ammonium were seaward.

Urea fluxes show that the mangrove exports urea in monsoon and postmonsoon and imports it during premonsoon.

DON transport was variable and did not reveal any particular pattern.

There was net import of phosphate in monsoon and postmonsoon and remained more or less balanced during the premonsoon.

Net transport of silicate into the sea during the monsoon and import and export remained in balance during the post monsoon. During the premonsoon the mangroves imported silicate.

The findings of the present study site suggest that there are sufficient new nitrogen input (Nitrate) in the monsoon months. While the non monsoon season is supported mainly by regenerative fluxes.

Biological and physical processes are therefore important in regulating the nutrient levels in these mangroves.