ASPECTS OF NITROGEN RECYCLING IN A CORAL REEF ECOSYSTEM

THESIS SUBMITTED TO GOA UNIVERSITY FOR THE
DEGREE OF **DOCTOR OF PHILOSOPHY** IN MARINE SCIENCE

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DECEMBER 1997

CERTIFICATE

This is to certify that the thesis entitled **'Aspects of Nitrogen Recycling in a Coral Reef Ecosystem'** submitted by **Rajan Rajkumar** for the award of degree of Doctor of Philosophy in Marine Science is based on the results of investigations carried out by him under my supervision. The thesis or part thereof has not been submitted for any other degree or diploma of any University.

CANDIDATE

RESEARCH GUIDE

Place: Dona Paula

Date: 12 Dec '97

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Acknowledgement

/ help Cometh from the Lord which made heaven and earth.Ps. 121.2.
fore I begin to thank them who helped me for my thesis, Dear Lord! let me feel it is ur love that has brought them near to me and be of great help.

y thesis, has taken shape to this stage due to

'. S.C.Goswami, who willingly agreed to take me as his student and guided me roughout.

:.E.Desa, Director, NIO gave the place to work, encouragement to continue and mplete my work.

r. Wafar, my intellectual Boss, I am so desperate to get his classic touch at every point my thesis and his obligation, which I did not completely deserve, all made me to say h! I am so fortunate that I had him for my thesis'.

r. D.Chandramohan, who tolerated me so much and never denied anything to help me the thesis.

would like to express my sincere gratitude to Dr. Mohandass, Sheelu and Pradeep for ieir timely help.

thank my dear friends, Thamban, Sukumar, Balakrishnan, Jayakumar, Jason, Ilango, avindran, Jayasree, Judith, Saji every one is so important that I do not know whom I hould owe most of my gratitude.

thank Cheryl, for being there to lend me the moral support at any point of time.

Besides the scientific help and the emotional attention got from them I mentioned above, also thank people from whom I derived technical help. I thank all of them who helped ne in drawings, xeroxing, printing etc. That amounts much too!

Though I did not mention every one by name, my sincere thanks goes to many senior colleagues in BOD and within the Institute who contributed in so many ways for the completion of my work.

This list, I feel is hardly complete, in terms of the quantity of help I derived from people who are concerned to me, whom I did not mention is not due to negligence but the proximity I have with them I owe it to their perfect love that tells me no matter who you are, you matter to us'.

I. Introduction.

The remarkable characteristic of the global ocean that covers more than 70% of the earth's surface is the diversity in its constituent seas and the resources, ranging from cold polar seas to the warm tropical waters. As one proceeds from the polar seas to the tropical waters one cannot fail to notice the increase in the biological productivity and the richness of the diversity of the marine organisms, culminating in some of the specialized tropical marine ecosystems. The latter include coral reefs, mangroves, seagrass meadows, algal ridges and banks, high saline lagoons, upwelling, estuaries and so on. Notwithstanding their structural diversity, all of them have several common traits: high biological productivity, high species diversity, abundance of endemic fauna, complexity of the trophic structure, high inorganic and organic resources and above all, their vulnerability to human intervention of any form.

Coral reefs have greatly fascinated mankind since centuries. Initially it was the fear of the dangers they posed for navigation which later gave way to wonder as man began to marvel at the underwater beauty of corals and other organisms of a reef and began to discover the riches (pearls, precious corals) from the reef. Gradually this aesthetic admiration gave way to the scientific curiosity - the central theme of which was what makes the reefs flourish in the midst of desertic oceanic waters. The esthetic admiration is back now, but in a different form - tourism to the reefs.

Sargent and Austin (1949)-1954 were the first to measure the community metabolism of a reef by flow respirometry. Their measurements showed a high level of

productivity by benthic organisms, among which corals were the dominant. This led them to conclude that, 'productivity per unit area is considerably higher than that of adjacent waters of any other open marine areas'. Subsequent studies confirmed the high productivity of coral reefs (a synthesis of all studies is given in Qasim et al., 1972), but at that time the question of how coral reefs sustain high production in the middle of oligotrophic water remained as yet unanswered.

Muscatine and Chernichiari (1969), Muscatine et al. (1981), Szmant et al. (1990) and Muscatine & Weis (1992)studied the elemental flux in the coral-zooxanthellae symbiosis and obtained evidence to demonstrate a conservation at this level. The carbon synthesized by the zooxanthellae is translocated back to the corals and the carbon dioxide released by the polyps is assimilated in turn by the zooxanthellae. Presumably this also happens with the other two macro elements of biological importance - nitrogen and phosphorous Pomeroy and Kuenzler (1969), Pomeroy et al.(1974) and D'Elia (1983) showed this symbiosis is equally efficient in conserving inorganic nutrients like phosphorous and nitrogen. Szmant et al. (1990) studied nitrogen excretion in reef corals (autotrophs, symbiotic with zooxanthellae) and showed that they conserve nitrogen by having relatively low rates of amino acid catabolism. The concept of efficient recycling of nutrients at individual and at whole ecosystem levels was then advocated as a driving force for sustaining the high production.

Though the reefs behave as closed ecosystems, influx and efflux of nutrients still occur. However, such sources are unimportant to supply large quantitites of nutrients. One such source is the upwelling of nutrient rich bottom waters. Andrews and Gentien

(1982) showed in the Great Barrier Reef that upwelling of the shelf thermocline waters can supply nutrients to corals in the reef. Another such source is endo-upwelling of the nutrients through the calcareous reef framework. Rougerie et al. (1992) demonstrated this in the Pacific atolls and hypothesised that the endo-upwelling model is completely compatible with the trophic relations and energy transformations outlined by Lewis (1981). However, the importance of endoupwelling is inconclusive. Tribble et al. (1994) showed that productivity on reefs does not require a large supply of 'exotic' nutrients, and that the data on nutrient concentrations in interstitial waters are easily explained by the oxidation of organic matter within the reef sediments, rather than through endoupwelling.

The general consensus is that coral reefs do not appear to be limited by the low concentrations of these nutrients in ambient sea water. Several studies have demonstrated that because reef autotrophs have typically have high C:N:P ratios, reef communities require a smaller quantity of nutrients than previously supposed to support the measured rates of production (Atkinson 1987, 1988, 1992; Atkinson and Bilger, 1992). Reef communities can also take up much larger quantities of nutrients than previously measured (Tribble et al. 1994).

The present study was intended to examine some aspects of nitrogen flux in a coral atoll. Nitrogen is a logical choice because, among the the three elements of biological interest - carbon, nitrogen and phosphorous- ambient nitrogen has so often been demonstrated to regulate the synthesis of organic matter at basic production levels in the sea. This limiting role could be especialy true with coral reefs, where the high productivity at low ambient N concentration present a contrasting situation. Furthermore, the diversity

of nitrogen species, with its five oxidation states avialable for uptake, add a complexity to the nitrogen cycle.

The aim of this study was to assess the relative importance of some of the biological processes that intervene in nitrogen recycling within a coral reef ecosystem and quantify the rates of nitrogen flux through these pathways in space and time.

The specific objectives were:

1)To study spatial and temporal variations of ambient nitrogenous nutrient concentrations.

2) To assess the relative importance of each of these nutrients to reef primary producers and seasonal changes in it - assimilation by phytoplankton.

3) To measure nitrogen flux through some bacterial pathways (e.g. nitrification) over seasonal scales and relate it with the availability of each nitrogenous nutrient.

4)Measure the nitrogen uptake by phytoplankton in oceanic waters around the coral reefs and relate them to the availability of nitrogen network.

2. Materials and Methods

2.1 Description of the study Area

2.1.1 Topography

The Lakshadweep archipelago, consisting of 12 atolls, 3 reefs and 5 submerged banks, is one among the largest offshore coral reef formations in the Indian Seas. Traditionally, the geographical limits of the Lakshadweep atolls and reefs are defined as 10 - 20° N and 71°40' - 74° E. The Minicoy atoll, which is also a part of the Lakshadweep group, lies outside these limits, at 8°18'N and 73°E, and is separated from the rest of the Lakshadweep atolls by the 9 degree channel. The Lakshadweep archipelago is contiguous with the Maldive archipelago in the south. To the north of the Lakshadweep, coral formation occurs mainly as submerged banks, prominent among them being Cora Divh, Basas De Pedro, and Sesostris Bank (depth 20 - 30 m). These are probably the reefs that got drowned during the Holocene transgression, but still retain an abundance hermatypic corals and other fauna and flora characteristic of coral reefs (Wafar, 1990).

Raised portions of the Lakshadweep atolls and lagoons form about 36 islands of varying sizes. Ten among them - Bitra, Chetlat, Kiltan, Kadamat, Amini, Agatti, Kavaratti, Androth, Kalpeni and Minicoy are inhabited. Some atoll islands such as Suheli Par and Bangaram are inhabited only seasonally, for fishing, coconut collection and tourism. The islands cover a total area of 36 km^2 and sustain an indigenous population of about 50,000. The predominantly calcareous nature of the soil restricts

agriculture primarily to coconut (*Cocus nucifera*) cultivation which, along with fishing, forms the staple source of revenue for the islanders.

With the exception of Androth where the lagoon is absent and Bitra and Amini where the atolls are circular in shape, all other atolls are elliptical in shape, extending in a NE - SW orientation, with the raised land mass lying on the east, the reef on the west and the lagoon in between. The length of the atolls is variable, with Minicoy being the longest (9 km). The width varies from a few hundred meters to about 2 km at the widest part of the Island. The width of the lagoon varies from 2 to 8 km. Minicoy has the widest lagoon among all the atolls whereas Chetlat has the smallest lagoon.

The seaward profiles of the atolls are typical of all oceanic atolls, with a steep drop to a depth of several hundred meters over a distance of 50 - 100 m. The reef slope is much wider on the western face than on the eastern face, and this is more marked especially when long stretches of land occur (Gardiner, 1903).

2.1.2 Climate

Climate is typically tropical. The Lakshdweep experiences both the South West and North East monsoons, and the combined total annual rain fall is about 1600 mm. The north east monsoon sets in over Lakshadweep by the end of November and continues until the end of March. During this period a more or less northerly wind prevails together with long calms but little or heavy weather. The south west monsoon is rather longer, prevailing from May until September and contributes to the bulk of

rainfall. Being in the cyclonic belt the atolls are occasionally affected by very severe winds and seas. However, damages to the reefs are usually minimal and have never occurred in the scale associated with hurricanes in Pacific atolls.

2.1.3 Physical parameters and Water mass characteristics.

The wave heights vary between 0.5 and 1.5m from October to February between 1 and 3m from June to September. The zero crossing wave periods predominantly vary between 5 and 6 s from October to February, and 5 and 8 s from June to September (Chandramohan *et al.*, 1993). The monthly mean significant wave height values reported for this region range from 1.5 to 2.7m during the south west monsoon period and are about 1m during the rest of the year (Kesavadas, 1979; Baba, 1988,). During low tide the major portion of the approaching waves dissipate their energy over the reef walls surrounding the lagoon. During high tide, part of the waves pass over the reef flat into the lagoon and break on the beach (Chandramohan *et al*, 1993). As the wave activity is intense during the southwest monsoon, more water flows over the reef due to waves and tides. The leeward sides of the islands have wide fringing reef beds, which dissipate the wave energy considerably and leave only the smaller waves to reach the shore.

There are no definite current patterns in the Lakshadweep, all sides of the atolls and reefs being probably washed equally at different seasons of the year (Gardiner, 1903). All lagoons, exhibiting geometrically similar shape and orientation, also show similar current patterns. The currents are generally weak. At the entrance channel in the north, the maximum velocity is about 15 $cm.sec^{-1}$ (average for Kalpeni, Kavaratti and

Agatti), and in the southern part of the lagoon it is lower than 1 cm.sec^{-1} - observed during both the flood and ebb tide (Chandramohan *et al*, 1993).

There are no regional observations of sea surface temperature in the vicinity of the Lakshadweep group of islands. Varkey *et al.*., (1979) described the distribution of temperature in the Lakshadweep sea showing a decreasing pattern towards offshore from the Indian shelf (i.e. from 76°N to 72°N) and from south to north (i.e. from 8°N to 14°N). Along meridional section 71°30'E in May, the surface temp. varied between 30.9°C and 30°C; in July, the meridional section was covered only up to 13°48'N and the surface temperature varied between 29°C and 28°C (Ramesh Babu, *et al* 1980).

The surface salinity increases sharply from south (8.5°N) to north (12°N) showing the presence of Arabian Sea High Salinity Water (34.6 to 35.64 ppt), as a distinct high salinity water mass all over the Lakshadweep sea in the surface layer (Varkey, *et al* 1979).

2.1.4 Faunal characteristics

Systematics, diversity and zonation studies of Lakshadweep corals are limited to Minicoy and Kalpeni Islands in the south and Chetlat Island in the north. So far 70 species of hermatypic corals representing 26 genera are reported from these islands (Pillai, 1971). Pillai (1969) has observed that the dominant corals are *Goniastrea retiformis, Diploastrea, Heliopora spp., Lobophyllia corymbosa* and various species of *Acropora* and *Porites*. While *Acropora* is dominant in the lagoon shoals, *Pocillopora damicornis* and *Porites* species are the commonest on the reef flat (Pillai, 1969). However, the systematics and diversity of other coral reefs in Lakshadweep archipelago

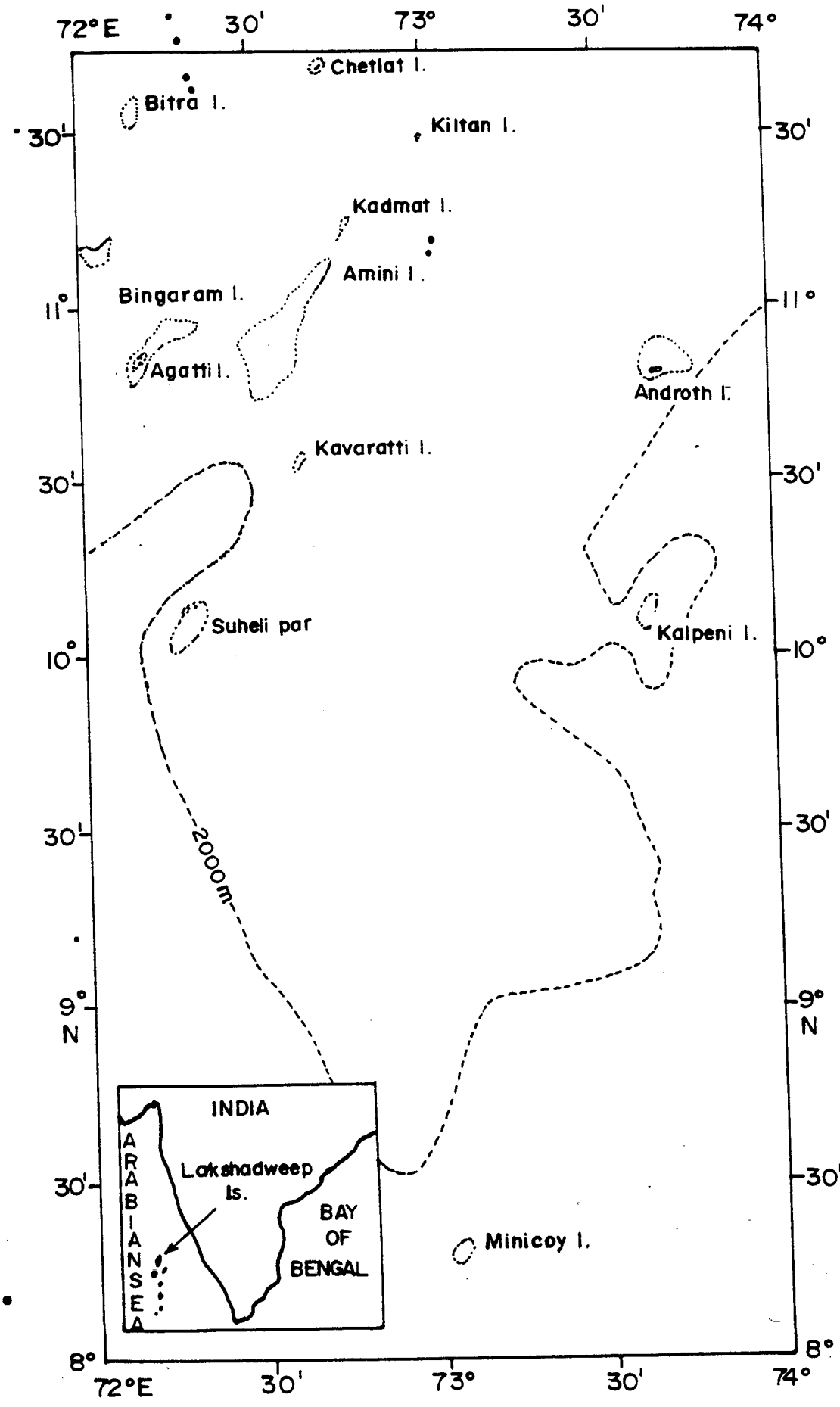
have not been studied in detail nor the deep water species, even from Minicoy, are known (Wafar, 1986). More study need to be carried out to understand the diversity of coral fauna from this region which is not greatly subjected to anthropogenic disturbances.

2.1.5 Kalpeni Atoll

Most of the present study was carried out in the Kalpeni-Cheriyam atoll (Fig.1). The land formations are restricted to the eastern part of the atoll with a relatively widened Kalpeni Island (5 km long and 1.3 km wide in the widest part, area: 4.2 km^2) oriented towards the south and an uniformly broad and narrow Cheriyam Island on the north (0.5 km wide and 2.8 km long). Both these islands are connected by a reef flat (3.5 line km), other wise called - theodolite traverse (Siddiqui & Mallik, 1975), which lies exposed during low tide. The small islets or other land formations on the southern tip of the reef are named Pitti and Tulakam and the one which lies in between Cheriyam and Kalpeni Island is called Kodithali. The reef flat on the western or the windward side is broad and slopes gently whereas the leeward side has narrow reef flat and slopes down sharply. Echo sounding indicated a 200-300 m wide wave-cut platform on the seaward reef; it is considerably wider at north of the Cheriyam island but narrowed appreciably towards the east (Siddiqui & Mallik, 1975).

The lagoon has an area of 8 km^2 which is 10.5 km long and 4.3 km wide in the central part. The depth of the lagoon varies from less than a metre to about 5 m. (Siddiqui & Mallik, 1975). It is connected to the open ocean by a deep boat channel that runs parallel to the main island and then takes a turn in the north-west direction to

Fig. 1 Lakshadweep Islands



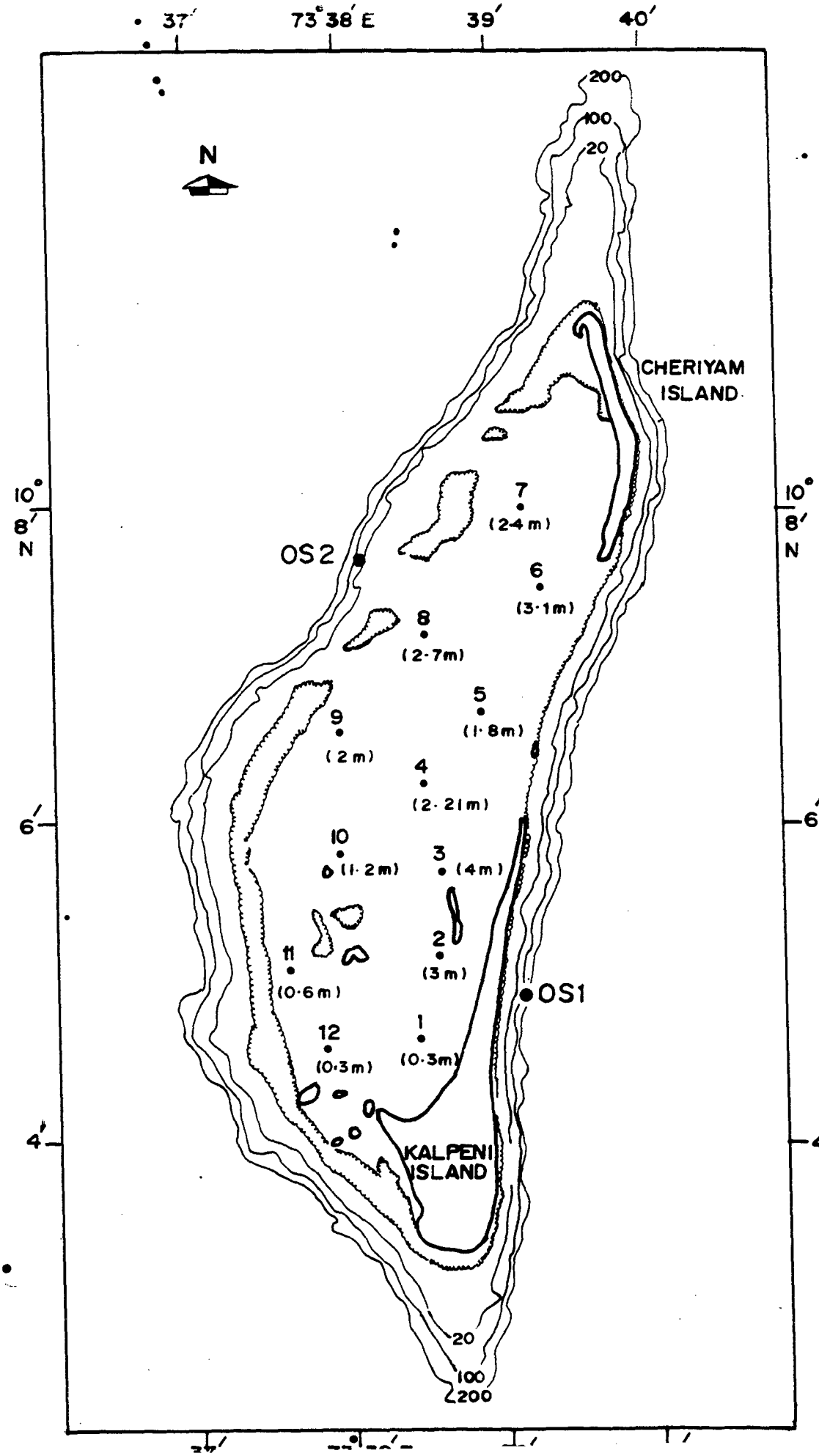
cut across the reef flat into the open ocean. Geomorphologically three disinct zones are apparent in the lagoon floor, starting from the island to the reef: a) zone of even topography bordering the island and covered with sand; b) central rugged part with protruding corals and coral knolls indicated by sharp reflections on the echograms and c) sand banks on the inner reef margin marked by steep slope towards the central part (Siddiqui & Mallik, 1975).

The many coral knolls (live coral colonies) arising from the floor in the central lagoon (zone b) reach almost the surface and render the boat movement in the lagoon difficult except along the channel. These are mainly colonies of *Acropora* situated in the deeper portions of the lagoon away from the shore, between the channel and the outer reef. Zone C is shallow and marked with very small coral colonies. Massive coral colonies are seen in the areas close to the channel, between the channel and the island shore where there is less human activity. The eastern side of the island is abundant with many branching and massive corals, and Gorgonians.

2.1.6 Description of stations

12 stations were selected (Fig.2) in the lagoon. The location distribution of these stations is such that there is a reasonably good coverage of the entire lagoon and the different biotopes (coral patches, algal mats, sea grass bed and sandy bottom) in it. The stations had the following characteristics with respect to their species richness and benthic structure. Prolific coral growth was observed at stations 4, 5, 6, 7, and 10. The stations near the shores (1, 2 & 3) were dominated with seaweeds and detrital material. The station 8 is deep and close to the entrance channel. No coral growth is possible there

Fig. 2. Kalpeni Atoll island showing station locations.



because of the frequent dredging to deepen the navigational passage. The other stations (9, 11 & 12) lie in the shallow, areas with small colonies of corals. The Cheriyam lagoon sampled frequently had a very good coral cover all over the lagoon with very high densities at its both northern and southern tips.

Two additional stations were selected in the open sea; The first one was on the eastern side (OS1) and the second one on the west (OS2), closer to the lagoon entrance in the open sea (Fig.2). The station OS1 does not resemble the open ocean conditions in the station OS2 is because it is close to the reef flat which is embedded with a very high biomass of encrusting algae.

2.2 Sampling methods

2.2.1 Strategy and facilities available

The study period extended from January 1993 to March 1995. A field station was set up in a hired building close to the lagoon, and provisioned with adequate facilities that would permit a year-round data collection and preliminary processing of the samples. Sampling was generally done at fortnightly intervals depending on the weather conditions. Most of the collection work started in the morning hours so that the analyses that could not be deferred until the next day could be finished on the same day. In all collections, sampling was restricted to surface because of the generally shallow depth in the lagoon and the homogeneity in the water column.

The stations in the lagoon (#1-#12) were selected for fortnightly observations of ambient concentrations of nitrogenous compounds, chlorophyll and particulate organic nitrogen. The station (OS1), along with station #1, close to the Jetty were sampled,

besides the regular fortnightly observations of nutrients and chlorophyll, more specifically for N uptake rates and for studies on nitrification in the water column and in the sediments. The outer sea station 2 (OS2) near the entrance was only sampled for the estimations of ambient nutrient concentrations, but not for other studies due to logistic constraints, mainly weather.

A fibre glass, out board engine fitted boat named 'Merulina', procured by NIO for this study was extensively used for all the collections in the lagoon and outer sea.

2.2.2 Sample collection and processing

Seawater samples for the measurements of all dissolved inorganic nitrogen (DIN) forms, except ammonium, were collected in pre-cleaned, oven-dried (45°C, overnight) polyethylene bottles. Immediately after collection, they were stored in an ice box and brought to the laboratory for immediate analysis. Special care was taken in the case of ammonium, where the samples were collected directly in stoppered 50 ml acid-washed reagent bottles and fixed immediately (on board) to avoid contamination.

Samples for urea and dissolved organic nitrogen (DON) were also collected in a similar manner, but these samples were kept at -20°C pending analyses.

Samples for particulate organic nitrogen (PON) were collected in pre-cleaned, acid-washed polypropylene carbuoys of 5 liters volume and brought to the laboratory, where 2 to 3 liters of each sample were filtered onto pre-combusted (2 hrs at 450°C) GF/C filters under vacuum. The optimum volume to be filtered was chosen depending on the concentration of particulate matter in the samples. Care was taken not to overload the filter but to collect as much particulate matter (generally defined > 1 μm) as possible,

since the most accurate results are obtained by filtering large volume of seawater (Gordon & Sutcliffe, 1973). Filtering about 2 litres for lagoon waters and 3 litres for of open ocean waters was sufficient to collect adequate amount of particulate material. The filter papers were then air-dried, folded in an aluminium foil and stored for pending further analyses. Blank filter papers were prepared in the same way. PON was estimated by Kjeldhal digestion described by Koroleff (1976a).

Samples for chlorophyll measurements were collected from the surface waters in 5 litre black carbuoys. Sample was pre-filtered through a nylon mesh of 300 μm size so as to remove large zooplankters and other suspended particles. The sample was then filtered through GF/C pads, and the filters were placed in centrifuge tubes of 15 ml capacity, taking special cautions not to expose the pigment matter to light. The volume of seawater filtered was restricted to 2 to 3 liters depending on the suspended load.

2.3. Measurement of ambient nitrogen concentrations

Methods for the measurements of dissolved nitrogen compounds in sea water have been refined in the last few decades to such an extent that detection of very low concentrations is almost a routine practice now. The methods employed here are sufficiently sensitive enough to detect the low levels of nitrogen concentrations typically encountered in reef waters.

2.3.1 Nitrite

Nitrite was estimated spectrophotometrically following the method described by Bendschneider and Robinson (1952). The principle of the method is that the nitrite in

sea water, when treated with sulphanilamide in an acid solution, results in a diazo compound that reacts with N-(1-naphthyl) ethylenediamine and forms a highly colored azo dye, the extinction of which is measured at 543 nm. Standards were prepared from KNO_2 and measured with every batch of sample.

2.3.2 Nitrate

Nitrate ion has an intense absorption band in the far ultra violet spectra. However, estimation of nitrate using this spectrum of light has limitations due to interferences from dissolved organic compounds and Bromide ions (D'Elia, 1983).

At present, nitrate measurement typically relies on the reduction of nitrate to nitrite by cadmium-copper and its determination by diazotization (see above). In this study, the procedure described by Parsons *et al.*, (1984), was adopted. The sample pH was adjusted to 9.5 by the addition of NH_4Cl (D'Elia, 1983) and the flow rate was adjusted to 100 ml in 8 - 12 minutes to obtain maximum reduction of NO_3. Phosphate interference predicted in the reduction procedure (D'Elia, 1983) was studied by spiking seawater samples from different locations with phosphate and then measuring NO_3 concentration. This showed negligible effect on the column under use. Column efficiency was checked at regular interval using simultaneous run of NO_2^- and NO_3^- solutions.

2.3.3. Ammonium

Ammonia (NH_3^+) exists primarily in the cationic form of Ammonium (NH_4^+)in seawater and since its determination is mainly by protonation to ammonia, the term ammonia is used (D'Elia, 1983). In all the methods the sum of $NH_3^+ + NH_4^+$ is recorded.

The widely accepted Indophenol blue method was preferred because of its most satisfactory results (Riley 1975; D'Elia, 1983). The formation of indophenol blue explained by Koroleff (1976a) is the result of ammonia that reacts in a moderately alkaline solution with hypochlorite to monochloramine, in the presence of phenol and the catalytic amounts sodium nitroprusside. In this study, trione (sodium dichloro isocyanurate (dichloro-s-triacine 2,4,6-trione), instead of hypochlorite was used as a chlorine donar (Grassoff & Johannson, 1972; Krom, 1980). The precipitation of Mg and Ca ions as hydroxides and carbonates at higher pH (9.5) were held in solution by complexing with sodium citrate (Solarzano, 1969). The reagents and blanks were prepared in ammonia-free water obtained through a deionised column. This gave satisfactory results compared to the blanks using ordinary distilled water.

2.3.4 Urea

Urea was estimated using the colorimetric method of Newell *et al.*, (1967). Urea in seawater in the presence of strong acidic solution reacts with diacetylmonoxime, the product of which then reacts with semicarbazide to form the chromaphore semicarbazone.

Reagents and blanks were made up with distilled water instead of de-ionised water, to avoid contamination through ammonium cyanurate, a major constituent in many of the deionising columns (Muvenna, 1992). After the addition of reagents, the flasks were covered with aluminium foil and placed in a water bath at 75°C for 2 hrs, then cooled to room temperature and the sample extinction measured at 520 nm. The temperature and timings were maintained constant throughout the seasonal study.

2.3.5 Particulate Organic Nitrogen (PON)

PON in the particulate material was estimated using Kjeldhal digestion method described by Koroleff (1976b). In this method, the PON contained in the sample is converted to NH_4SO_4 by digestion with H_2SO_4 and a catalyst mixture. The ammonium is then measured by the indophenol blue method (see above).

Separate reagent blanks and standards for ammonia were prepared anticipating the high ammonia concentration in the final estimations. Blank measurements on the GF/C filters and the digestion mixture were done with each series of measurements. The Kjeldhal 'N' then calculated from the following expression using indophenol blue absorbance at 630 nm (Koroleff, 1976b).

$$\mu g \text{ at Kjeldhal - N } l^{-1} = \frac{50}{\text{Volume taken (l)}} F (As - Ab)$$

where As is the Absorbance of the sample,

Ab the blank absorbance,

F calibration factor, obtained from a standard curve.

The particulate organic nitrogen content was obtained by subtracting the amount of NH_4 determined separately (before digestion).

3.6 Dissolved Organic Nitrogen (DON)

DON was estimated by the persulphate oxidation method (Koroleff, 1976b). his procedure has a wide application and has a good precision (D'Elia, 1983). Besides, ie common drawback of interference from large quantities of nitrate or nitrite is lleviated as the ambient concentration of these two components are relatively much ow. The problems associated with turbid waters (Nydahl, 1978) are unimportant here as he samples had very low particulate loads. The samples were then pipetted directly into he oxidation flasks, without filtration to avoid contamination from ammonia.

The determination here is by wet oxidation using persulfate (Koroleff, 1976b) where the difference between the concentration of total dissolved nitrogen (i.e. nitrate + nitrite + ammonium + organic nitrogen) measured after the digestion and that of the dissolved inorganic nitrogen (nitrate + nitrite + ammonia) gives the dissolved organic N content. The oxidation of combined nitrogen compounds into inorganic nitrogen is achieved under alkaline conditions by boiling (100°C) with potassium peroxodisulphate.

50 ml Erlenmeyer flasks with glass stoppers tied to the neck were used as oxidation flasks. The samples were pipetted directly into the oxidation flasks without filtration to avoid contamination from ammonium. The oxidation was then performed in an ordinary pressure cooker for half an hour. The rest of the oxidation procedure as well as the reagents for oxidation were as given in the Koroleff's (1976b) method.

No_3 standards at concentrations ranging from 1-20 µg at l^{-1} were prepared using potassium nitrate (KNO_3) and the column efficiency checked. The calibration factor 'F' was obtained from the linearly occuring values which normally lie within 12 µg at l^{-1}. At higher concentrations (usually >12 µg at l^{-1}) the values are not generally linear due to

chloride ion interferences in the azo dye formation. Hence samples with net absorbance above 1.0 measured at 1 cm cell were analyzed again after a 10-fold dilution.

The organic N standards using EDTA were run at various intervals and the 'F' value compared with that of nitrate. Blank values with oxidizing mixtures were determined for every set of samples.

The amount of total nitrogen is calculated from the expression (Koroleff, 1976);-

$$\mu g\ at\ l^{-1} = \frac{50}{ml\ sample} F\ (As - Ab)$$

Where As is the absorbance of the sample

Ab is the absorbance of the blank

F the calibration factor.

2.4 Chlorophyll a and Phaeopigment estimations

The extraction and measurements were done as described by Strickland and Parsons (1972), where the total quantity of Chlorophyll and Phaeopigments can be measured. In this method, the extinction of an acetone extract of plant pigment is measured before and after treatment with dilute acid. The pigments were extracted with 90% acetone. The filters with the particulate matter were ground with a glass rod, and the extracts were allowed to stand for 10-20 hrs in the refrigerator for a total extraction of the pigments.

The acetone extract was then centrifuged and the clear supernatant was taken for spectrophotometric measurements, where the optical density of the extract was

measured at 665, 645, 630 and 700 nm. The extract was then acidified with 2 drops of 50% HCl, and the optical density was measured again at 665 nm. The Chl a content was calculated using the trichometric equations of Strickland and Parsons (1972). The phaeopigment concentration was calculated using the equation of Lorenzen (1967).

2.5 Uptake studies

2.5.1 Principle

The radioactive isotope of carbon , ^{14}C, has been used since 1950's to measure carbon assimilation and productivity of phytoplankton. This method is relatively easier and sensitive, and has come to be accepted, despite several shortcomings, as a standard method in oceanography. However, this method has one distinct disadvantage: it cannot provide information on the state of nitrogenous nutrition of the phytoplankton. This constraint becomes all the more serious in marine environments such as oceanic waters or coral reefs where carbon is in unlimited supply whereas nitrogen is not.

Dugdale and Goering (1967) pioneered the use of stable isotope ^{15}N to measure nitrogen assimilation by phytoplankton. By using nitrate and ammonium labeled with ^{15}N, they were able to measure the uptake rates of these nutrients separately. This classical work also led to the birth of the concepts of 'new production' and 'regenerated production', and later, of the export production and *f*-ratio (Eppley and Petersen, 1979) which have greatly enhanced our knowledge of global biogeochemical cycles of nitrogen. Again in the last 30 years, ^{15}N isotope was

also used to measure uptake of urea (McCarthy, 1972), nitrite (Kiefer *et al.*., 1976; McCarthy *et al.*., 1977) and amino acids (Wheeler *et al.*., 1981) thus allowing us to gain insights into the uptake and assimilation of each of these N sources. In addition, ^{15}N has also been used to measure the rates of N transformations (nitrification, denitrification and N fixation), and has come to be recognised as an indispensable tool in measurements and quantification of productivity processes.

Basically, the method is like that of any other tracer study. Compounds labeled with ^{15}N (enriched to 95-99%) are added in trace quantities to a seawater sample, which then is allowed to incubate for a certain time interval. At the end of the incubation, the particulate matter is recovered by filtration, and the ^{15}N:^{14}N ratio (i.e. atom % excess of ^{15}N relative to its natural abundance, 0.365%) is measured either in a mass spectrometer or an emission spectrophotometer.

Though elegant, this method is not without constraints. The first is the ability of the present day analytical methods to measure subnanomolar concentrations of the ambient nutrients, especially of ammonium in oceanic waters. The second is the contamination with atmospheric N during sample preparation. This can occur during evacuation stage when the atmospheric nitrogen is removed from the analytical system prior to conversion of the PON to dinitrogen or during the conversion stage itself, if the catalysts used in the chemical reaction are not adequately cleaned of the contaminant N. The precautions needed to avoid these problems render the method somewhat tedious and time-consuming. These constraints have also limited the use of ^{15}N to only a few laboratories around the World.

2.5.2 Field studies

2.5.2.1 Stations

Station OS1 and stn #1 were selected for nitrogen uptake studies. The former represents oceanic conditions i.e. before the oceanic water flow over the reef water to the lagoon. The second station represents the lagoon conditions i.e. a situation where the chemical and biological properties of the ambient water have probably been modified by flow across the reef and lagoon. Uptake measurements at both stations were made at fortnightly intervals over an annual cycle.

2.5.2.2 Incubation

Seawater samples were obtained from surface and dispensed into 2 l stoppered acid-cleaned glass bottles. Uptake experiments were done with nitrate, ammonium and urea. Nitrite uptake was not measured since earlier studies demonstrated that its uptake is generally unimportant. The tracers were in the form of sodium nitrate, ammonium chloride and urea, each enriched to 99% with ^{15}N. Two types of uptake measurements were made. The first one was trace uptake in which the tracer was added in truly trace concentration so as not to perturb the ambient concentration and by consequence unnaturally elevate the uptake rates. Generally this is done in such a way that the amount of tracer added does not exceed 10% of the ambient concentration of the nutrient under study. When it is possible to analyse nutrients by automated methods such as onboard research vessels, it is possible to measure ambient concentrations within 15 minutes of sampling and add the tracer in the correct concentrations required. However, with the field lab where measurements

were done by manual methods, this was not possible. Hence, the addition of tracer was always made at fixed concentrations of 0.05 μg at l^{-1} to all the incubations. Comparisons with ambient concentrations measured later showed that the tracer addition in most of the cases were in fact at <10% of the ambient.

The second set of incubations was designed to measure saturated nitrogen uptake. In this type of experiments, the tracer is added in such a concentration, that the uptake is not substrate - constrained. The *V* measured under these concentrations becomes equivalent to V_{max}. In our experiments the tracer is added at a concentration of 5 μg at l^{-1}, which was sufficient enough to saturate the uptake processes.

When saturation and trace uptake rates were measured on the same sample, their ratio is a useful indicator of whether the uptake is nutrient- constrained or not (Gilbert and McCarthy, 1984; Wheeler *et al.*., 1982). Thus when the ratio is close to 1, then the uptake of the nutrient in question is not substrate-constrained.

After addition of the tracer, the incubation vessels were placed in tubs filled with seawater and incubated in ambient sunlight for 2 hr (1000 hrs - 1200 hrs). This was followed in all the cases so that a constancy in the incubation condition was possible which, in turn, was useful when uptake rates of different nutrients at different periods were compared. The 2 hr incubation was sufficient to detect ^{15}N incorporation and uptake rates over the length of this time are generally linear (Goldman *et al.*, 1979).

At the end of the incubation, the samples were filtered through pre-ignited GF/F filter pads under a vacuum not exceeding 200 mm Hg. The filters were then

dried at 40°C in a hot air oven, wrapped in precombusted aluminium foils and held pending analysis of their $^{15}N;^{14}N$ ratio in an emission spectrophotometer.

2.5.3 Sample preparation and analysis

Analysis of $^{15}N:^{14}N$ isotope ratio by emission spectrometry requires that the nitrogen is present in dinitrogen (N_2) form and that the final pressure of N_2 in the emission tube is 4-5 torr.

The filter with the particulate matter was ground with CuO (pre-ignited at 400°C) and then introduced into a pyrex emission tube (length 140 mm; ID 7 mm). A batch of 6 tubes thus prepared was evacuated in a glass manifold mounted on a IBP VPM-120 model vacuum system capable of attaining a vacuum of 10^{-6} atmosphere when a liquid nitrogen trap is used. However, the emission tubes were generally evacuated only to 10^{-4} - 10^{-5} atm (contamination with atmospheric N_2 at this vacuum is less than 0.001%) and sealed with a blow torch. the tubes were then heated overnight at 500°C in a muffle furnace and cooled. Heating dissociates CuO to Cu and oxygen which combines with PON to form oxides of nitrogen. On cooling the oxides of nitrogen are reduced by copper to N_2. The required 4-5 torr was achieved by sub-sampling a suitable fraction of the filter, based on a knowledge of PON measured previously in a duplicate sample in a CHN analyser.

The principle of the emission spectrometry is as follows. The nitrogen molecules in the sealed tubes are excited by a radio frequency source to produce an emission. The nitrogen molecules consist of $^{14}N_2$, $^{14}N^{15}N$ and $^{15}N_2$ and the emission spectrum, accordingly will contain vibrational spectra for each of these three

molecules, which are measured at spectral band heads of 297.7, 298.3 and 298.9 nm respectively. The intensity of these spectra are proportional to the number of corresponding molecules.

A JASCO 150-N heavy nitrogen analyser (specifications include: RF source of 13.56 Mhz and 30W Czerney - Turner monochrometer, a PM tube detector and a built in recorder) was used to measure the emission spectrum of the sample after freezing out the impurities (CO_2, H_2O) with liquid nitrogen.

As the atom % excess of ^{15}N of each sample is measured with reference to total N content, a standard curve is generally unnecessary. However, since the calculated atom % excess of ^{15}N tends to be higher than the true values at lower enrichments (<0.5%) and lower at higher enrichments (>20%), suitable corrections to the measured atom % excess of ^{15}N are necessary. This was done by preparing a calibration curve of a range of atom % excess ^{15}N values (0.365% - 22%) against true values of a set of standards supplied with the instrument.

2.5.4 Calculation of uptake rates

The specific uptake rate ($V\ h^{-1}$) was calculated from the expression

$$V = \frac{\text{at \% excess in PF}}{\text{at \% excess in Df}} \times \frac{1}{t}$$

Where,

at % excess in PF is the at % excess of 15N measured in the particulate fraction,

at%excess in DF is the at%excess of ^{15}N in the dissolved fraction

and t = the duration of incubation.

The absolute uptake rate (ρ) was calculated as

$$\rho\ (\mu g\ at\ N\ l^{-1}\ h^{-1}) = V\ h^{-1}\ X\ PON\ (\mu g\ at\ l^{-1})$$

$$= N\ \mu g\ at\ l^{-1}\ h^{-1}$$

2.6 Nitrification measurements

Rates of nitrification are conventionally measured as the rate of production of nitrite and nitrate when a seawater sample is incubated with ammonium (substrate), and the end product nitrate + nitrite measured colorimetrically. However, this method has a limitation : Incubations need to be done over longer time intervals, at times of the order of a week or more, if the concentration of nitrite + nitrate produced is to be statistically higher than the initial concentration.

Nitrification can also be measured using ^{15}N isotope. The substrate is given in the form of $^{15}NH_4$ and the atom % excess of $^{15}NO_2/^{15}NO_3$ produced is measured in a mass or emission spectrometer (Miyazaki *et al.*., 1973, 1975). This method also requires incubations for several hrs, at times up to a day, to get measurable incorporation of ^{15}N into nitrate. The procedure for extraction of nitrate (Wada and Hattori, 1972) for the measurement of $^{14}N:^{15}N$ isotopic ratio is also quite tedious and prone to contamination, both of which preclude its routine use in a field laboratory.

The nitrifying bacteria, during the process of oxidation of ammonium to nitrate also assimilate carbon. Since carbon assimilation by biological process can be easily measured, and with a better precision than with ^{15}N, the rate at which carbon is assimilated by the nitrifying bacteria can be used as a proxy for nitrifying activity. This consideration led Billen (1976) to propose and measure the nitrifying activity of

bacteria by measuring carbon assimilation in two samples - in one where the bacteria were allowed to nitrify and the other where they were prevented from doing so.

In brief, this method consists of obtaining 2 samples, either of water or sediments, one of which is treated with an inhibitor of nitrification such as N-Serve or allylthiourea. Both the samples are then added with ^{14}C in the form of bicarbonate and allowed to incubate for a certain time interval (usually 2 hrs). At the end of incubation the samples are assayed for ^{14}C activity. Nitrification rate is then calculated as the difference between the ^{14}C activity between the two samples and converted to N equivalents using the molar ratio of 0.12 µmol bicarbonate to each µmole of ammonium oxidised (Billen, 1976).

In this work, nitrification rates were measured both in the water and sediment samples. The inhibitor used was N-Serve, at a final concentration of 5 µg N-serve l^{-1} in the water column, and 5 µg N-serve/core (~5 g dry wt) in the sediments. The ^{14}C was obtained as $NaH^{14}CO_3$ (activity 5 µci ml^{-1}) from BARC, Bombay. Water samples were directly filtered with 0.22 µm membrane filter at the end of the incubation. Sediment samples at the end of the incubation were agitated vigorously with about 100 ml of 0.22 µm filtered sea water to release the particle-attached bacteria, and the sample filtered with 0.22 µm filters. After drying, the filters were extracted with 5 ml of scintillation cocktail and assayed for radioactivity in a Hewlett Packard scintillation counter.

3. Results and Discussion

3.1 Seasonal flux studies

Temporal changes of nutrients in coastal marine system are subjected to the influence of terrigenous inputs (Atwood *et al.*,1979, Eppley *et al.*,1979, Thomas and Carsola.,1980). These inputs also add lots of N to the system. Knowing N is limiting in many of the oceans, there was an early interest in comparing near shore and offshore waters and also in the influence of freshwater inputs on the seasonal abundance of nitrogen (Nixon and Pilson, 1983). The following studies quoted by them (Nixon and Pilson, 1983) prove this statement. They were, 1) Jhonstone (1908)'s, that claimed that the greater density of plant life near land is directly due to the fact that there is greater amount of the ultimate food materials, nitrogen compounds and carbon dioxide, there, than far away from land. 2) Cooper (1933)'s, who found that 'land drainage may be of great importance' for ammonia and nitrate in the Plymouth sound. However, it is very lately (in the 60s) came the umpteen numbers of studies in coastal and estuarine systems dealing with the seasonal abundance (annual cycles) of nitrogen pertaining to such terrigenous fluxes. At present, there are studies available on the spatial and temporal variations in the concentration of ammonia, nitrite and nitrate, over at least one annual cycle, reasonably well described for perhaps several dozen estuaries, lagoons, and nearshore marine waters around the world (Nixon and Pilson, 1983).

The situation is quite different in coral atolls where such studies on seasonality are minimal . As coral atolls are located far from terrigenous influences, a seasonality induced by such fluxes is hardly conceivable and it is probably one

reason why seasonal studies on coral atolls are sparce. Nevertheless, since the productivity of an atoll equals or exceeds the productivity of any coastal/estuarine systems, several authors introduced the concept of an external input from sources other than terrestrial that can sustain such high productivities. These were, upwelling near the reefs (Andrews and Gentien, 1982), geothermal upwelling (Rougerie *et al.*, 1992), water-mass drift (Andrews, 1983), etc. These studies, except that of Andrews (1983)' were on short time scale / on-the-spot estimations and do not have a seasonal basis.

Another reasoning for seasonal patterns was given by Sharp (1983). He suggested *in situ* seasonal patterns caused by biological regeneration (if no physical phenomena have caused any seasonal variability) in the pelagic layers of the oceanic systems. Menzel and Rhyther (1961), Fogg (1975) and Deuser and Ross, (1980) demonstrated that there are annual cycles in the primary productivity in much of the ocean. This *in situ* changes can be important in coral reefs because of the still valid hypothesis that coral reefs sustain such high productivities in these low nutrient waters is due to efficient recycling by biological means. With respect to nitrogen it is further more important because the nitrogen cycle, unlike those of other nutrient elements such as phosphorous and silicon, is primarily mediated by biological, not chemical processes (Webb, 1981). Table 1 & 2 give the list of biological nitrogen processes and the values of major N species that has been studied in coral reefs (Sharp, 1983). In the present study, though all these processes are not considered, emphasis is given to the assessment of many of the important processes in a seasonal basis.

Table 1. Major n Nitrogen cycle processes and important organisms involved.

S. No.	Process	Important organisms	Comments
1.	Nitrogen fixation	Blue-green algae (Cyanobacteria), for instance Calothrix crustacea	Well studied, rates well quantified
2.	Ammonification	Grazers, for instance fish, echiniderms Detritivores, for instance polychaetes Filter feeders, for instance sponges Bacteria	Studied, but not well understood or quantified
3.	Nitrification: ammonia oxidation	Bacteria	Studied and quantified
4.	Nitrification: nitrite oxidation	Bacteria	Studied and quantified
5.	Dissimilatory nitrate reduction and denitrification	Bacteria	Not well studied or quantified
6.	"Assimilatory" nitrite reduction	Macrophytes Corals Foraminiferans Bacteria	Well studied and quantified
7.	"Assimilatory" nitrate reduction	Macrophytes Corals Foraminiferans Bacteria	Well studied and quantified
8.	Immobilization and assimilation	Macrophytes Corals Foraminiferans Bacteria	Well studied and quantified

Table 2. Major nitrogen species in the Sea*

Species	Surface oceanic (0 - 100 m)	Deep oceanic (>100 m)	Coastal	Estuarine
Nitrogen gas (N_2)	800	1150	700 - 1100	700 - 1100
Nitrate (NO_3^-)	0.2	35	0 -30	0 - 350
Nitrite (NO_2^-)	0.1	<0.1	0 -2	0 -30
Ammonium (NH_4^+)	<0.5	<0.1	0 - 25	0 -600
Dissolved organic N	5	3	3 -10	5 - 150
Particulate oranic N	0.4	0.4	0.1 - 2	1 - 100

* Approximate average values are given for oceanic waters and approximate ranges are given for coastal and estuarine waters. All values are in μg at N l^{-1}.

Therefore, this is one among the few studies where the changes in nutrient stock levels were estimated together with the assessment of biological processes that mediate production and consumption. The importance of this study lies in the fact that coral res (especially atolls) completely lack such data where there is an urgent necessity for one.

3.1.1 Ambient concentrations

3.1.1.1 Nitrate

Nitrate has often been attributed an important status as a nitrogen source for marine phytoplankton because of two reasons. The first one is that, next to N_2, it is the most abundant species of nitrogen in dissolved form in the sea and second one is that it is the most abundant one among biologically assimilable forms. Hence, the availability of NO_3^- has often been associated with the magnitude of primary productivity, especially in the oceanic waters where it its low abundance limits primary production. Though the importance of NO_3^- has been revised after the recognition of other regenerated nitrogen (NH_4^+ and urea) sources as possible alternatives (Vaccaro, 1963; McCarthy et al,1977), as a new nitrogen component, nitrate is still responsible for the particulate carbon production meant for export/losses from surface waters, except under quasi-steady-state conditions where phytoplankton incur no losses whatever (Dugdale and Goering, 1967, Vezina and Platt, 1987).

The supply of nitrate in the sea is mostly based on physical processes such as riverine input (Garrels *et al.*, 1975; Delwiche and Likens, 1977; Soderlund and Svensson, 1976, Edmond *et al.*, 1981), upwelling (Dugdale and Goering, 1967; 1970) and atmospheric washouts (Soderlund and Svensson, 1976). The biological processes, in the mean time act as sinks as well as sources. The sources can be by nitrification and nitrogen fixation (indirectly by supplying the substrate ammonium for nitrification), and nitrate assimilation and dissimilatory nitrate reduction help in the utilization of nitrate. These biological processes are discussed in detail separately in the following chapters. Dissimilatory nitrate reduction was not considered important in the present study because anoxic conditions are rarely discernible in atolls.

In coral reefs, the supply of nitrate from external sources can be important as this can support high total production and export of the particulate organic matter export from the reef to the surrounding ocean. Marsh (1977) showed that nitrate in ground water, terrestrial runoff and upwelling have large local effects on reef biota. Johannes (1980) and D'Élia et al (1981) also reported influx of ground water nitrate into reef systems. The biological pathways mentioned earlier have also been shown to have a major role in mediating nitrate concentrations in reefs (see below).

Sharp (1983) presents a review of studies on oceanic nitrate distribution. A general depth-wise profile shows increasing concentrations of nitrate beneath the photic layer, usually reaching a maximum in the area of oxygen minimum layer, and decreasing to a lower concentration below that (Sharp, 1983). The values in the surface layers, integrated from 0 to 100 m, show an average value of 0.2 μg at N l^{-1}

and in the deep waters, they reach upto 35 μg at N l^{-1}. His review did not support a good seasonal pattern in the surface layers (integrated in the 1 - 150 m). However, the concentrations varied seasonally in the surface layers of the coastal waters. The annual cycles here (coastal waters) exhibited surface nitrate values that are usually close to zero in summer where there is no upwelling and several μg at N l^{-1} in the winter (Sharp, 1983).

In reef waters, variations in nitrate concentrations were shown with respect to their occurrence in oceanic and coastal areas. In the oceanic reefs, the estimations show almost non-existent to trace levels of nitrate (0.02 - 2.50 μg at N l^{-1}) that did not show much variations from the tropical oceanic values. The coastal reefs, for e.g. high-moated and high latitude reefs show increased concentrations (0.54 - 5.17 μg at N l^{-1}) that reflect the effect of nutrient input from sources such as upwelling (Andrews, 1983), ground water and terrestrial runoff and ground water intrusions (Marsh, 1977; Wade, 1976). Table 3 gives the values of nitrate from different reef formations of the world (reproduced from Crossland, 1983).

Nitrate concentration in the present study varied from 0.0 to 2.25 μg at N l^{-1} (Table. 1 in Appendix), comparable with the values reported by Crossland (1983) for oceanic atolls. The mean value was 0.55 ± 0.226 μg at N l^{-1} that is moderately higher than the average oceanic surface values (0.2 μg at N l^{-1}, calculated by Sharp, 1983), and suggest that the production rates of nitrate is higher than in most of the oceanic surface waters. However, Wafar et al (1986) measured in the Lakshadweep sea (open ocean), nitrate concentrations ranging from <0.1 – 0.5 μg at N l^{-1} which

ıble 3.Dissolved inorganic and organic nutrient concentrations in the coral reefs (μg at N l^{-1}).

Type and Location	Nitrate	Nitrite	Ammonia	DON	Urea	Reference
c						
ı Atoll, Lagoon	0.02-2.40	-	-	-	-	Smith & Henderson (1973)
ak Atoll, offshore	0.02	-	.030	3.0	-	Smith & Jokiel (1975.
all Is.), reef	0.06-0.30	-	0.20-0.29	1.7-2.3	-	Odum & Odum (1955)
					-	Webb et al. (1975)
					-	Johannes et al. (1972)
g Atoll	0.48-1.98	-	-	-	-	Marshall et al. (1975)
					-	Krasnick (1973);
ı Atoll, offshore	0.01	-	0.27	3.8-5.6	-	
t Is.), reef	0.04-0.68	-	0.31-0.54	-	-	Johannes et al. (1979)
ıto Atoll, offshore	0.36	-	0.10	-	-	
ɔtu Is.), lagoon	0.22	-	0.10	-	-	Sournia & Ricard (1976)
ıc Bay, i)	-	0.05-0.94	1.60-2.40	3.4-7.5	0.4-2.0	
reef	0.21	-	-	-	-	Henderson, Smith &
agoon	0.09-0.32	-	-	-	-	Evans
gin Is.,	0.12-2.50	0.00-0.50	-	-	-	(1976).
ɔn Harbour	-	0.10-4.75	-	-	-	Birkeland et al. (1976);
ɔa)						Randall et al. (1978)
						Dong et al. (1972)
loated						Wade (1976).
Is., offshore	0.54	0.14	0.32	5.0	-	
ırrier Reef), lagoon	0.59-0.82	0.17	0.25-0.34	4.2-4.6	-	
atitude						Crossland & Barnes
os Is., rn Australia)	0.79-5.17	0.01-0.50	0.07-11.00	0.1-7.4	-	
						Crossland (unpublished)

are closer to the present estimations in the reef. That shows, with the present reef two different conclusions are possible when concerned with the ambient nutrient concentrations. That is, either the reefs do not show any differential production of nitrate with that of the open ocean, or the production of nitrate at one point is compensated by the consumption in the other.

The second assumption may be considered more apt because of the efficient recycling of nutrients operating in a reef system, by which any leaking of nutrients into the surrounding water mass is minimized. The following studies prove support this statement. Webb and Wiebe (1978) at Lizard Island, Great Barrier Reef observed that nitrification in the coral community elevated the nitrate concentrations to above that of the nearby open ocean water, but also showed that it is efficiently utilized by reef corals and zooxanthellae-bearing foraminiferans. A lag period was absent in the uptake indicating that the responsible enzymes did not require induction. Crossland (1983) with a nutrient flow study in the same reef system arrived at a conclusion that depletion or elevation of nutrient levels in one benthic zone appeared to be balanced by the production in the other. So, while individual reef communities caused measurable changes, the reef system as a whole caused little net change to the nutrient chemistry of the water (Crossland, 1983). Wafar *et al.*, (1990) also confirmed this with their studies on nitrification in corals. They showed that NO_3^- production rates were equal to NO_3^- uptake rates by the zooxanthellae, suggesting a close coupling between these processes.

The evidence for the different biotic zones of production and consumption in the present study is clearly demonstrated from the station-wise differences in the nitrate distribution in the lagoon. Fig.3 shows the values of the 12 stations, average for the three seasons (pre-monsoon, monsoon and post-monsoon). The following features become apparent.

1) The stations covered in the lagoon showed increased values of nitrate than the outer sea stations, probably because the processes responsible for its regeneration are intense in the lagoon.

2) Webb *et al.* (1975) referring to nitrification state that corals and sponges release nitrate and nitrite into the surrounding waters. This is evidenced in this study as the distribution of nitrate shows higher concentration over coral patches. Transect studies also showed a marked station-wise variability (see Fig.35 in Chapter.3.2)

3) The nitrate values in the stations close to the wind-ward reef, with little coral cover and flushed with oceanic waters, remained low during most of the study period. However, relatively higher concentrations (>1.0 μg at l^{-1}) were observed in these stations during the monsoon months. Though it was difficult to delineate the source of this high nitrate water, it could be stated that nitrate is supplied from the oceanic waters to the reef in the monsoon months.

Fig.4 shows the seasonal distribution of nitrate for all the 12 stations. As a distinct spatial variability (differences between the stations) is evident, a distinct

|. 3. Seasonal average nitrate values.

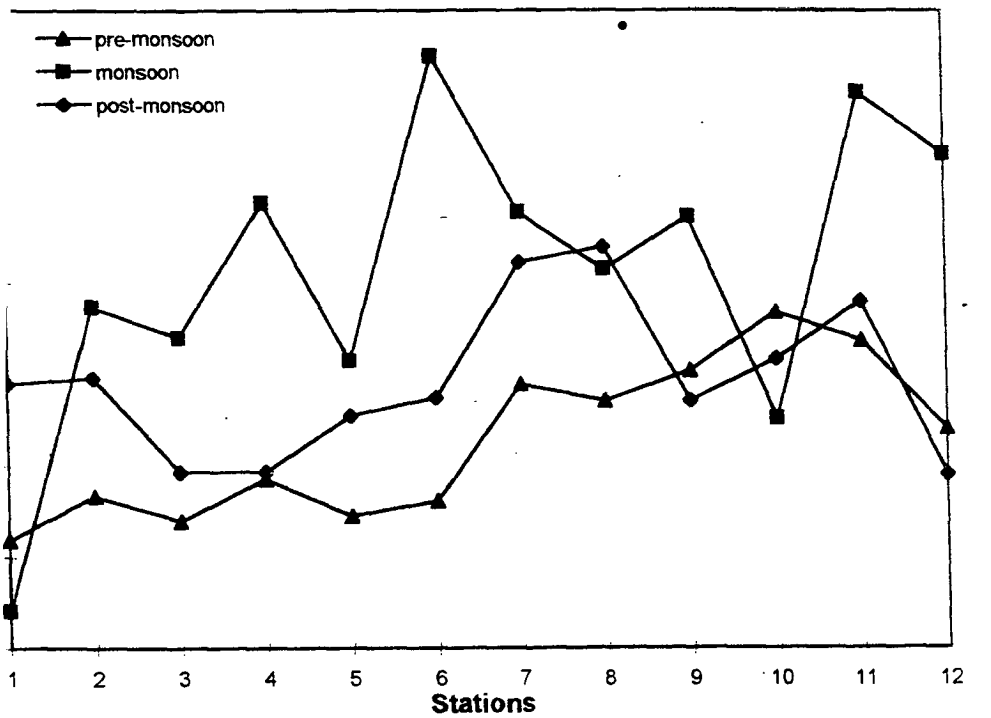
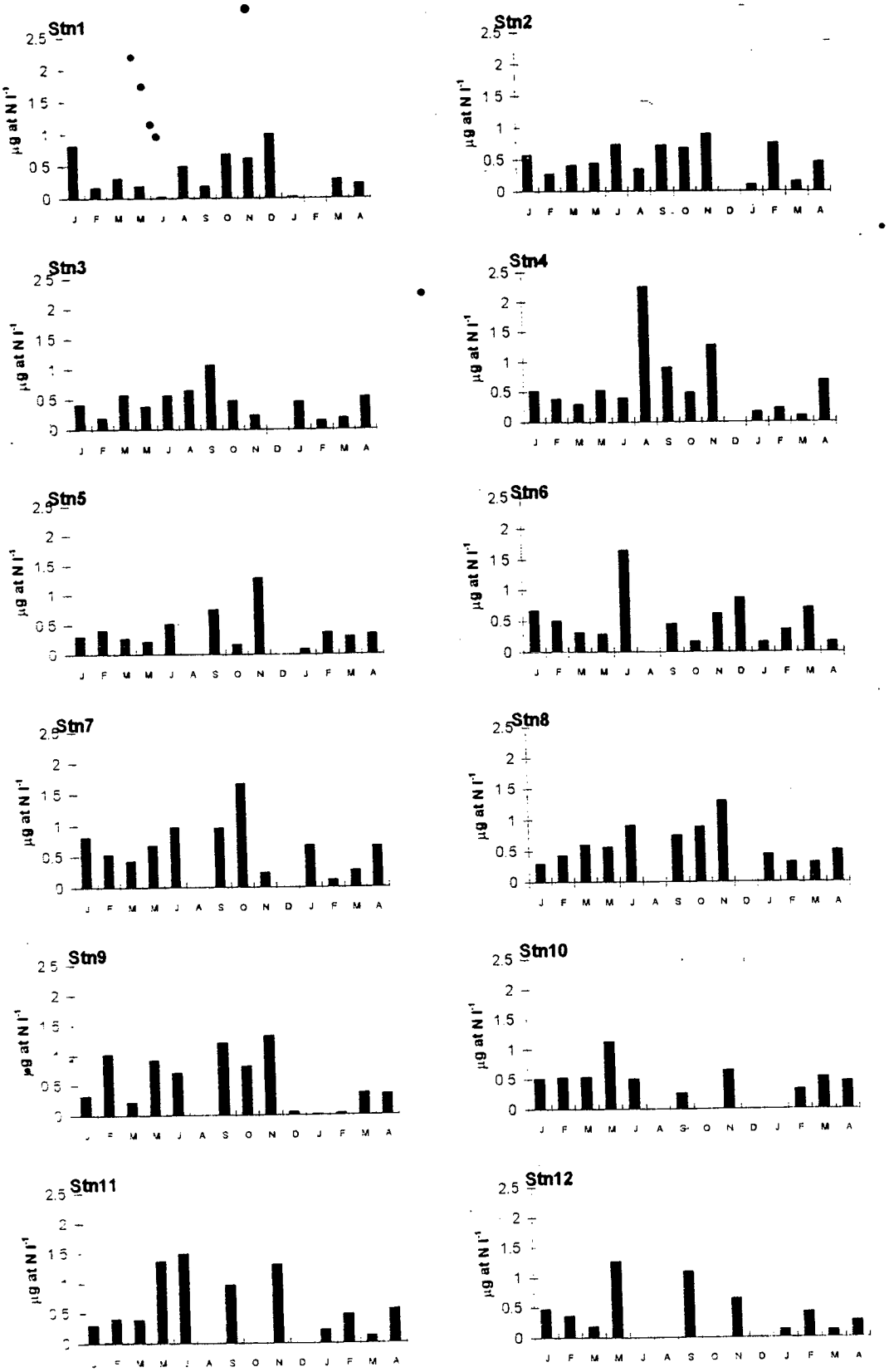


Fig.4. Distribution of nitrate in the lagoon stations



seasonality is also clearly discernible from these observations. ANOVA tests showed significant variations at 95% level (F = 5.071) between the three seasons and a higher significance of variation, between non-monsoon and monsoon months at 99% level (F = 13.255, n= 35) Table 4. The trend is clear from the monthly mean values integrated from the 12 stations (Fig.5a), that shows a distinct peak in the monsoon months (range: >0.5 - 1.5), with a declining phase in the post-monsoon months (range: >0.5 - 0.6). The values remained low through the entire pre-monsoon season (>0.2 - 0.5), with out any peak value.

As mentioned earlier in the introduction, the nitrate supply can be from external sources by physical processes or from *in situ* regeneration by biological processes. The distinct seasonality of nitrate in this case suggests that supplies by external sources may be more important than *in situ* regeneration. The reason here is discussed based on the following observations.

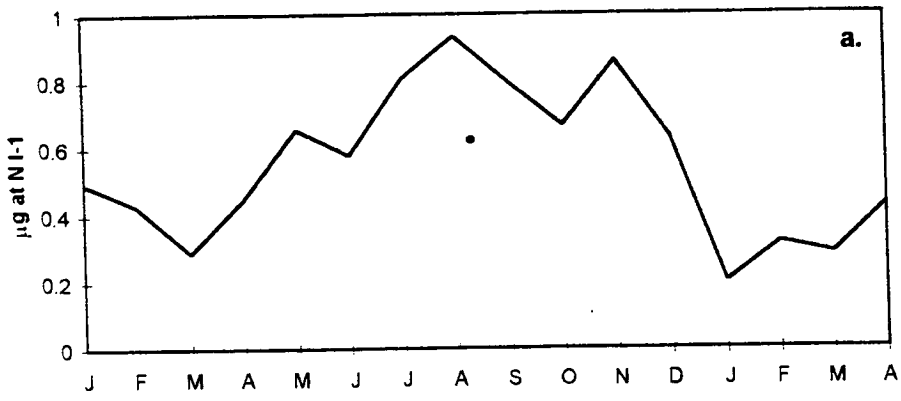
1) All the other compounds of nitrogen, except nitrate, exhibit seasonal peak in the post-monsoon months that could be explained by the high biological productivity in this season. The chlorophyll *a* values were correlated well with the ambient concentrations of these compounds. The possible explanation for this is the *in situ* regeneration by the biological processes (see for details in the respective chapters for NH_4^-, urea and DON). Where as nitrate concentrations exhibit a reverse trend that could not be explained by the seasonal high in the biological productivity (Fig.5b).

able 4. F values of the ANOVA tests for the different nutrients to show variations etween the seasons. (S - *significantly varied*, NS - *not significantly varied at 99% vles).*

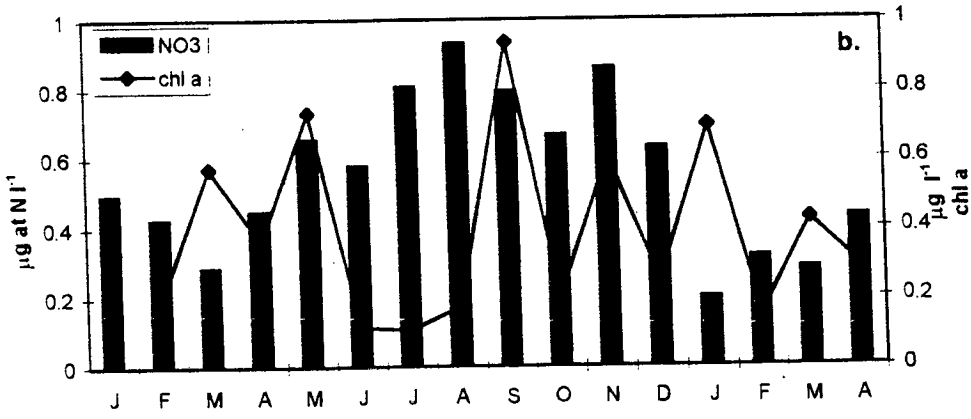
utrient	Between the seasons (n)	pre-monsoon and monsoon(n)	monsoon and post-monsoon(n)	monsoon and non-monsoon(n)
O_3^-	7.7311*(35)	12.0704 *(23)	5.0711(23)	13.255*(35)
O_2^-	5.724 *(35)	5.44 (23)	0.354 (23)	0.825 (35)
$H4^+$	19.184 *(28)	36.91 *(16)	32.77 *(16)	34.45 *
rea	7.522 *(35)	23.203 *(23)	10.527 *(23)	13.695 *(35)
ON	41.68 *(35)	58.087 *(23)	7.115 (23)	25.355*(35)
ON	2.804 (34)	4.73 (NS) (22)	5.103 (23)	5.507 (34)
hl a	19.07 *(32)	16. 014 *(22)	27.838 *(20)	15.607 *(32)

= Significant at $p<.01$ level.

Fig.5 a. Average nitrate from the lagoon stations.



b. Comparision of nitrate concentrations with chlorophyll a.



2) The second evidence comes from the results on nitrification studies. Previous studies (Webb *et al.*, 1975; Webb and Wiebe, 1975; Wafar *et al.*, 1990) showed that nitrification enhances nitrate concentration in the reef waters than in the oceanic waters. Though the present results on nitrate showed spatial distribution with reference to the different sites of nitrification (e.g. coral communities) the values did not show any comparison with the seasonal pattern of nitrification rates(Fig.29b and c)

3) The third evidence is from the increased values of nitrate in the stations close to the outer reef in the monsoon months (see #3 in the discussion for station-wise differences.

3.1.1.2 Nitrite

Nitrite (NO_2^-) is an intermediate compound in the nitrogen cycle in the sea. It is produced during 1)nitrification (NH_4^- to NO_2^-), 2)denitrification (NO_3^- to N_2O), 3)dissimilatory nitrate reduction (NO_3^- to N_2 or ammonia in some cases - see Sorensen, 1978) and 4)nitrate assimilation or assimilatory nitrate reduction (NO_3^- to NH_4^+). Here, the first three processes are mediated by bacteria and the fourth one, by organisms bearing chlorophyll i.e. autotrophs, including phytoplankton and a number of aerobic bacteria and fungi (Hattori, 1983).

Nitrite produced during any of these processes may be released into the ambient waters. The rate at which these processes proceed vary in the sea depending on the quantity of substrate available and its supply (either through biogenic or external sources), physical conditions (light, O_2 etc) and with the efficiency of the organisms responsible for each. For example, most of the profiles of NO_2^- distribution in the sea show a secondary nitrite maximum. The primary nitrite maximum usually occurs just below the euphotic zone. The cause for this is the nitrite excretion during assimilatory nitrate reduction that is coupled to photosynthesis. When the requirements of light for photosynthesis are not met with (light limitation), the nitrate reduced to nitrite is not reduced any further in the cells and nitrite is excreted (Vaccaro and Ryther, 1960; Packard *et al.*, 1978). The second one, the deep secondary nitrite maximum usually located after the nitrate maximum, in oxygen - depleted waters. This is caused by nitrate reduction by heterotrophic bacteria i.e. denitrification (Brandhost, 1959).

In the surface oceanic waters (0 - 100 m) nitrite concentration are usually at limits below detection or not more than 0.1 μg at N l^{-1}, compared to the concentration of nitrate (0.2 μg at N l^{-1}) and ammonium (<0.5) (Table.2 Sharp,1983). The reason may be that the processes mentioned earlier (nitrite excretion by phytoplankton and denitrification by bacteria), that are responsible for the nitrite maxima are inhibited by light oxygenated conditions in the photic zone. In coastal waters, nitrite concentration range from trace to 2 μg at N l^{-1} in the estuarine waters, from traces to 30 μg at N l^{-1} (Table.2). The concentrations in these environments may owe their origin to external sources such as freshwater advection through river flow and land run-off.

Concentration of nitrite measured in coral reefs are shown in Table.3 (reproduced from Crossland, 1983). The values listed here are considerably higher than those reported from the oceanic areas. The possible sources by which nitrite is produced in these waters may be biological rather than supplies from external sources (see introdutory chapter on seasonal flux studies). However, given the physical conditions of a reef (sufficient light and saturation of oxygen O_2, upto, and at times beyond, 100%, nitrite excretion and denitrification would not account for these concentrations. The most plausible process that can contribute significantly to nitrite production is nitrification. This can be supported by two observations. Firstly, nitrification in reef waters are several times higher than other oceanic systems (Webb and Wiebe, 1975; Webb *et al.*, 1975; Andrews and Muller, 1983, Szmant and Froelich, 1983). Secondly, during nitrification, oxidation of ammonium to nitrite is relatively rapid (Rajendaran, 1974), and can lead to an accumulation of nitrite being its oxidation to nitrate.

The processes of denitrification and dissimilatory nitrate reduction may not be operating significantly in coral reefs, because of the highly oxigenated conditions. Hence, nitrite production through these processes could be considered insignificant. Recent investigations, however, have identified several microhabitats in coral reefs that are anoxic (Sansone, 1985; Risk and Muller, 1983; Skyring and Chambers, 1976; Cohen, 1984). However the extent of nitrate production in these habitats is unknown.

Nitrite concentrations measured in the present study ranged from below detection limits to 1.57 μg at N l^{-1}, over the entire study period (Table 2 in appendix). The average value (0.12 ± 0.12 μg at N l^{-1}) estimated here is considerably lower than those from reefs associated with high islands (see Table 2). These fringing reefs may be receiving more

nutrient inputs through ground water (Marsh, 1977) and surface run-off (Wade, 1976) compared to oceanic atolls as the present one. However, the average and the range in nitrite concentrations in the present study compare well with those of high, moated (e.g. Great Barrier Reef) reefs (range: 0.07 - 0.17 μg at N l^{-1}), possibly because of the location of the barrier further away from the shore.

Average values of nitrite concentration in the three seasons showed the highest value in the post-monsoon months (0.15 ± 0.16) followed by a slightly lower monsoon value (0.14 ± 0.19) and a remarkably low pre-monsoon value (0.07 ± 0.02). The values show a reverse trend to that of nitrate with the monsoon months (June - August), exhibiting very low concentrations that at times fell below the limits of detection (Fig. 6 and 7). A significantly high peak was observed in the month of September at most of the stations (Fig. 7). This peak becomes sharpen the values from all stations are integrated: the peak starts from September and extends into the post monsoon period (Fig. 9). ANOVA tests showed significant variations in NO_2 concentration between the three seasons ($F = 5.724$, $p < 0.01$, $n = 35$), but did not show significant variations when any two seasons were compared (Table 4). This is because of the extension of the high peak into both the monsoon and post-monsoon months. Hence, the discussion on the seasonal variability is confined more towards an explanation of the high values in the months of September to November (0.3 ± 0.17), in comparison with the moderate values during the rest of the period (0.07 ± 0.05).

As mentioned earlier, among the biological processes responsible for nitrite increase in the sea, nitrification is the only process that is significantly active in coral reefs. In the present study, however, seasonal changes in the nitrification rates in the sediment and lagoon waters showed a negative relation with the increase in NO_2^- concentrations (Fig. 29b

Fig. 6. Distribution of nitrite in the lagoon stations.

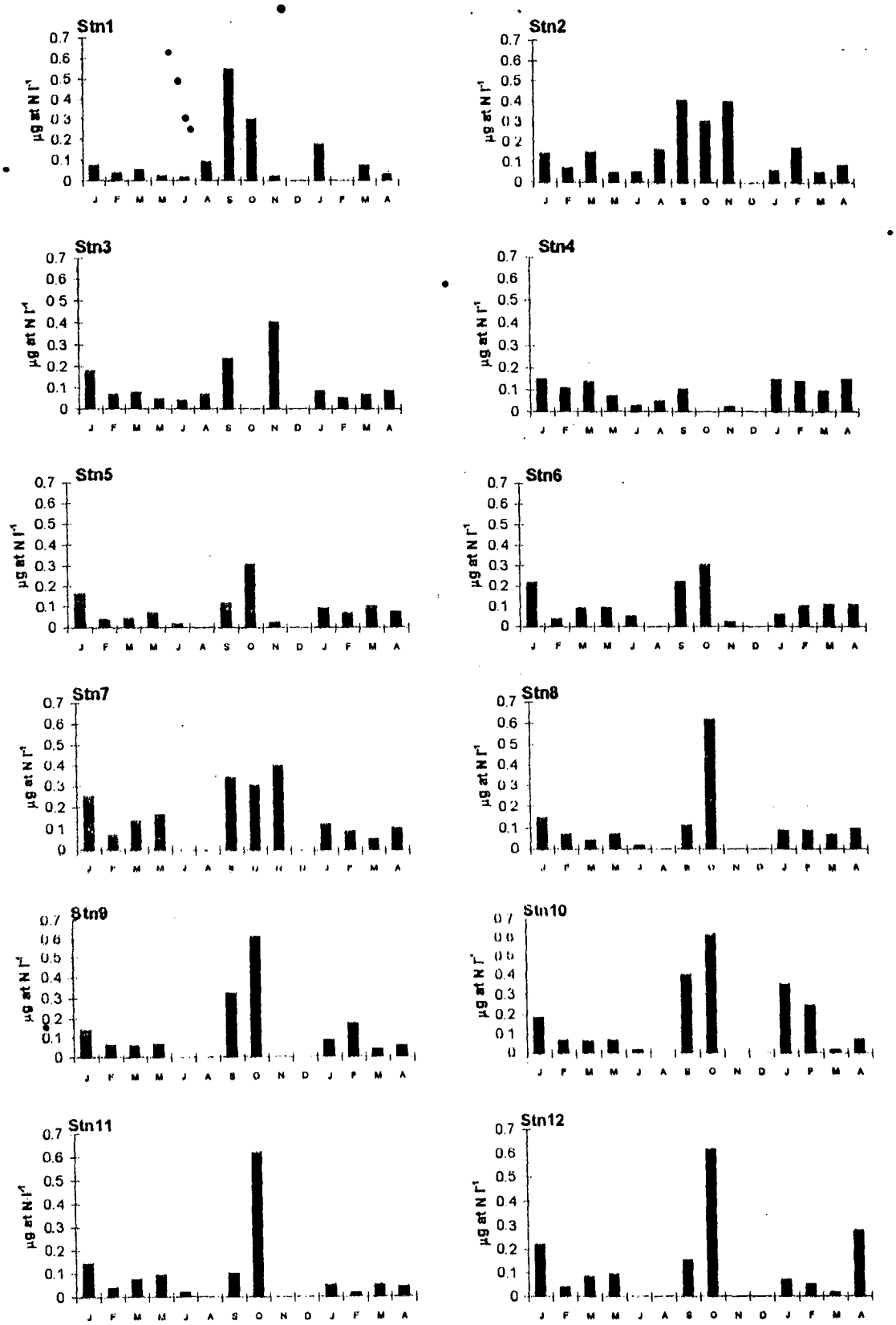
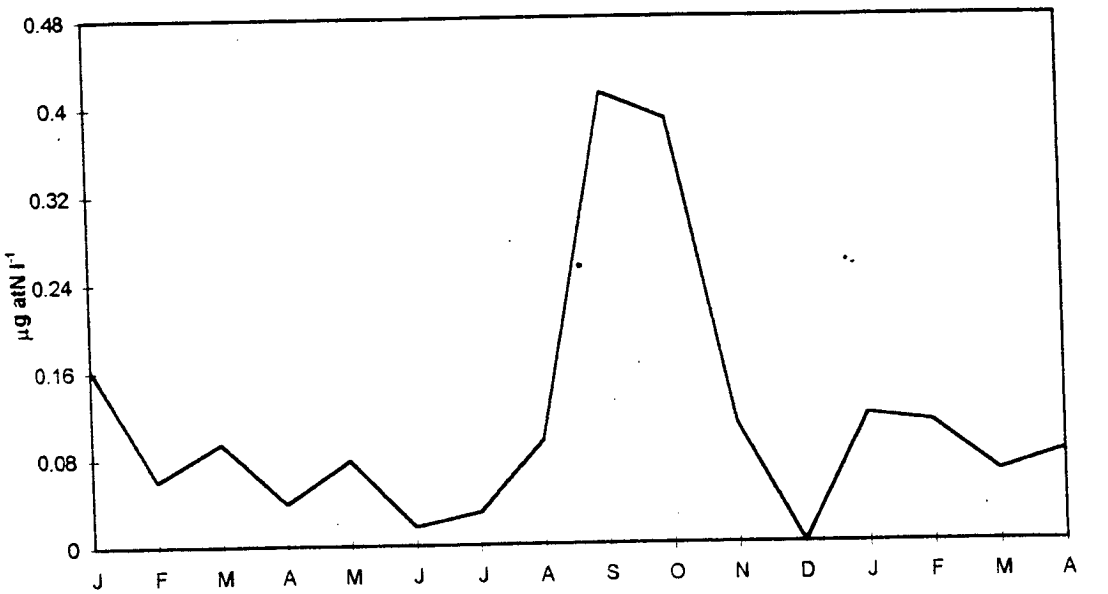


Fig. 7. Average nitrite values from the lagoon stations.

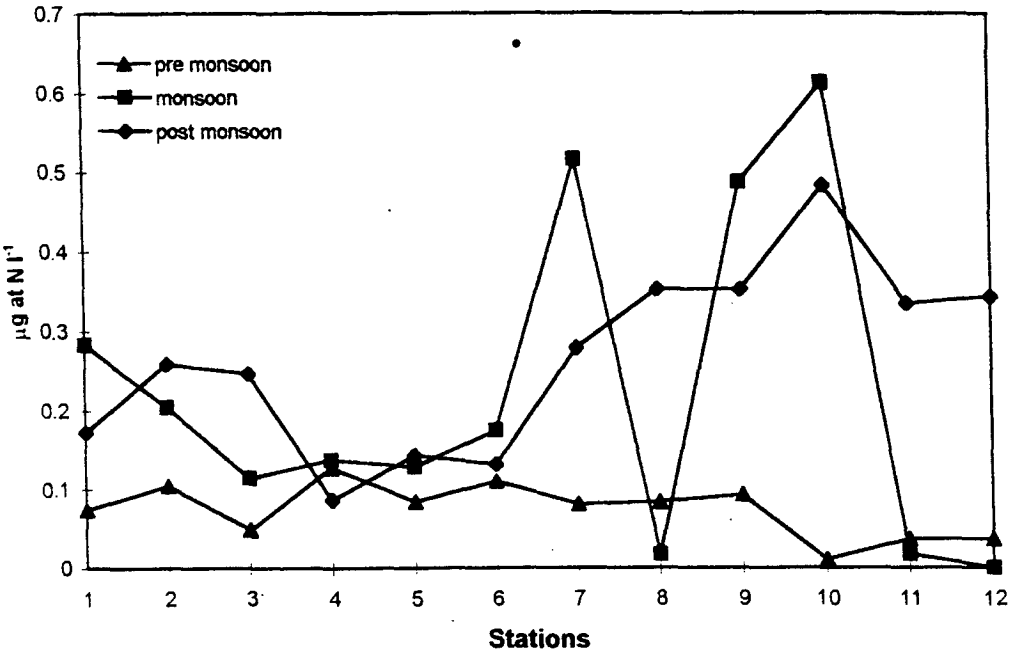


and c). The highest nitrite peak observed in September to October coincided with very low nitrification rates. A similar trend, where nitrification rates did not correlate with the nitrate concentrations also, was observed in the present study (see nitrate).

Compared to the changes of nitrate, those of nitrite follow a completely different seasonal trend. This shows that the external sources that supply nitrate may not be supplying nitrite (high NO_3^- concentrations in the monsoon months are attributed to external inputs). A comparison of the trends of the seasonal cycles of these two compounds shows that the nitrite peak closely follows that of nitrate. Nitrite production, after a nitrate peak can only happen through assimilatory and/or reduction of dissimilatory nitrate. Assimilatory nitrate reduction is unlikely to be of significance in reef waters, except at deep sediment layers or on the deeper waters of outer reef. Similarly dissimilatory nitrate reduction may not be a wide spread occurrence in reef, even though it is a possibility. The most likely explanation is that the nitrite peak is part of the nitrogen cycle, but the resultant nitrate peak is not apparent because of a rapid oxidation. Besides, the time interval between two samples is not short enough to detect a nitrate peak after the nitrite peak (the nitrate peak precedes the nitrite peak has an external origin).

The average values obtained for three seasons at the 12 stations are plotted in Fig. 8. The station-wise variability is not clearly marked in the pre-monsoon months, but becomes marked in the monsoon and post-monsoon months. While the lagoon waters undergo extensive physical disturbances during the monsoon, they exhibit high biological productivity associated with calm conditions in the post-monsoon season. Thus, the variations associated with the nitrite concentrations have distinct physical and biological

Fig.8. Seasonal average nitrite(NO_2^-) values.



causes. The very low values observed in the pre-monsoon period could be due to low biological productivity since other factors (nutrients) may be limiting in this season.

The stations 4,5,6 and 8 which lie close to the open ocean had very low concentrations (<0.2 μg at N l^{-1}) owing to the mixing with oceanic water. This trend is clearly observed in the monsoon season but less marked in the post and pre-monsoon months. Comparatively higher values (>0.4 μg at N l^{-1}) are observed in the coral patches which are located in areas of low exchange with oceanic waters (stations 7 and 10). NO_2^- availability is also more in the shallow stations (9, 11 and 12).

These observations show that biological processes can be responsible for active nitrite production at different sites of a reef. The high concentrations in coral dominated zones may presumably be due to nitrification (see below). Denitrification/dissimilatory nitrate reduction can also be occurring widely in coral reefs (Wiebe, 1985). However, the studies are very few. In the shallow stations, the availability of NO_2^- may be more due to efflux from the sediments. The proof is the high rates of sediment nitrification observed in the present study. Denitrification in the sediments can also cause sufficient efflux.

To conclude, the nitrite levels in the present study do not suggest any external input. If any input had been there, it was not associated with NO_3^-. Secondly, the processes, dissimilatory and assimilatory nitrate reduction are assumed to be active in the present reef. Thirdly, efflux from sediments should be considered as a significant source of NO_2^-.

3.1.1.3 Ammonium (NH_4^+)

The generalized picture of vertical distribution of ammonium in the ocean shows a maximum near the bottom of the euphotic zone. This distribution, however, is not clearly demonstrated as compared to nitrite (Sharp, 1983). Sharp (1983), from observations on distribution of ammonium from other oceanic region, concluded that ammonium occurred in deep waters in measurable concentrations but they did not show a clear depth- dependant pattern.

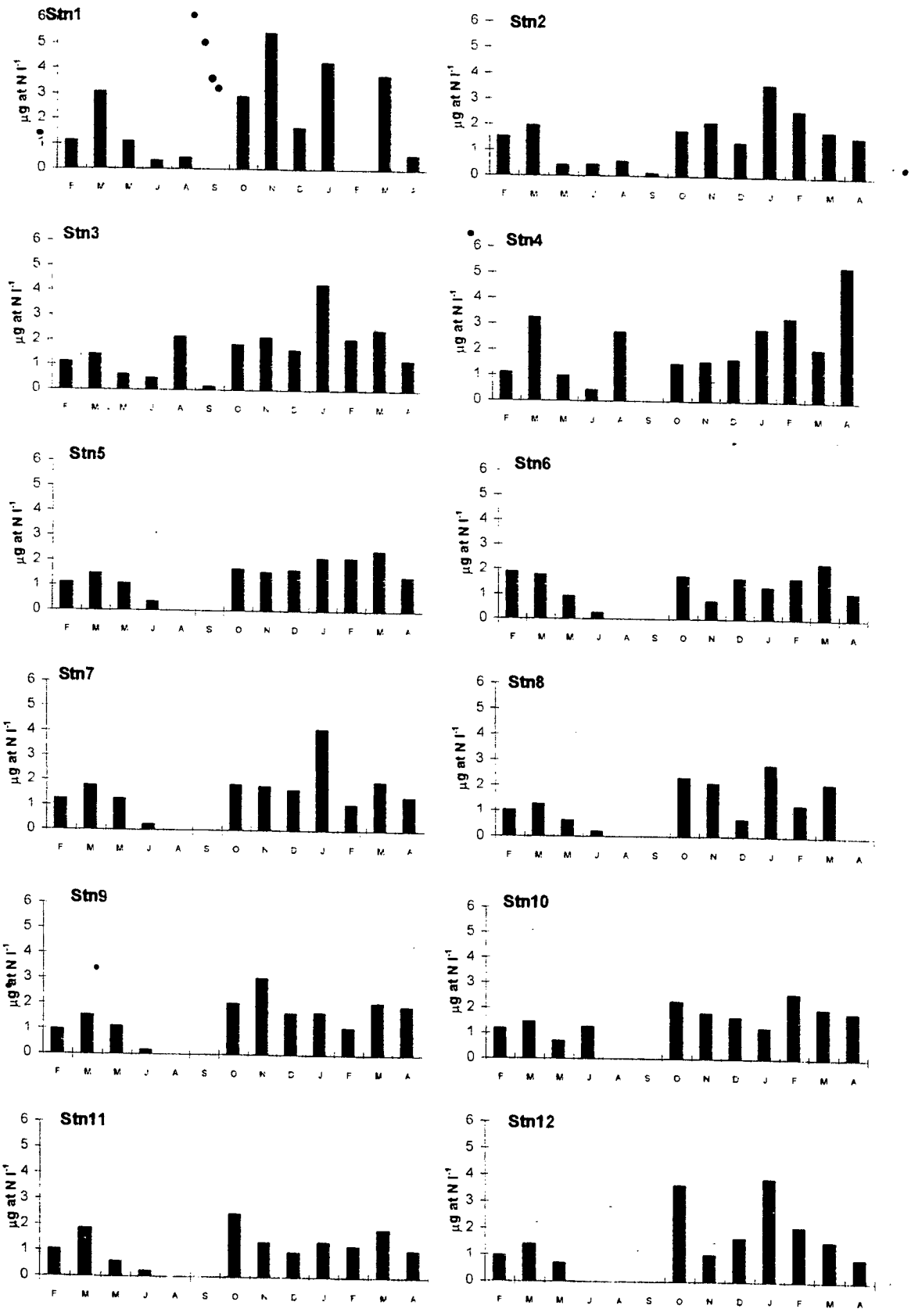
The average values of ammonium estimated for surface oceanic, deep oceanic, coastal and estuarine waters are summarised in Table 2. Though the concentrations were higher than those of nitrate and nitrite in the surface oceanic waters, in the deep waters they were very low compared to those of nitrate. Similarly, estuarine and coastal waters also have generally lower concentrations of NH_4^- compared to NO_3^-. However, as far as its role as a nitrogenous nutrient in the marine environment is concerned, ammonium has a role as important as, are more important than, of nitrate.

The significance of ammonium in the marine environment can be recognized from the following facts. They include, 1). the most preferred form of dissolved inorganic nitrogen (DIN) by phytoplankton (McCarthy, *et al.*, 1977; Eppley *et al.*, 1979; Billen, 1984) as well as heterotrophic microorganisms 2) major form of biogenic input to the ocean (Sharp,1983) and 3) central component in the regeneration pathway (Boucher *et al.*, 1994). So far, the estimations of nitrogen concentrations in coral reefs (mainly tropical) have shown NH_4 as the most available form of dissolved inorganic nitrogen (Crossland, 1983). This is in contrast to the majority of the open ocean situations where almost all of the ionic nitrogen is in the thermodynamically stable form of nitrate (Sharp,1983). The high percentage of regenerated production compared to new production estimated in coral waters of Lakshadweep (Wafar *et al.*, 1986) lend support to the importance of NH_4^-.

Almost all of the measurement of ammonia in coral reefs (Table 3), show that the concentrations are low and lie in a narrow range (0.2 - 0.5 μg at N l^{-1}) except for some observations (e.g. Canton atoll lagoon where the values ranged from 0.09 - 1.30 μg at N l^{-1}). Values from high latitude reefs (temperate), on the contrary, were generally high and also varied greatly (0.07 to 11 μg at N l^{-1}). Compared with the atolls, reefs around high islands also showed high concentration of ammonium, in the range of 0.3 - 2.6 μg at N l^{-1}.

In the present study, ammonium concentration in the lagoon ranged from 0 - 5.38 μg at N^{-1} . However, majority of the observations were in the range of 0 - 1.5 μg at N l^{-1} and concentrations >1.5 μg at N l^{-1} were not frequent (Table 3 in appendix Fig.9). Except for the high values the NH_4 concentration compare well with many of the earlier estimations from oceanic reefs(Table.3).

Fig. 9. Distribution of ammonium in the lagoon stations.

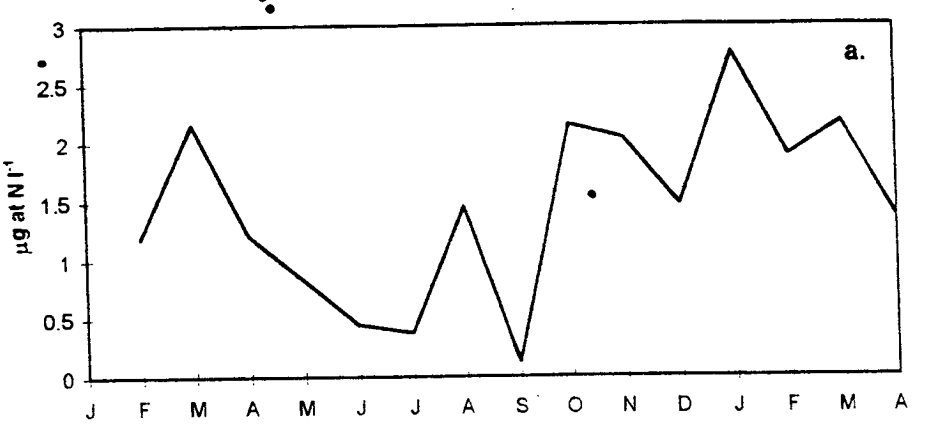


The monthly average of NH_4 concentration from the 12 lagoon stations showed highest values (2.8 µg at N l^{-1}) in the month of February and lowest values in the month of September (0.126 µg at N l^{-1}) (Fig.10a.). Concentration in the monsoon months (mean: 0.60 ± 0.59 µg at N l^{-1}) were remarkably lower than those of the pre- and post-monsoon seasons. The post-monsoon values (mean: 2.11 ± 0.53 µg at N l^{-1}) were comparatively higher than the pre-monsoon values (mean: 1.1 ± 0.18 µg at N l^{-1}). Analysis of the data for statistical variation showed significant variations at 99 % level, between three seasons (F = 19.184, n= 28) and between monsoonal and nonmonsoonal months (F = 34.452, n= 35) (Table 4). The seasonal variability patterns as a whole did not differ much among the stations (Fig.11).

Annual cycles of NH_4^- in most of the coastal and estuarine waters are controlled by terrigenous inputs. Sharp (1983), observed that terrigenous inputs, often from sewage, can affect the NH_4^- values. Coral atolls situated in oceanic waters hardly receive any such inputs. Nitrate values of the present study are the first to show some input from external sources (see nitrate chapter) - this needs to be ascertained further by direct estimations. However, the same cannot be assumed for ammonium since these two compounds (ammonium and nitrate) do not always have a similar behaviour or distribution pattern in their seasonal abundance. The seasonality in this case therefore can be explained only by *in situ* changes (mostly the biological processes of production and regeneration within the reef) and an attempt here is made to expalin the present seasonal cycles on the basis of this.

The elevated concentrations of NH_4^- in the post-monsoon season attest to the fact that ambient concentrations of NH_4^- are considerably influenced by the high biological productivty associated with this season. Lerat *et al.* (1990) in temperate waters observed that seasonal cycles in water column NH_4^- concentrations are associated with phytoplankton

Fig 10. a. Average values of NH_4^+ from lagoon stations.



b. Comparative plot of NH_4^+ concentration with chl. a.

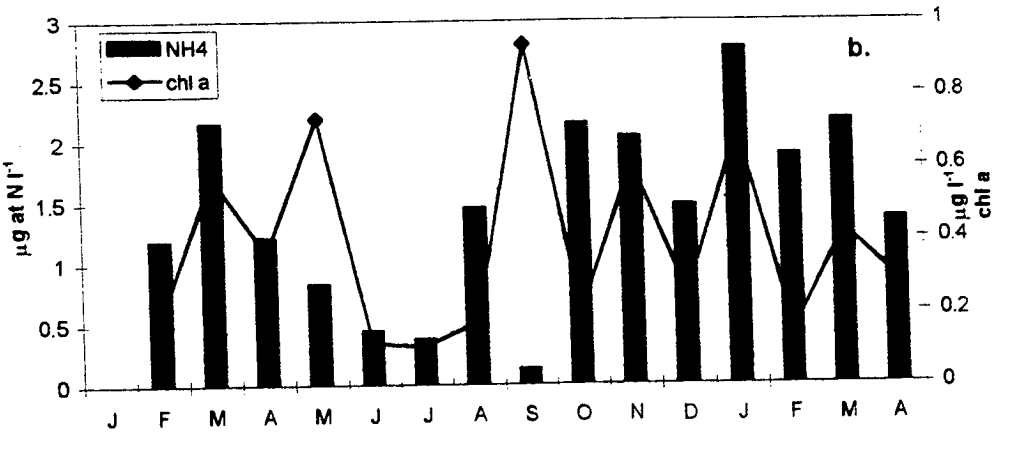
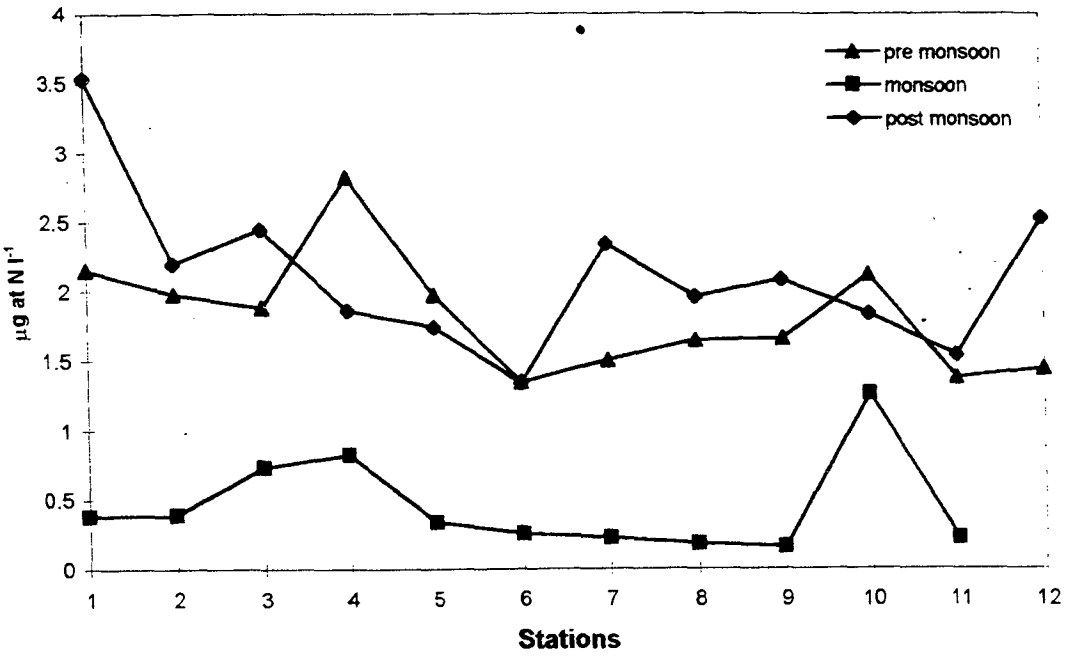


Fig 11. Seasonal average ammonium values.



development. In reef waters, however, the water column $NH4^+$ concentrations can hardly be seriously altered by phytoplankton because of its low biomass.

Fig 10b. shows a comparative plot of NH_4^+ concentrations aginst chlorophyll *a*. At most instances the ammonium values showed good correlation with chlorophyll *a* except for some points where they differed from each other (e.g. high Chlorophyll a peak in September did not coincide with the NH_4^+ value in that month). This shows that increase in phytoplankton biomass occurred with the increase in NH_4^+ concentrations. One clear inference from this observation is that phytoplankton here is dependent on NH_4^+ availability for its growth and they utilize this compound efficiently during the times it is availble in sufficient quantities (see ammonium uptake by phytoplankton).

A relationship similar to that of phytoplankton has also been seen with the nitrifying microorganisms. This is evident from the increase in nitrification rates with the increase in ammonia concentrations (Fig 29b and c). This aspect is discussed in more detail in the chapter on nitrification.

The above mentioned processes (phytoplankton abundance/assimilation and nitrification) cannot be responsible for the increase in ammonium concentrations, because 1) it is utilized in both the cases and 2) increase in concentrations are found to enhance the rate of the processess and not *vice-versa*.

Lerat *et al.* (1990) identified the oxidation of soluble organic nitrogen (SON) as a major source for NH_4^+ accumulation in the sediment pore water. This can be effluxed into the water column and enhance the water column NH_4^+ levels. Since the SON (Soluble Organic Nitrogen) input is strictly seasonal. owing to the rate of production of sedimentary organic material and its mineralization by endofauna, it can impart a seasonality to the water

coloumn NH4 concentration. Boynton and Kemp (1985) also reported significant correlations between C:N:P ratio of high organic matter at the top of the sediment and nutrient fluxes (NH_4, PO_4). Therefore, to conclude, the enhancement of NH4+ levels in the nonmonsoon months can be largely attributed to the organic material production which in turn produce ammonium through its degradation and remineralization.

In contrast to the marked seasonal patterns, the station wise data did not show a clear spatial variability. The trend shows that the values from stations 5, 6, 7 and 8 remained low for most of the period, compared with other stations. The same trend is also observed at stations 11 and 12 except for pre-monsoon (mainly February). Nutrient flux studies across the reef system of Lizard island, Great Barrier Reef, showed that NH_4 is taken up in the winward and leeward reefs and there is a net consumption of this nutrient (Crossland, 1983). The present data, however, did not show any marked spatial variability for ammonium among the 12 stations that can be used as clear evidences of exchange of nutrients at different community assemblages of the reef during the flow of water across the reef.

Several reasons can be put forward to explain why there are no spatial variations in ammonium.

There is no concrete evidence to show that the corals themselves are strictly ammonotelic. Kawaguti (1953) was the first to infer that ammonium is one of the excretary products of corals. Johannes and Webb (1970) observed that nitrogen is lost from corals as free amino acids along with products of protein catabolism (presumed to be ammonia). Later studies stated that ammonium is also produced largely from excretion by heterotrophs such as zooplankton (Wafar *et al.*, 1986), fishes (fish shoals and fish larvae accumulation) and other organisms (Meyer and Schutlz.,1985; Bishop and Greenwood,1994) that are

resident around the coral colonies and other parts of a reef. Kawaguti(1953) reported the absorption of ammonium by reef corals in the light while there is production in the dark. He concluded that zooxanthellae were responsible for the consumption of ammonia in the light. Lewis and Smith (1971) Muscatine and Cernichiari (1969) proved that zooxanthellae accumulate inorganic nitrogen compounds from solution and then translocate the organic N compounds to the animal host where they becomes incorporated into protein. Muscatine and D'Elia (1978) also proved that intact corals still remove ammonium from ambient waters as much as in light in dark.

It was proved that heterotrophic mode of feeding produced more ammonia than the autotrophic mode of feeding. This was observed from studies in which corals were fed zooplankton and the ammonium production compared with the corals that were not fed (Szmant-Frolich and Pilson, 1984). Hence, the autotrophic corals (mostly hermatypic or reef building or zooxanthellae dependent) will release very little NH_4. Thus it can be concluded from many observations that reef corals can maintain a low nutrient environment if they are actively autotrophic. The ambient levels of NH_4 estimated in this study support the hypothesis as already suggested by Wafar *et al.* (1993) that the algae would be limited of 'N' if there be no regenerative 'N' supplied.

Transect studies, however, show the accumulation of NH_4 over coral patches, suggesting that coral excretion may be responsible for this. This condition owes to the heterotrophic mode of feeding when there is enough animal food material (zooplankton) and when autotrophy is limited for other reasons.

3.1.1.4 Urea.

According to Remsen (1971), until the work of Vaccaro (1963) most measurements of available nitrogen included only nitrate and ammonia. Ryther's (1954) work was the first to introduce the measurements of urea along with NO_3 and NH_4 in nitrogenous nutrient studies and many followed suit (Degens *et al.*, 1964; Guillard, 1963). The importance of urea, that it can be used as a nitrogen source in the marine environment, as well as in the fresh water systems, has been realised later in the studies of phytoplankton uptake and regeneration processes.

The demonstration of urea uptake by phytoplankton has been done with laboratory cultures and also in the natural samples. The following studies form examples of the laboratory culture assays. Hodson *et al.* (1975) and William and Hodson (1977) studied urea metabolism and transport in fresh water Chlorophyte *Clamydomonas reinhardi*. In their studies, urea was taken up at higher concentrations (3 mM, and at lower concentrations it was repressed by ammonium (K_m = 5.1 μM). Carpenter *et al.* (1970) observed in *Skeletonema costatum* that this algae could use urea at ambient concentrations typical of some inshore habitats. Antia *et al.* (1975) who examined growth rates in 26 marine algae observed that 88% of the organisms showed good growth (often better than on ammonium) when urea was the sole nitrogen source. Rees and Syrett (1979a), in urea-grown cultures of the marine diatom *Phaeodactylum tricornutum*, observed an active transport system with high affinity for urea (Ks = 0.6 - 1.0 μM) and that addition of ammonium (0.1 - 10 mM) did not inhibit the short-term uptake of urea. However, the ammonium-grown cells could not take up urea and the capacity to transport urea appeared only after conditions of nitrogen

starvation (Rees *et al.*, 1980). The conclusion drawn from these and several other studies(Lui and Roles, 1970; McCarthy and Eppley, 1972; Syrett and Bekheet, 1977; Bekheet and Syrett, 1977; Horrigan and McCarthy, 1982; Goldman and Dennet, 1983; Molloy, 1987; Molloy and Syrett, 1988) demonstrate that phytoplankters possess a urea uptake system that follows saturation kinetics; they are able to accumulate urea intracellularly at a rate and to a concentration, that suggests that uptake is mediated by an active transport process (Antia *et al.*, 1991).

Several studies have reported on the uptake of urea in natural seawater samples. McCarthy and Eppley (1972) carried out seawater enrichment experiments to study uptake using 15N compounds. Their findings showed that in natural populations also, as that of pure cultures, the urea uptake is repressed under conditions of ammonium enrichment and that urea ranked second in importance to ammonium for phytoplankton nutrition. McCarthy *et al.* (1977) later proved this in Chesapeake Bay phytoplanktons; the order of preference as measured by uptake relative to availability was NH_4^+ > urea > NO_3^- >NO_2^-. Studies of Sorensson and Shalsten (1987) agreed well with these findings.

A large number of other studies also have shown that urea may be a significant source of available nitrogen for phytoplankton in both coastal and offshore waters, especially during periods when nitrate levels are limiting. Remsen's (1971) work in surface waters off the continental shelf between Panama and Callao, Peru, are in confimation of this. Other studies of importance which support this are as follows: McCarthy (1972), in stations off the coast of southern California, showed that urea accounted for 28% (range: < 1 to

60%) of the total 'nitrogen productivity'. Eppley *et al.* (1973) from their studies, recorded urea was as important a nitrogen source as ammonium for assimilation by phytoplankton and with excretion by zooplankton. Contrary to earlier studies, their results, also showed that urea is a much more important metabolite in the oligotrophic ocean. Price and Harrison (1988) used ^{15}N isotopes, with Sargasso Sea phytoplankton and showed that the uptake rates were saturated at ambient *insitu* concentrations of urea. An important aspect of these findings is that urea utilization is mostly associated with the photosynthetic activity of the phytoplankton (Mitamura and Saijo, 1975), rather than with heterotrophic assmilation. Therefore, the importance lies in the fact that, unlike ammonium, the utilization of urea is mostly by phytoplankon rather than by heterotrophic microorganisms, since it has been observed that a substantial fraction of ammonium assimilation is mediated by heterotrophic microorganisms(Webb and Hass, 1976 ; Laws *et al.*, 1985; Wheeler and Kirchman, 1986).

Another reason for urea to be recognised as an important N component is it's rapid turnover cycle. It is turned over rapidly to yield NH_3 and CO_2 and contribute significantly to the production of NH_4. The turnover times estimated in the euphotic zone of the sea were found to vary. Remsen *et al.*,(1974) in the North Atlantic, showed longer duration, ranging 59 to 98 days. Compared to this, Herbland (1976) in tropical Atlantic found very short turnover times (24 hours to 48 hours in the mixed layer). Similar short turnover times (mean 1.58 day.) have been estimated subsequently (Kokkinakis and Wheeler, 1988). Still shorter turn over times in a scale of hours has been estimated from marine sediments (Lomstein *et al.*, 1989; Lund and Blackburn, 1989; Lomstein and Blackburn, 1992; Pedersen *et al.*. 1993 a and b). Therkildsen and Lomstein (1994) also estimated rapid turnover times, varying between 36 and 133 min in the sediment surface (0 - 1 cm) and

between 38 and 17 hrs in the deeper sediments. They estimated that the urea turnover could account for 80% of the calculated maximum net NH_4 production (2.9 mol $N/m^2/yr$). Enhanced urea production also stimulated turnover rate (Lomstein *et al.*, 1989; Lomstein and Blackburn, 1992) From their observations, the enhanced urea production is concomitant with the production of high quality organic material (low C/N ratio) and with the presence of benthic macrofauna. Pedersen *et al.*. (1993 a) found that turnover rates of urea constituted up to 100% of the net NH_4 production rate in an afaunal sediment sample. This can account considerably in the NH_4 uptake by phytoplankton and consequently to the primary proctivity.

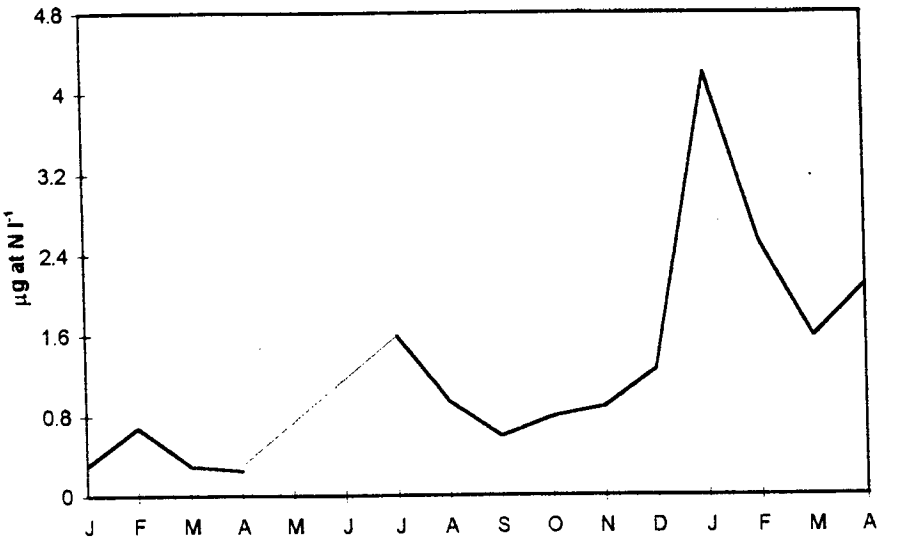
Lastly, the varied sources from which urea can be derived in the marine environment identify it's significance as an important N nutrient. It's importance as the exceretory product is secondary to the ammonium N. The following studies reveal the importance of urea production rates through zooplankton excretion: Corner and Newell (1967) reported that as much as 10% of the total nitrogen excreted by *Calanus helgolandicus* may be in the form of urea. Dagg *et al.* (1980) reported that urea formed 6-53% of the total nitrogen excreted by copepods from the Peru upwelling system. Reviewing works on urea excretion by marine zooplankton, Bidigare (1983) stated that urea and amino acids together represent ~20% of the total nitrogen released. Urea production through excretion from migrating fishes (Meyer and Schultz, 1985), larval fish aggregations (McCarthy and Whitledge, 1972) and shark infestations also form considerable inputs. Terrestrial outputs from sewage outlets and freshwater discharge can form localized urea enrichments in many environments (Remsen, 1971; Paasche and Kristiansen, 1982). Bacterial decomposition of organic matter is another important source of urea recognised in

the studies of Satoh (1980) and Pedersen *et al.*,(1993 a, b). Degradation of arginine and purines also contribute to the production of urea (Remsen *et al.*, 1974; Vogels and Drift, 1976).

Earlier estimations of urea in surface waters of World Oceans showed higher concentrations usually in coastal areas and relatively lower values in the oceanic waters. Newell (1967) found concentrations of urea as high as 3.07 μg at N l^{-1} in surface waters of the English channel, brought in perhaps by fresh water discharge. Remsen (1971), observed extremly patchy concentrations ranging from 0.54 - 5.00 μg at N l^{-1} in surface waters off the continental shelf between Panama and Callao, Peru. Sharp (1983) observed that the urea values estimated elsewhere in oceanic waters ranged from 0.1 - 1.0 μg at N l^{-1} and is in many orders higher than the average surface oceanic values of other inorganic nitrogen sources. In coral reefs, the estimations of urea were hardly been done. The data available from the Kaneohe Bay (Hawaii) showed that the values ranged from 0.4 - 2.0 μg at l^{-1} (Smith, 1977; Marshall *et al.*, 1975)

The concentrations of urea for the entire study period ranged from a low of 0.03 μg at l^{-1} to a high of 7.23 μg at l^{-1} as against the narrow range observed in the open ocean situations (Table 4 in appendix). ANOVA showed significant differences (99%) between all the three seasons and between monsoonal and non-monsoonal months (Table 4). The values decreased considerably in the monsoon than in the non-monsoonal months. Seen from the monthly observations the increased concentrations are in the months of November to February (Fig. 12.), which represent both the non-monsoon seasons of the year. The trend is still clear from the seasonally integrated values, which showed a highest value (2.53 μg at

Fig 12. Average urea values from all the 12 stations.



Dotted line = Data not collected

l^{-1}) in the post monsoon season followed by a slightly lower value (2.04 μg at l^{-1}) in the pre-monsoon season, and a lowest (0.87 μg at l^{-1}) in the monsoon period.

This definitive seasonality can to a certain extent mask the possible spatial variability. This is shown during the time of peak value and the lowest value observations. The peak value (7.23 μg at l^{-1}) for the whole observation lies in the month of January where the values did not fall below 2.0 μg at l^{-1} at all the 12 stations. Similarly the lowest values (0.03 μg at l^{-1}) are in the month of September and the concentrations were never higher than 0.5 μg at l^{-1}.

The prominent feature in this study is the distinctively lower concentrations in the monsoon months, compared to the almost similar values in both the non-monsoon seasons. Since the variability between both the calm seasons (non-monsoon) being less pronounced, the drop in the monsoonal values becomes an important parameter to discuss. The urea production from different sources and the level at which these sources are influenced by seasonal changes explains this trend. From the earlier studies, most of the urea production in the marine environment can be attributed to zooplankton excretion in the water column (Bidigere, 1983; Pandian,1975), or to macrofauna in both sediment and water column (McCarthy and Whitledge, 1972; McCarthy and Kamykowski, 1972). Other localized inputs studied are fish larvae aggregation (McCarthy and Whitledge, 1972), shark infestation (McCarthy and Kamykowski, 1972) and flux of terrestrial origin (Remsen, 1971). These studies, however, lack a seasonal coverage.

Remsen *et al.*, (1974) and McCarthy, (1980) identified microbial degradation of organic N compounds as 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,b). In coral reefs, the supply of organic matter can come from varied sources. Organic matter wastes from corals and associated macrofauna form the important part. Decomposing litter from seaweeds also contribute significantly. Wastes from migrating fishes has also been identified as an important source of detritus and nutrients(Smith and Marsh, 1973; Meyer and Schultz, 1985). Therkildsen and Lomstein (1994) observed a seasonality in the production of urea through microbial decomposition of organic matter. They found that the highest urea production rate is concurrent with the maxima in C- mineralization, temperature, the quality of organic material (low C/N) and a high macrofaunal biomass. Seasonal patterns are also observed in the level of organic matter input from migrating fishes (Meyer and Schultz, 1985). From these observations, it can be derived that organic matter can contribute significantly as a source of urea in coral reefs and with a defined seasonality. The normally high values in the non-monsoon seasons, observed in the present study can be explained with the enhanced supply of organic matter that is associated with the increase in biological productivity and the concomitant increase in biomass.

In monsoon months, however, all these processes may be operating in a low scale. leading to a decrease in urea concentrations. Moreover, the monsoonal influx of urea through continental sources (e.g. riverine input, ground water runoff etc.) may have very little influence in coral atolls, due to their location in oligotrophic oceans and away from these terrigeneous fluxes. The present observations therefore, suggest that the regenerative

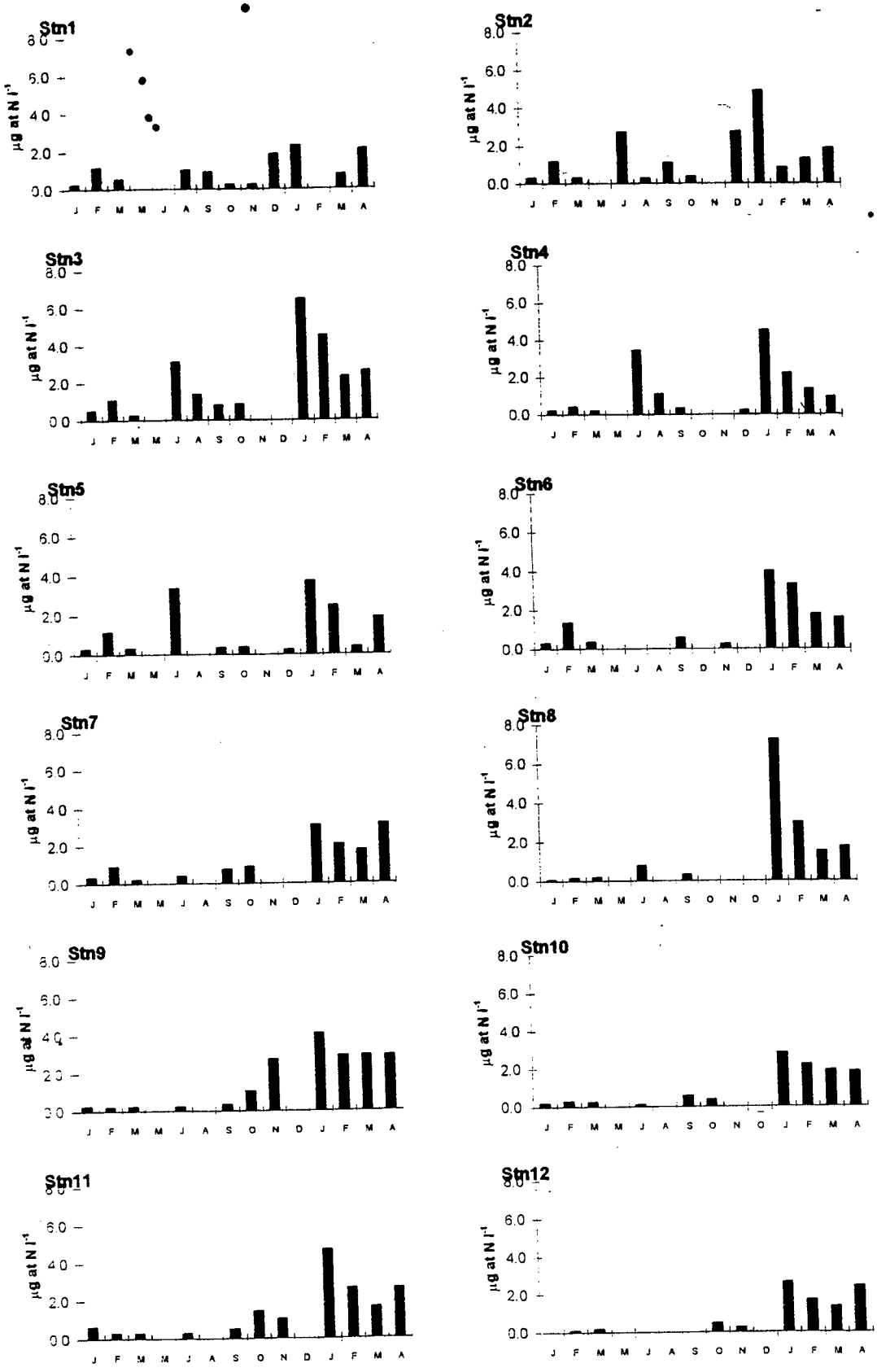
processes play a dominant role in the flux of urea than any input derived from external sources.

The absence of a spatially heterogenous distribution of urea is in sharp contrast with that of NO_3 and NH_4 in this study and the patchiness characteristic of urea observed elsewhere (Harrison *et al.*, 1985). Slightly higher values, however, were measured from the stations close to shore and along the coral patches (Fig 13). This can be due to more localized sources of urea enrichment (McCarthy and Whitledege, 1972; McCarthy and Kamykowski, 1972) and from other sources of organic matter input responsible for urea production(see above). However, such local increase is not substantial to justify a truely heterogenous distribution.

3.1.1.5 Dissolved Organic Nitrogen

The estimation of dissolved organic nitrogen (DON) in sea water is always beset with the problem of defining what exactly constitutes the limits between particulate, colloidal, and dissolved fractions and how to separate them without cross-contamination. Antia *et al.*(1991), in view of the difficulties in separating the minutest particulate material (i.e., picoplankton and femtoplanktonic particles and colloidal organic matter) from truly dissolved matter, suggested that it is useful to define the dimensions of DOM (or DON) in terms of filter pore size that enables its seperation from particulate material in a given water sample. Goldman and Dinnet (1985) suggested the error due to breakage of cells during filtration of the delicate athecate nanoplankton (mostly naked flagellates and

Fig.13. Distribution of urea in the lagoon stations.



coccoids) and leakage of fluids from the broken cells may also add to the DOM in the filtrate, thus introducing yet another error (Goldman and Dinnet, 1986).

Despite these shortcomings, the methodology as such for the estimation of DON has undergone considerable developments since the 70's. In Kjeldhal's (1883) procedure, the DON is digested to produce ammonium. This process was considered tedious and lacked sensitivity (D'Elia, 1983). It was followed by UV oxidation by which organic nitrogen is oxidized photochemically to produce nitrate. Though elegant and easy to use, this method is less precise with samples containing a large amount of nitrate (plus nitrite) and inefficient in decomposing N-N bonds. Koroleff's (1970) method of wet oxidation by persulphate was the most widely used for the measurement of organic nitrogen. As in the case of photochemical oxidation, persulphate technique also has a poor precision in the presence of large quantities of nitrite and nitrate. The dry combustion method of Gordon and Sutcliffe (1973) is the most accurate method in use where the seawater sample is freeze-dried and the residue ignited at a high temperature. This method is not widely used in routine analyses due to handling difficulties in the field conditions. All these methods are prone to contamination and need an ammonium correction with most of the eutrophic samples (e.g. Holm-Hansen *et al.*, 1966; Butler *et al.*, 1979). Sharp *et al.* (1983) observed that these methodological problems rendered most of the values reported in of the 1960s and 1970s appear either somewhat high or low.

In the present study, DON was measured by persulphate oxidation. This method, though lacking precision on samples with high turbidity and high nitrite plus nitrate content, is still practical for routine use and a better one among all the wet oxidation processes. The

dry combustion method was not used due to the difficulties discussed earlier. The values of DON discussed in this study is inclusive of urea though urea *per se* is discussed separately (see above).

Characterization of DON and its role in the marine nitrogen cycle have been the subject matter of several studies. Estimates of hitherto identified and quantified constituents of DON in offshore seawater suggest that some 70 - 80% of total DON still remain undefined (Antia and Landymore, 1975; Gardner and Stephens, 1978). Billen (1984) characterized DON in natural waters as:

1) a small free amino acid fraction directly usable by microbes,

2) dissolved proteins and polypeptides (combined hydrolyzable amino acids) constituting a much more important part (16 - 50%, Tuschall and Brezonik, 1980), and

3) a bulk fraction probably made of humic compounds, refractory to microbial attack (Thomas *et al.*, 1971).

However, theoretically, DON may be divided into high and low molecular weight nitrogen compounds (Antia *et al.*, 1991). Applying this in the above characterization by Billen (1984), the free amino acid fraction can be a low molecular weight component and the rest two can be grouped under the high molecular weight category.

According to Billen (1984), DON makes up 25 to 80% of the total nitrogen as a function of the season and represents both a nitrogen and an energy source for heterotrophic micro-organisms in the sea. Though literature on this topic began to accumulate since the elegant measurements made by Dursma (1961), the importance of DON as a nutrient has not yet been fully assessed due to its inherent complexity (Butler, *et al.*, 1979; Paul, 1983). In spite of

that, review studies on the concentration ranges of dissolved organic compounds showed that these values are correlated with the fluctuations of several biological processes that occur locally or diurnally or seasonally (Butler, *et al.*, 1979; Antia *et al.*, 1991). This is because of the close interdependence of micro- and macro-organisms (includes both fauna and flora) in a system which either produce or utilize the compounds at various rates and at different molecular levels.

Review work on DON and phytoplankton by Antia *et al.* (1991) states that with the exception of RNA and ATP virtually all the low molecular weight compounds (Ureides and Amidines, Amino acids and sugars, purines, pyrimidines, nucleotides, pteridines and flavins) are either excretory products or else derived from functional extracellular (cell surface-linked) metabolites of aquatic organisms.

With regard to nucleotides, RNA and ATP are believed to arise from the death and decay of aquatic organisms, replete with pools of such metabolites (Antia *et al.*, 1991) and DNA is produced by heterotrophic bacteria through their death and lysis (Paul *et al.*, 1987). The DCAA compounds (high molecular weight dissolved combined amino acids, presumably in the form of polypeptide or protein) have been found to be produced through excretion of microalgae (Newell *et al.*, 1972) and release of bacterial cell wall mucopeptide material (Salton, 1960). Billen (1984) lists these sources as three main process of DON production in the sea:

- extracellular release of dissolved organic matter by phytoplankton
- spontaneous lysis or spillage during zooplankton feeding
- excretion by zooplankton

The relevance of utilization and mineralization process of DON to marine nitrogen cycle has been investigated in many studies. Antia *et al.* (1991) reviewed studies on the utilization of DON compounds by microalgae with special reference to urea and amino acids. Their review shows that many species of marine phytoplankton cells can take up and assimilate urea as well as amino acids as nitrogen and energy sources. Billen (1984) in his review addresses its utilization by heterotrophic micro-organisms in the sea. He observed that heterotrophic utilization of amino acids is dominant than the algal uptake. Nevertheless, according to Rogers (1961), the high molecular weight polymeric material (proteins and peptides) which forms majority of the stocks and fluxes of DON (proteins and peptides) needed exoenzymatic hydrolysis before adsorption by bacteria. With mineralization, micro-organisms again are considered the direct mineralisers of organic matter (Billen, 1984). So, all these processes can cause direct changes in the DON levels at spatial and temporal scales in a system and predictably in a measurable magnitude. The seasonal and spatial scale estimations of DON can therefore be the first step towards understanding its flux. The DON estimations in the lagoon and open sea waters, in the present study is discussed in the following paragraph in order to address the changes in DON with respect to the biological processes.

The concentration of DON in the marine environment varies widely between surface, deep, coastal, oceanic and estuarine waters. DON concentrations in marine systems measured earlier are presented by Sharp (1983), Billen (1984), and Antia *et al.* (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})

waters (Table 2). Billen's (1984) review also listed highest DON concentrations (105 - 200 μg at N l^{-1}) in the estuaries. The coastal waters had lower concentrations (20 - 70 μg at N l^{-1}) followed by still lower oceanic upper layer values (5.2 - 8.2μg at N l^{-1}) and very low open ocean deep layer (3.3 - 6.9 μg at N l^{-1}) values. Gordon and Sutcliffe (1973), estimated DON by a dry combustion method and found the levels average 0.44 mg/l in surface waters and 0.12 mg/l in deep waters.

Very few studies in coral reefs have dealt with DON estimations. The studies that included DON estimations are in relation to benthic fluxes, eutrophication and other natural and man-made external inputs (Laponte and Clark, 1991; Alongi, 1996) rather than in the understanding of reef nitrogen cycling. Crossland's (1983) review work on dissolved nutrients in coral reefs lists the DON estimations from three major reef systems (oceanic atolls, high islands and high latitude reefs). The values ranged between 1.7 and 5.6 μg at N l^{-1} in oceanic atolls, 3.0 and 7.5 μg at N l^{-1} in high island reefs and 0.1 and 7.4 μg at N l^{-1} in high latitude reefs. The important observation is the low values reported and the narrow range in which they occur, in the oceanic atolls, compared to high island and high latitude reefs. The high values reported for these two systems attest to the role of continental sources in supplying DON to the reef waters.

The concentration of DON in the present study varied from 0.15 to 48.1 μg at N l^{-1} (Table 5 in appendix). These are remarkably higher than what were reported earlier from the oceanic atolls but lie within the range reported from the coastal locations (i.e., 3 - 10 μg at N l^{-1} - Antia *et al.*, 1991; 6 - 70 μg at N l^{-1} - Billen, 1984). Most of the data were, in the range of 10 - 25 μg at N l^{-1}. Only at rare occasions did the concentrations exceed 30 μg at N l^{-1}.

Seasonal changes in DON concentrations showed distinctive peaks in the months of July and November, with very high values for July (15 - 48 μg at N l^{-1},) and relatively higher values in the months of November (6 - 15 μg at N l^{-1},). The mean values obtained for these two months (July and November) are 25.7 μg at N l^{-1}, and 11.9 μg at N l^{-1}, respectively.

The monthly values integrated for the three prominent seasons shows elevated values in the monsoon period followed by reduced post-monsoon and pre-monsoon values (Table 5). The ANOVA shows significant ($p < 0.1$) variations among the three seasons and between the monsoon and non-monsoon seasons demonstrating seasonal differences associated with the monsoon climate (Table 4).

Seasonal variation of DON has been investigated in many marine ecosystems that are influenced by the coastal processes like river runoff, ground water discharge/subsurface fluxes (Wandzell and Swanson, 1996), nutrient enrichment by river plumes (Lopez and Cifuentes, 1994) etc. Estuaries and tidal creeks are the major recipients of DON through these processes. Most of these studies are related to coastal conditions. In coral reefs, at least as in the present case, external inputs of DON are unlikely to be of substantial importance, and hence the distinct seasonality observed in the present study, can only be explained by *in situ* changes in biological characteristics.

Table 5. Seasonal variability of DON values (μg at N l^{-1})

Stations	Pre monsoon	Monsoon	Post monsoon
1	--	15.97	7.76
2	9.04	11.87	5.32
3	0.622	16.496	15.159
4	1.985	21.98	7.226
5	1.466	25.39	7.64
6	0.999	6.102	6.43
7	--	19.54	8.918
8	1.984	24.27	9.334
9	1.20	18.39	5.6
10	1.82	34.28	6.429
11	2.45	12.94	6.009
12	1.44	--	12.18

Several other factors which can influence changes of DON concentrations are discussed below. Butler *et al.* (1979) reported a distinctive seasonal variation in total dissolved organic nitrogen concentrations at the English Channel Station E1, following the period of intense phytoplanktonic activities. Zher *et al.* (1988) also reported increased DON concentrations during periods of senescence of diatom blooms. *Trichodesmium* dinitrogen fixation has been accounted for the release of NH_4 and DON (Letelier and Karl, 1996). Unlike the other (external) processes discussed earlier, these processes can add nutrients to coral reefs and consequently influence the size of DON pool. However, these compounds are low molecular weight category and may get utilized very fast. Therefore, the changes in DON concentration should be due to compounds which are refractory to microbial attack and are of high molecular weight category. The following studies support this.

Billen (1984) in his review of the annual cycles of total amino acid concentrations from diverse areas (Andrews and Williams, 1971; Riley and Seagar, 1970; Crawford *et al.*, 1974; Billen *et al.*, 1980) did not find any clear evidence of important seasonal changes. It is because the pool size of the amino acids remained same, though there are differences of two orders of magnitude in the heterotrophic utilization of amino acids at some seasons and different locations (Billen, 1984). Moreover, the speedy assimilation by algal communities also helps the removal of amino acids from the water column so that any addition to the original amino acid pool does not become apparent. This applies to coral reefs where the efficient utilization and heterotrophic processes do not allow any apparent change in the easily labile DON concentrations. More emphatically, therefore, it should be the high molecular weight compounds that can add a seasonality to the DON concentrations and in coral reefs these should be the products of community metabolism. Humic compounds can

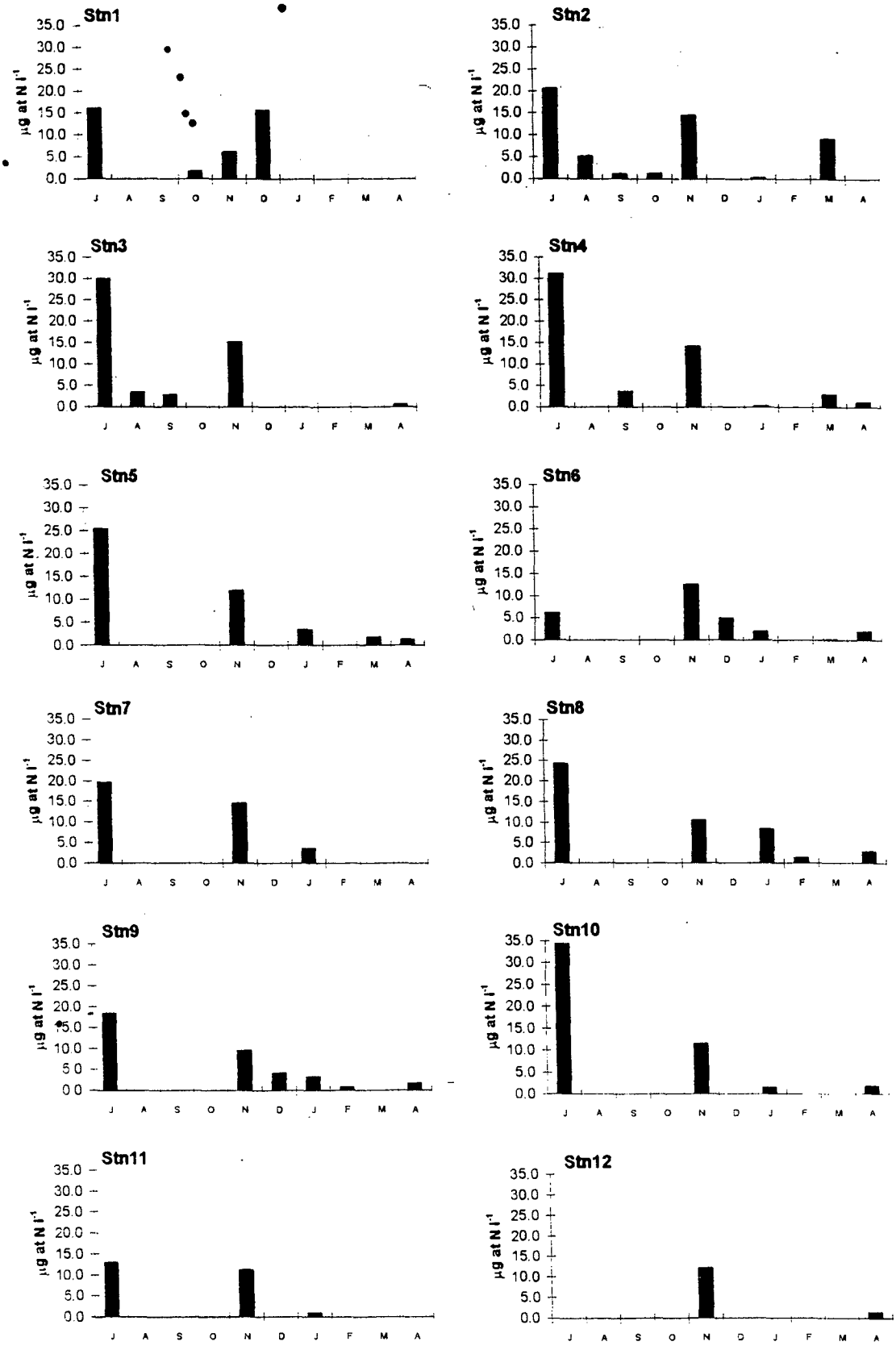
form such a product released by community metabolism in coral reefs. Billen (1984) showed that the humic compounds form the significant part of the dissolved organic matter which are refractory to microbial attack. The production here comes from seagrass beds, coral colonies and other macroalgal niches. This may be induced by the climatic conditions also.

The importance of seagrass beds in coral reef nutrient cycling is little studied. As suggested earlier, they are a rich source of humic compounds, and contribute significantly to the dissolved organic matter in coral reefs depending on their total biomass. Quantification of N contribution by decomposition of seagrass litter showed that it could meet 6-8% of the nitrogen requirement in salt marsh plants (Callagher *et al.*, 1984). The argument here is, the seagrass beds which can supply enough detritus so and enrich the organic N pool can introduce seasonality in the DON concentrations. Studies on seagrass beds showed distinct seasonal production and decomposition cycles. Leaf growth, leaf initiation, biomass and primary production were minimum in the winter months and maximum in summer, influenced by changes in water temperature and length of daylight hours. There was a seasonal thinning of dense seagrass beds due to foraging by migrating fishes. The export of material from the seagrass beds into the subtidal habitats is also seasonally coupled with the active physical forces like wind patterns. water motions and wave actions etc. (Kiler and Noris, 1988). Clearly, the seagrass beds undergo a seasonal cycle acted upon by various physical forces. Therefore, the production and release of organic material from this community are likely to bring change in the DON concentrations both seasonally and spatially. In the present study this can be understood in the following way.

In the Kalpeni Island, the lagoon widens in the northwest of the atoll, with much of the seagrass bed lying close to the shore on the west. In the monsoon months the winds, from the southwest direction can cause sufficient disturbances to these seagrass beds and lead to a resuspension of organic detritus. As argued earlier these humic compounds can serve as a rich source of organic material and enrich the organic N pool. In the present observation, this could have been the cause for the elevated DON levels close to the shore as well as for the high values reported for the monsoon months (see Fig. 14) (See also the stationwise variability).

Mucus produced by coral colonies is the second such source of organic material. The rate of mucus production was estimated as 10.8 $mg.m^{-2}/d$ and in terms of contribution to shallow reef, this value is equal to 88 $mg.m^{-2}/d$. In most cases the mucus production is reported to be elevated during unfavourable environmental conditions. These conditions are: extreme low tide exposures (Krupp, 1984), prolonged exposure to siltation mainly due to dredging (Marszalek, 1981) and sublethal exposure to pollutants (Segal, 1982). Biochemical estimations on the elemental composition of mucus revealed that it contained high carbon (31.7 ± 1.4 % w/w) with relatively low nitrogen (5.20 ± 0.93 % w/w) and phosphorous (0.287 ± 0.024)contents (Krupp, 1981). Estimated by the same author, the organic composition showed a high protein content next to carbohydrate. But Daumas *et al.* (1981) observed that a high proportion of the nitrogen contained in the mucus is in a non-protein form and this fraction seemed to decrease during the transformation of polyp mucus to floating mucus aggregates. Krupp (1984) also observed that consolidated mucus strands were rich in organic material while pure mucus was low in trophic quality. An overall view

Fig.14. Distribution of dissolved organic nitrogen (DON) in the lagoon stations.



of these studies shows that the mucus contains less N, either in the protein or non-protein fraction. From the view of the present study, however, the following observations have been made.

As with the case of seagrass detritus in the water column, the mucus production also is enhanced by the unfavourable weather conditions in the monsoon. This source may be smaller compared to detritus organic matter. Transect studies, however, demonstrate elevated levels of DON over live coral patches (Stations 7, 8, 9), than over the seagrass beds. In both the cases (seagrass beds and mucus), it is the overall abundance of organic material from these sources which substantially increases the organic N loading.

Zimmerman and Montgomery (1984) showed that decomposing algal mat reversed the nutrient concentration gradient in the sediment and was responsible for the subsequent build-up of dissolved nutrients in the sediment resulting from continued decomposition. These decomposing algal mats occurred seasonally and are found to load 'N'. Preliminary work on the decomposition rates of *Microcoleus lynbaceus* indicate a release of 3.8 μg N g^{-1} dry wt d^{-1} in the early stages of decomposition (reviewed by Zimmerman and Montgomery, 1984). In a similar study on the decomposition of tropical macroalgae *Caulerpa cupressoides*, William (1984) observed a release of 1.8 m mol N from 25 g wet weight algae within 7 days of the experiment. The predominant form of nitrogen released in these experiments was dissolved organic nitrogen (William, 1984). These studies prove that if the mat occurrence is a regular phenomenon, it can alter the DON concentrations considerably to show significant seasonal variations. However, no such studies have been

done so far to assess the impact of drifting algal masses and decomposition of macroalgae in coral reef nutrient cycling.

Many studies on nitrogen fixation claimed that the coral reef productivity is mainly supported by this new source of 'N'. Glibert and Bronk (1994) demonstrated that DON release from diazotroph *Trichodesmium* sp. can be a significant source of recently fixed nitrogen. The bloom of *Trichodesmium* sp., if it occurs in a seasonal pattern, can bring a seasonality to DON concentrations in the water column. The present study, however, does not have any evidence to support such a hypothesis, though the most favourable conditions in the post-monsoon months can favour such a bloom with the utlization of nutrients brought in during monsoon months.

Cornell *et al.* (1995) reported that atmospheric input of DON is another factor which could contribute to the oceanic 'N' input and that it is ubiquitous and significant component of precipitation. No estimations of this has been known so far from the Arabian Sea. Hence it would be critical in the present study to evaluate the importance of this source on the seasonal changes of DON.

3.1.1.6 Distribution Particulate Organic Nitrogen (PON)

Particulate matter in the sea is not a well categorized one. The simple definition that the organic matter retained on a membrane filter (or the filter in use, for that matter) called as 'particulate' is a very poor description. To define it in proper terms, particulate matter is mainly dependent on the choice of filters. and also on the sampling procedure involved. The following studies give a clear understanding on this subject. Sharp (1973, 1974) distinguished that the organic matter retained by a membrane filter does not comprise the

whole particulate matter in the water column because, many smaller particles that easily pass through this membrane are missed out. Secondly, the production of particulate matter and the flux to deep water of large particles are spatially heterogenous; thus water collections made with smaller samples may not include all of the particulate matter. Nonetheless, a large number of PON estimations were made by traditional water bottle collections, except in instances involving studies on particle flux and settling velocity.

Problems encountered in the determination of PON, however, are very few. Much of them arise out of contamination in the tedious digestion procedures involved. The two working procedures currently in use are Kjeldhal wet digestion by Kjeldhal (1883) and Dry combustion procedures by Gordon and Sutcliffe (1974). The present estimates were by Kjeldhal digestion method due to its easy use in a feild lab and inexpensive apparatus.

There is relatively more information availbale on particulate organic nitrogen than on dissolved organic nitrogen (DON) (Sharp, 1983). The common interest in the estimation of POC and PON, in most of the marine research is to use them as indicators of biomass, assess biological and ecological properties of plankton and as a parameter in the nutrient studies.

Most of the studies when POC and PON are measured relate them to phytoplankton productivity. To quote some of them: investigations of Fraga (1966), Garfield *et al.*. (1979), Packard and Dortch (1975), Slawyk *et al.*. (1978) and Vallespinos and Estrada (1975) suggest that PON and particulate protein concentrations tend to be positively correlated with biomass indicators (e.g., cholorophyll-a). Fraga (1966) observed a C/N ratio of 6.54 in the water column, the same as that of phytoplankton suggesting that the nitrogen was associated with the phytoplankton cells. Montegut and Montegut (1983) observed that the

POC, PON and PP are variable according to depths, seasons, and areas and are linked to ambient fertility (phytoplankton production). Their (Montegut and Montegut, 1983) observations also suggested that in surface waters, the phytoplankton and partly degraded cells of dead phytoplankton form the major part of the particulate matter composition, with the bacteria and living or dead zooplankton contributing to the minor part. All these observations suggest that phytoplankton in surface layers influence to a greater extent the concentration and composition of the particulate matter.

Another important reason for PON estimation is in the relationship of nitrogenous nutrients to particulates. Emphasis on this relationship is placed when Banse(1974) pointed out that the ratio of disappearence of nitrogen and phosphate ions from the water represents the net result of removal of the elements into the various particulate and dissolved organic pools and their release from any of the pools into the inorganic pools. This predicts that the estimations of PON will help to prove that relationship with reference to nitrogen. All studies on this topic depend on the fact that the geochemical cycle of the elements in a marine system is strongly dependent on, or influenced by the biological activity. More clearly, the production of organic matter acts as a major process of transfer of elements from the dissolved to the particulate form. It is therefore essential here to assess the particulate nitrogen distribution with reference to the nitrogen parameters in this study.

The following studies are examples which demonstrate that the elementary composition of plankton changes with a change in the nutrient content of the seawater. Garfield *et al.* (1979) observed a particulate protein maximum (which normally account for most of the PON) that was coincident with the secondary nitrite and particle maxima found

at 200 m in the Peru upwelling. Montegut and Montegut (1983) obtained results that were consistant with the experiments made on phytoplankton cultures (Antia et al, 1963), who observed that the protein content of phytoplankton decreased and carbohydrates and lipids increased as nitrate became exhausted. High PON production was also observed in the areas of strong upwelling, due to increased phytoplankton production with the influx of nutrients (Suzuki and Matsukawa, 1987).

Besides phytoplankton production, decomposition and remineralization of dissolved organic nitrogen compounds play a major role in determining the PON pool. The cycle is described as follows.

PON is produced by phytoplankton in surface waters. It sinks out of the euphotic zone or usually enters the marine food chain through zooplankton grazing. Heterotrophs convert the organic N from the fecal pellets and particles of dead plankton into inorganic N. This inorganic N can then serve once more as a nutrient for phytoplankton growth.

Estuaries and coastal areas are different from oceanic systems where the cycle described here is not completely applicable since it receives external supplies of both nutrients and particulate matter. However, studies still remain inconclusive about such allocthnous inputs in coastal systems. Estimations of Bhosle *et al.* (1985) is one such example. They estimated low POC/PON, POC/Chl-a, and PON/Chl-a ratios at two stations in a estuarine system (Mahe, Western India), indicating, autochthonous production (*in situ* production) contributes to the majority of the particulate production and consequently the carbon and nitrogen compounds.

The different roles of PON in marine N cycle has been explained in the following studies. Firstly, it helps in the downward removal of nutrients from the upper water coloumn. Steele and Baird (1972) and Davies (1975) using sediment traps have shown that that 30 - 40% of annual water column production N may be transported to bottom sediments. Secondly, it can act as a source of N in the subsurface and bottom waters as it is getting utilized and remineralized (Garfield *et al.*, 1979).

Earlier measurements of particulate organic nitrogen show that the concentrations vary regionally and in both surface and deep waters. In surface oceanic environment, particulate organic nitrogen values are usually in the range of 0.1 - 0.5 μg at l^{-1}, while deep water values are usually below 0.07 μg at N l^{-1} (Gordon, 1971; Ichikawa and Nishizawa, 1975). In coastal waters, it is found in the range of 0.1 - 30 μg at N l^{-1} (Postma, 1966; Haines, 1979; Culberson *et al.*, 1982). Estuarine values have been reported to lie in the range of 5 - 100 μg at N l^{-1} (Postma, 1966; Haines, 1979; Culberson *et al.*, 1982). Garfield *et al.* (1979) used particulate protein as a measure of PON and observed that the surface values ranged from 0.7 to 24.4 μg at N l^{-1} in 1969 and from 0.3 to 13.2 μg at N l^{-1} in 1977 in the Peru upwelling system. On comparison, they found that these values were higher by a factor of 10 from those of non-upwelling areas.

Variations in surface and deep waters has also been reported in several studies. Garfield *et al.*, (1979) observed that the particulate protein concentrations decreased exponentially with depth in water column down to 1000 m with no further decrease below 1000 m. They also reported a subsurface maxima of protein concentrations between 130 and 230 m coinciding with the secondary nitrite maximum.

Yanada and Maita (1978) studied seasonal variations of PON in Funka Bay, Japan. They estimated an average concentration of 22 μg N l^{-1} (range: 4 - 59 μg N l^{-1}) with the maximum values in early spring and in July coinciding with the high productivity in the surface waters. Seasonal variations are also attributed to the high productivity due to strong upwelling during different times of the year (Pak *et al.*, 1980; Yanada and Maita, 1978).

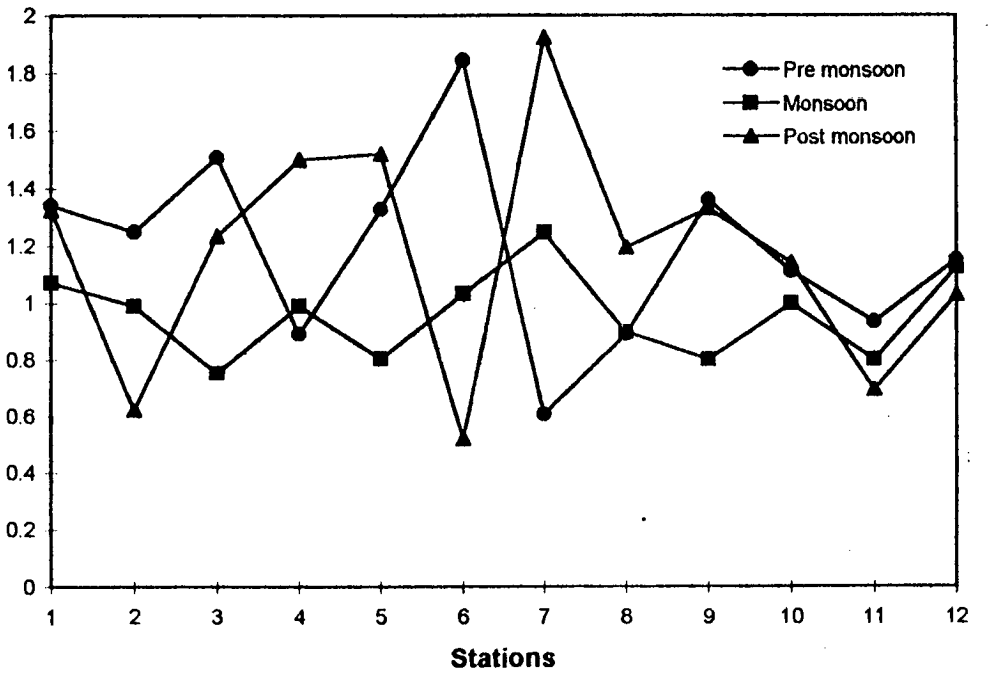
The PON flux studies also have been carried in different ecosystems. For example, Morrel and Corredor (1993) in a mangrove lagoon, calculated the overall mean fluxes through particulate organic matter input to the sedimentary environment as 789 μ mol m^{-2} h^{-1}.

In coral reef ecosystems the PON esimations are few, and are limited to those of Coles and Strathman (1973), Sorokin (1974), Crossland (1983), and Rothans and Muller (1991).

The present study on PON in the reef water had the following objectives: 1) to understand the seasonal variability in the ambient PON distributions; 2) to understand the spatial variability with reference to the special biotopes of the coral atoll and 3) to examine the interrelationship of ambient dissoved inorganic and organic N concentrations with the availability of PON at seasonal and spatial scales.

The concentrations estimated in the lagoon varied from 5.74 μg N l^{-1} to 34.86 μg N l^{-1} over the whole study period (Table 6 in appendix). Monthly observations show that the concentrations are elevated in the non-monsoon months than in the monsoon months. The integrated values obtained for the three seasons show a reduced average of 12.62 ± 1.62 μg N l^{-1} for the monsoon months with the pre- and post- monsoon seasons showing nearly uniform values (16.68 ± 2.8, 16.4 ± 2.7 μg N l^{-1}) (Fig 15). Analysis of variance (Table4)

Fig. 15. Seasonal distribution of particulate organic nitrogen(PON).



showed that the difference between monsoon and non-monsoon months are statistically significant at 95% level. No significant variations were showed among the three seasons, unlike it was the case with the major N forms (Table 4).

The station-wise variability is remarkable during certain observations within the study though the averaged values tend to mask these. The increase in concentrations occurred at stations (5, 6, 7, 8) above the live coral cover patches. Very low concentrations were observed from the shallow areas representing sandy patches.

The PON concentrations measured at the lagooon and reef stations in the present study are similar to those reported from coastal waters (Postma, 1966 ; Haines, 1979), but lie within a comparatively narrow range. The values were also ten times (in a way similar to the Peru upwelling system) higher than the oceanic values reported (Gordon, 1971; Ichikawa and Nishizawa, 1975). However, it should be noted that the PON values from oceanic waters in this region are low and resemble those of any other oceanic/oligotrophic waters.

There are two ways by which coral reefs can be enriched of particulate nutrients. Firstly, the intrinsic sources in which materials are produced within the reef system through primary and secondary producers and secondly the extrinsic sources from the neighboring environments (e.g. mangroves, estuaries), migration of animals and particulate input through pollution and other man-made inputs (Rothans and Muller, 1991). In case of atolls, the extrinsic sources are few which suggests that the PON enrichment in this system should come mainly from the internal sources. This is true in the present study area where there are no reports of any exteranl particulate matter input. The very low oceanic values, comparable

to those of the oligotrophic systems also suggest that it is the production from the reef which constitute much of the available PON in the lagoon and outer reef waters.

Crossland (1983) studies have shown that the *in situ* production of PON in the lagoon is the major source for its abundance in the outer reef. They observed that the POC/PON ratio decreased considerably in the leeward reef flat and suggested nitrogen enrichment of organic particulates in the lagoon as a possible reason for the enhanced PON (low POC/PON ratio) over the leeward reef flat as the organic materials produced in the lagoon are being transported there. However, migrating fish communities may also form a distinct source of particulate matter enrichment of external origin (see below).

One important observation in the present study is the characteristic patchiness of PON concentrations in the lagoon. It varied distinctly between the lagoonal stations. This is noted only at certain observations during the calm seasons when there is no sufficient mixing in the lagoon, but doesnot become apparent when data from all the observations are pooled. Earlier studies give a general description of lagoonal enrichment without characterising the various zones of enrichment. Crossland (1983), for example, observed significantly greater levels of NH_4, POC and PON in waters within the lagoon and the front of leeward reef flat. In the present study, PON estimations from stations characterized as sea grass beds, live coral zones, and sandy patches give a clear picture of varied enrichment of PON, which can lead to the overall increase in the lagoonal concentrations as well. It also indicates clearly that the particulate concentrations in the water increased with the increase in biomass at various locations. Coral colonies harbour lot of organisms and play a host for migrating communities of foraging fishes. These fish communities forage

off the reef and return to shelters in the reef. The fecal material released during this time could be an important source of organic and inorganic nutrients to reef community. This can be one source of PON enrichment since corals as such cannot contribute much for PON budget as they produce low trophic quality (low nitrogen content) metabolic wastes which include mucus material (Krupp, 1981).

The topography of Kalpeni would also explain the station-wise variability. It is such that the entire stretch of leeward region is covered by the island land mass except for a small patch of reef flat exposed in between the Cheriyam and Kalpeni islands. This prevents sufficient mixing of lagoon waters under conditions of calm weather and also does not allow the unidirectional flow of water towards the leeward reef. The export of nutrients also therefore, must take place only during flood tides or through the well connected channel passages in the wind ward side. The station-wise variability is better pronounced due to this well defined reef structure.

The PON values did not show well marked seasonal differences. The concentrations did not vary significantly between the three seasons, in contrast to those of other major N forms. Differences at 95% level (ANOVA) however, were observed between the monsoon and the non-monsoon months. As reported earlier (Funka Bay, Japan- Yanada and Maita, 1978) this can be related to the high productivity period with the increase in chl a concentrations showing a phytoplankton-dependent PON production. The same situation has also been reported during upwelling at different times of the year (Pak *et al.*, 1980; Yanada and Maita, 1978).

In the present study, though the phytoplankton dependent PON production appears to dominate during favourable weather conditions (availability of light, nutrients), the

increase is only marginal (in other words, the monsoon values are only marginally reduced), attesting to the role of heterotrophs in the PON production.

Sorokin (1974) estimated the production of bacteria in coral reefs. His values ranged from 0.8 - 436 mg C/g/day as against the photosynthetic production of 3.2 - 550 mg C/g/day. This shows that bacterial production forms a considerable portion of the total microflora in coral reefs. This probably explains why the PON concentrations are not much varied throughout the year.

To conclude, the PON is not solely dependent on the primary producers (phytoplankton production), as it is shown from the seasonal studies. Therefore it is difficult to assume that the PON production is dependent on new nitrogen sources. It might probably come from the regenerated material mostly supplied within the lagoon.

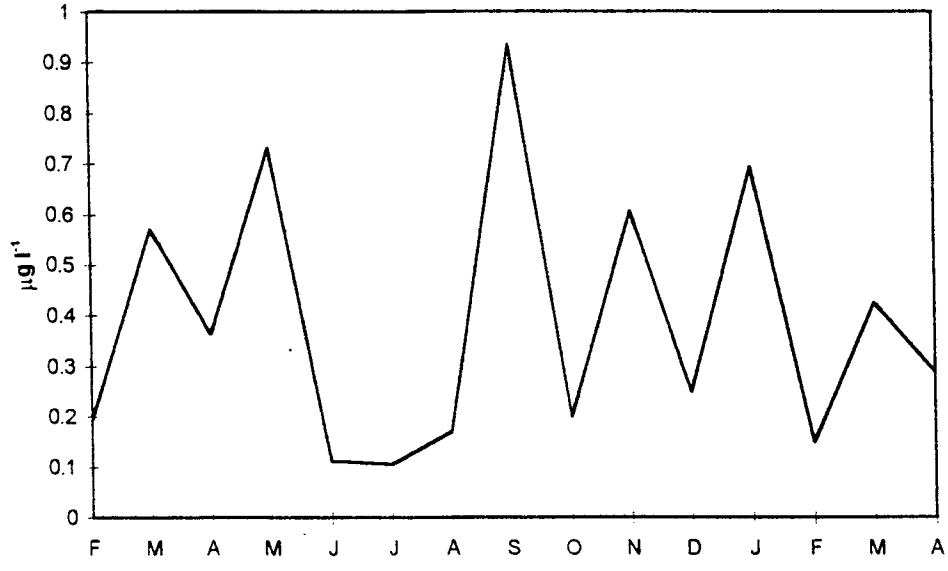
3.1.1.7 Chlorophyll a and Phaeopigments

Chlorophyll and other plant pigment measurements are convenient and rapid methods of measuring phytoplankton biomass in the sea. Besides the composition of the plant pigments (Chl *a*, *b*, *c* and carotenoids) and the state of their degradation phaeo and chlorophyll a are indicators of several other characteristics of phytoplankton assemblage. (Strickland and Parsons, 1972; Harris, 1996). Therefore, their applicability found wide usage in marine systems. To cite a few : Jeffrey (1974) documented the use of accessory pigments as specific biomarkers for marine algal groups. Trees *et al.* (1985) used variations in chlorophylls *a*, *b*, and *c* and their degradation products to investigate changes in phytoplankton biomass and physiological conditons in the North western Atlantic Ocean.. Lorenzen used the phaeo/chlorophyll *a* to demonstrate the state of

decomposition of plant pigments. Wafar *et al.* 1986 found a good correlation between phaeo/chlorophyll a ratio and ammonium concentration which suggest that the dead planktonic matter is rapidly mineralised within the euphotic zone itself. Baines *et al.* (1994) used these estimations to understand the relationship between sinking flux and planktonic primary production. Smith *et al.* (1996) observed increase in biomass and primary productivity in the southern Ross Sea during mid-January, when surface chlorophyll concentrations averaged 4.9 $\mu g\ l^{-1}$. Nitrogen utilization studies also used chlorophyll measurements to differentiate between new and regenerated production associated with the deep chlorophyll maximum (Harrison, 1990).

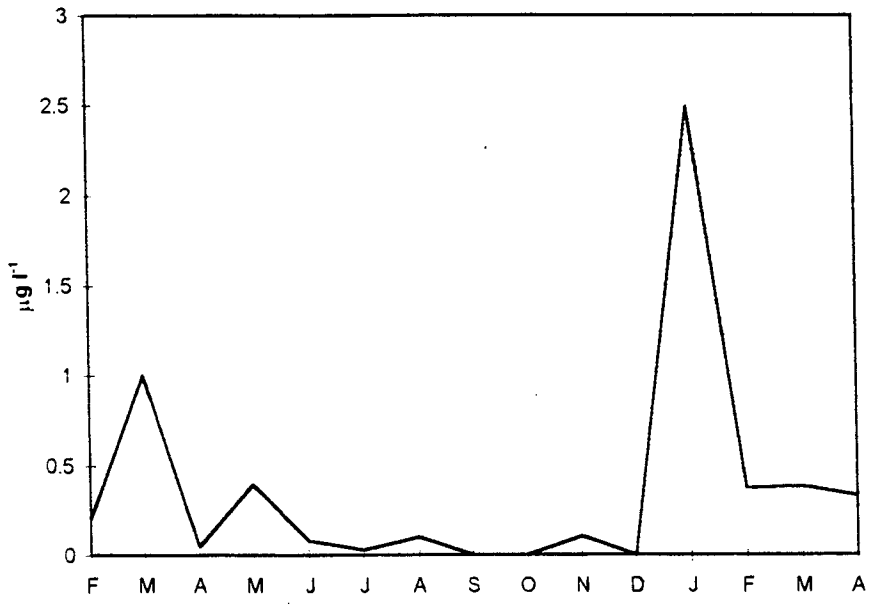
In the present study the spatial and temporal distribution of chlorophyll in the lagoon of Kalpeni atoll was also measured. The values fall in the range known for the resemble the oligotrophic situations (0 - 2.305 $\mu g\ l^{-1}$) (Table 7. in Appendix). The concentrations in the coastal waters were remarkably higher (0.49 - 2.69 mg chl a m^3). This proves that the present atoll also has the characteristic low net productivity that is typical of the oceanic atolls. Average values from the stations to show monthly variations shows a clear post monsoon high and a very low monsoon (Fig.16). The reasons for this are obvious as post monsoon months favour high biological productivity with more available nutrients and favourable weather conditions, whereas monsoon months exhibit low nutrient concentrations and limiting physical conditions (e.g. light). These estimations are made use in the uptake studies of nitrogenous species in the present study.

Fig. 16. Chlorophyll a values of the lagoon stations.



The trend in the seasonal phaeopigments in the present study clearly showed that the peak followed that of the chlorophyll (Fig 17).. This may be due to the degradation of the phytoplankton.

17. Phaeo pigment concentrations from the lagoon stations.



3.1.2 Uptake studies

The role of nutrients in regulating primary production has been recognised since almost from the beginning of this century, when it was realised that nitrate and phosphate are removed from seawater (by phytoplankton activity) in the same ratio in which they occur. This eventually gave rise to the classical concept of 'Redfield ratios'.

Studies on the kinetics of nutrient uptake by phytoplankton began earnestly in 1960's. Earlier studies on uptake of nitrogen by phytoplankton species were undertaken by following spectrophotometrically the ambient concentration changes. Nitrogen-depleted media were thus spiked with nitrate at concentrations ranging from 10 to 20 μM, and the depletion of nitrate in the medium during growth of the culture was followed over time (Caperon and Meyer 1972; Eppley *et al.*., 1969; Carpenter and Guillard, 1970). This approach is useful only when phytoplankton cultures with high biomass are used, and are not applicable to marine systems where the phytoplankton standing stocks are low. Again the sensitivity of the spectrophotometers (in the range of 0.05 - 45 μM for nitrate) is often not significantly different from the rate of nutrient removal by natural populations at lower ambient concentrations over several days incubations. Another major limitation for this approach in the natural systems is that the cause of depletion may not be due to phytoplankton alone but may also be due to bacterial processes, which lead to transformation from one compound to another. Therefore, there was a need for another technique where the different compounds can be labelled and their utilisation followed. Dugdale (1967) proposed the use of tracer methods, in order to have a direct measurement of the kinetics of uptake of a particular nutrient.

The use of radiotracers has come a long way ever since the development of ^{14}C method (Steemann and Neilson, 1952) for the measurements of marine primary production. Notwithstanding its extensive application, this method cannot help to distinguish the utilisation of individual nutrients by phytoplankton, especially with nitrogen, and hence primary production alone is inadequate to evaluate the export production. Dugdale and Goering (1967) showed from their studies on nitrogen

balance that the rate of export of organic nitrogen away from the euphotic zone cannot exceed the rate at which new production (production due to newly incorporated nitrogen i.e., NO_3-N, N_2) becomes available to replace it, if the phytoplankton production is to maintain itself in a steady-state. They also showed the advantages of using nitrogen rather than carbon and phosphorous as a tracer. The first reason is that nitrogen is a major structural component of cells and is reasonably constant in its ratio to carbon and phosphorous. Secondly, measurements of population growth using nitrogen may show less scatter than those using carbon or phosphorous, because the latter two are not only structural components but are continuously turned over in the energetic processes of organisms.

^{15}N has been identified as the ideal isotope to study the N processes, especialy N_2 fixaion (Dugdale *et al.*., 1961). Later studies by Goering *et al.*., (1964) and Dugdale and Goering (1967), focused on the use of ^{15}N for measuring the assimilation rates of dissolved inorganic nitrogen by marine phytoplankton. By using the stable isotope of ^{15}N, it was possible to measure the new and regenerated production rates separately, based on $^{15}NO_3$- and $^{15}NH_4$+ uptake. Since then ^{15}N remained the most widely used tracer for measurements of combined inorganic nitrogen assimilation in oceanographic studies (Harrison, 1983) and also for some dissolved organic nitrogen species such as urea (McCarthy, 1972).

So far, uptake studies in marine ecosystems were concerned with resolving the following: How abundance and availability of micronutrients regulates the phytoplankton productivity, are the rates of uptake of different nutrients ambient levels limiting, which of the nutrients that are limiting in the real sense, do phytoplankton compete for nutrients, and what if they are given in excess (saturated levels), were the prime questions asked and answered in most of these studies. Also addressed is how nutrient availability, either through physical transport processes or through biologically regulated regeneration processes, controls the growth and primary production rates of marine phytoplankton populations (Goldman and Glibert, 1983).

Dugdale (1967)'s study can be quoted as the first in this respect. He proposed that rates of phytoplankton nutrient uptake could be related to nutrient availability according to the rectangular hyperbolic equation. The equation he used was the modified equation of Monod which is defined as:

$$V = V_m \frac{N}{K_s + N}$$

in which V is a specific growth rate (time $^{-1}$) in terms of limiting nitrogen concentration N (mass.volume^{-1}), V_m is the maximum uptake velocity (= maximum growth rate) (time^{-1}) in terms of N, and K_s is the concentration of N for which $V = 0.5\ V_m$ (mass.volume^{-1}).

Goldman and Glibert (1983) observed two major drawbacks in the application of Dugdale's equation. Firstly, the nutrient uptake and growth processes are coupled (in balance and equal) only under certain well - defined laboratory conditions that seldom are replicated under natural conditions. In natural marine environments, particularly in impoverished oceanic waters, steady-state conditions for bacterial or phytoplankton nutrition are seldom established (McCarthy and Goldman, 1979). Secondly, there are intra- and interspecific differences among phytoplankton in their abilities to take up and assimilate different nitrogenous nutrients (e.g., NH_3, NO_3, NO_2, and organic N) and also temporal and spatial variations in the availability of these nitrogen nutrients (Goldman and Glibert, 1983). They summarise to say that uptake and growth processes are equal only under steady state conditions.

Other nonlinearities observed in the assumptions based on the use of Michaelis-Menten equation are (Goldman and Glibert, 1983)

1) Cell physiological state which plays a major role in influencing nitrogen uptake rates by phytoplankton.

2) The use of $\rho = V(PN)$, where the use of V leads to an underestimate of uptake proportional to the fraction of detrital N present.

3) the possibility that inorganic nitrogen uptake over time could be non-linear.

They concluded that protocols have to be developed more on the basis of analytical considerations than on the best representation of the natural phytoplankton situations. However, without an appreciation of the appropriate temporal scales of phytoplankton response to environmental perturbation, future progress in understanding such relationships will be restricted (Goldman and Glibert, 1983). The experimental protocol generally followed in this study is explained in detail in the materials and methods section.

Measurements of uptake of inorganic nitrogen by phytoplankton have been carried out both under laboratory conditions and in the natural environment. Studies on laboratory maintained cultures are reviewed by Goldman and Glibert (1983). These studies have helped to understand the inherent mechanisms involved in phytoplankton uptake which could later be explained in the natural environments. For example, chemical composition of phytoplankton varies tremendously with the degree of nutrient limitation (Goldman *et al.*., 1979) as has been earlier demonstrated with phytoplankton cultures (Eppley and Renger, 1974; McCarthy and Goldman, 1979).

The following paragraphs list the field observations of phytoplankton uptake for different ecosystems:

Phytoplankton uptake kinetics has been studied extensively in coastal areas because of the possibility of various sources of N input to these areas. Phytoplankton in these systems has been known to utilise these newly derived N and contribute to new production. Glibert *et al.*. (1991) studied nitrogen uptake by phytoplankton in the plume of Chesapeake Bay estuary. By studying the plume during different seasons, they observed that highest specific and absolute rates of uptake occurred when the availability of total N was at a seasonal high. They also observed that urea contributed up to 70 - 80 % of the total N utilized during winter and summer; in spring, most of the nitrogen uptake was in the forms of NO_3^- and NH_4^+. Comin and Valiela (1993) reports the drainage from paddy fields into the coastal lagoons of Ebro Delta. This results in a shift from the sea-water dominated phase to a fresh water dominated

phase and accordingly to a shift in the phytoplankton metabolism. This is shown with the dominance of DIN metabolism in the seawater phase, to a shift to the dominance of P uptake in the freshwater phase. They observed that the loss of dissolved nitrogen is concurrent with the increase in particulate N in the seawater phase (Comin and Valiela 1993). Pearl and Fogel (1994) studied the significance of atmospheric N input. They observed that the phytoplankton productivity and biomass increased with the addition of rain water as the $\delta^{15}N$ of particulate matter is considerably reduced. The reduced $\delta^{15}N$ is the result of utilisation of isotopicaly lighter N from the rain water, which shows that the atmospheric N input is an important parameter for the enhanced production. Short-term effects on N uptake have been observed for other environmental disturbances also. Garside *et al.*. (1976) studied the influence of sewage-derived input on the Hudson estuary and NewYork Blight. MacIsac *et al.*. (1979) in the same way studied the effect of sewage effluent on nitrogen and carbon productivity of natural marine phytoplankton near two California out-falls. The results showed inhibition in the NH_4^+ uptake at much lower effluent concentrations than was carbon uptake.

Other studies of significance on coastal waters which dealt with preferences phytoplankton for N nutrients and the f-ratio are listed below. Glibert *et al.*. (1982) investigated nitrogenous nutrition of the phytoplankton in Vineyard Sound, Massachusetts, over a period of 15 months and noticed that uptake rates of ammonium exceeded those of nitrate throughout the year except during the winter bloom. Koike *et al.*. (1986) addressed the importance of heterotrophic microorganisms in the regeneration of ammonium for phytoplankton assimilation in coastal waters of southern Scotia Sea. Like earlier and many other observations, ammonium was the most preferred (93%) form of assimilation, in spite of high nitrate (21 to 29 μM) present in these waters. Harrison *et al.*. (1987) evaluated the relationship between f-ratio [NO_3 uptake/(NO_3^- + NH_4^+)uptake] and ambient nitrate concentration from coastal waters; the f-ratio increased asymptotically with increase in nitrate concentration. Vezina (1994) assessed the mesoscale variability in nitrogen (NH_4^+ and

NO_3^-) uptake rates in the estimations during a summer phytoplankton bloom in a physically complex coastal system of lower St. Lawrence estuary. The data showed dependency of f-ratio with environmental condition. It (f-ratio) varied smoothly in a hyperbolic relationship with ambient NO_3 levels but only at 50% surface light. Kaufman *et al.*. (1983) in their studies observed the importance of urea as a nitrogen nutrient for phytoplankton in a nutrient rich coastal lagoon of Barrier Island estuary, Great South Bay, New York. The significant part of their observations was that the nitrogen uptake as measured with ^{15}N exceeded the cell requirements, at times by two or three-fold in the summer of 1979 which points to the N utilisation, by organisms other than phytoplankton.

Nitrogen utilisation in specialized coastal ecosystems also has been addressed. Harrison *et al.*. (1990) studied nitrogen utilisation in ice algal communities of Northwest territories of Canada and showed that these communities are not nitrogen-limited. They observed a temporal shift from NO_3 dominated metabolism during early stages of algal biomass accumulation under the ice to NH_4 dominated metabolism later on when the biomass was in decline. All these studies pointed out the species response to nutrient variability in these systems and proved that coastal systems never seem to be devoid of nitrogen to limit productivity.

N limitation in the sea was the prime concern in the studies of nitrogen uptake in oceanic waters. The concentration of N observed in the euphotic zone of oceans are often below the detection limit of 0.03 μg at l^{-1}. The capacity of the phytoplankton to grow at rates approaching μ (i.e., the maximum specific growth rate) in these levels has been, however, observed from the earlier culture studies (reviewed by Goldman and Glibert, 1983). These observations prompted the need to understand the mechanism of how the resident phytoplankton can grow under such low N levels in these systems. McCarthy and Goldman (1979) offer a hypothesis which suggest that the microenvironment surrounding a phytoplankton cell probably determines the magnitude of the supply of nitrogen to the cell. Such minute patches that could not be detected using available techniques may come from the excretory wastes of

zooplankton, bacterial degradation of particulate and dissolved organic nitrogen etc. Overall, the increase in ability to take up nitrogen compounds during conditions of N-deprivation is of ecological significance. Uptake studies in oceanic waters are listed as follows: Dugdale and Goering (1967) measured nitrate uptake as a fraction of ammonia plus nitrate uptake from the northwest Atlantic and the northwest Pacific oceans. They conclude by saying, for phytoplankton in the sea, ammonia is an important nitrogen source when nitrate levels are low, whereas nitrate and nitrogen fixation are the most important parameters with respect to nitrogen limitation of primary productivity. McCarthy (1972) studied the uptake of nitrate, ammonium and urea by natural phytoplankton population in 36 samples collected at 9 stations off the coast of Southern California. At a station characterised by highest biomass and carbon productivity, he observed low ambient concentrations(< 1.0 μg at N l^{-1}) of all three nutrients, owing to the high utilisation rates - An average of 39.7% of the available nitrate, 60.1% of the available ammonium, and 56.4% of available urea was utilised per day. Kanda *et al.*. (1985) reported on kinetic parameters for nitrogen uptake and rates of inorganic carbon uptake by natural populations of phytoplankton obtained over a large area of the Pacific ocean. They suggest that phytoplankton in the open ocean is in general not physiologically nitrogen deficient; it appear to be adapted to the nutrient regime of their habitat, and this adaptation is reflected by the affinity for nutrients. Le Bouteiller (1986) in studying environmental control of nitrate and ammonium uptake by phytoplankton in the equatorial Atlantic Ocean observed that when NO3- concentration exceeded 0.1 μM, nitrate uptake was strongly related to chlorophyll abundance. Their size fractionation experiments suggested that <3 μm phytoplankton which predominates the mixed layer have a preference for ammonium and the larger ones (>3 μm), relatively numerous only in the chlorophyll maximum, prefer nitrate.

The upwelling regions are distinct from the average oceanic systems in that the ratio of new to recycled nitrogen uptake is much higher here (Codispoti, 1983). Codispoti (1983) further quotes that the ratios of nitrate- supported primary

production to nitrate plus ammonium-supported rates frequently exceed 0.5 and may be as high as ~0.8 in upwelling regions, while values of <0.1 has been found in the oligotrophic zones. Very high nitrogen uptake rates were encountered in upwelling systems. Off Peru the values averaged 40 mg.atoms N m^{-2} d^{-1}(nitrate + ammonium), and were 22 mg.atoms N m^{-2} d^{-1} in area off NW Africa (Codispoti *et al..*, 198 , Dugdale, 1976).

The values of uptake estimated from natural marine samples in the earlier studies are listed below (Table.6) Wheeler (1983) lists the nitrogen-specific rates for transport and assimilation (V_{max}(h-1)) of nitrogenous compounds estimated on different phytoplankton cultures by many authors.

Nutrient uptake kinetics of phytoplankton in reef environments has been little studied earlier. Sournia and Ricard (1976) states the reason as this: there is evidence strongly to suggest that the bulk of planktonic food in these environments belongs to such detrital forms as mucus, aggregates, and organic particles; comparatively little work has been devoted to the phytoplankton component. Therefore, the main focus for the nutrient uptake studies on coral reefs has been on the symbiotic associations ie. intact corals (Bythel, 1988, ; Muller-Parker *et al..*, 1988; Ferrier, 1991; Atkinson *et al..*, 1994), Giant clams (Fitt *et al..*, 1993, 1995) and isolated zooxanthellae(Muller-Parker *et al..*, 1988; Goldman *et al..*, 1979; Wafar *et al..*, 1990, 1993). Community metabolism and uptake of nutrients at different communities of the coral reef system also have been addressed. Atkinson and Bilger (1992), calculated the production of a coral reef flat by assuming phosphate uptake is mass transfer limited and then scaling P uptake to Carbon - C fixation. Atkinson *et al...* (1994) studied the effect of water velocity on a community of *Porites compressa*. They found that NH_3^+ uptake by the corals can be correlated with the water velocity. Studies on primary production (new and regenerated production) in coral reefs also considered in most part the macrophytic community than the free living microalgae.

Table 6. Uptake values from earlier estimations.

n	NO_3		NH_4		Urea		*f*-ratio %	Reference
	V h-1	ρ µg at $l^{-1} h^{-1}$	V h^{-1}	ρ µg at $l^{-1} h^{-1}$	V h-1	ρ µg at $l^{-1} h^{-1}$		
& Coastal								
ıern ırnia	2.033	0.1709	1.817	0.106	1.46	0.0856	-	McCarthy, 1972
ragansett Rhode Island	0.005	na	0.012	na	0.0045	na	-	Furnas.1983
rier Island ry, Great Bay, NY.	na	na	na	0.165	na	na	na	Kaufman *et al.*, 1983
S, Peru	0.075	0.35	0.05 cu	0.39 cu	na	na	82.	Wilkerson *et al.*, 1987; MacIsaac *et al.*, 1985.
Blanc, NW	0.019	0.033	-	-	-	-	70	Codispoti *et al*, 1982; Dugdale, 1985
conception,	.023	0.046	na	na	na	na	57	OPUS83 prod.dat Wilkerson et al, 1987
California	0.023	.083	na	na	na	na	78	Wilkerson *et al*, 1987
olm Bay, eastern gat, Sweden	na	0.0172	na	0.0232	na	0.0172	-	Sahlsten, *et al* 1988
ic Sea	na	0.0161	na	0.0441	na	0.2941	-	Sahlsten & Sorensson, 1989
trophic								
tral North c Ocean.	na	na	na	0.0005	na	0.0004	-	Eppley et al., 1977
rling, Guyot	0.0009	0.00035	-	-	-	-	9	Kopezak *et al*, 1990 Wilkerson *et al*, 1990
literranean	0.0029	0.00058	na	na	na	na	21	Mac Isacc & Dugdale, 1972
gasso Sea	0.0018	0.0002	0.0052	0.0026	0.004 /h	0.0021	4	Glibert *et al* , 1988
f Stream	0.0005	0.0001	0.0024	0.0009	0.0009 /h	0.0004	3	Glibert *et al*, 1988
nutrient, low ctivity								
artic: Scotia	0.0026	0.0027	0.0025	0.0019	na	na	37	Glibert *et al*, 1982

	NO_3^-		NH_4^+		Urea		f ratio (%)	Reference
	V	ρ	V	ρ	V	ρ		
	0.0036	0.0027	0.0024	0.0019	na	na	54	Olson 1980
s sea	0.0032	0.0071	0.0034	0.0073	na	na	40	Olson 1980
quatorial Pacific -1°S, 150°W	0.0022	0.0016	0.0025	0.0019	na	na		WEC'88 productivity data
lation P, th east Pacific	0.0047	0.007	0.0018	0.0052	0.0137	na	48	Wheeler & Kokkinakis, 1990 Miller *et al*, 1988
velling								
lorth east ific	na	0.402	na	0.0897	na	na		Kokinakis & Wheeler, 1987
eru	na	0.1215	na	0.129	na	na		Kokinakis & Wheeler, 1987
lenguela	na	0.278	na	0.0557	na	na		Kokinakis & Wheeler, 1987
lamibian ar	0.0032	0.1635	0.0044	0.2373	0.0019	0.936		Probyn, 1988
Eastern nadian Arctic	na	0.1616	na	0.0627	na	0.0788		Harrison *et al.*, 1985

Few studies, were actually carried out with the phytoplankton community in coral reefs. The following works can be cited where the effect of nutrient loading and phyto plankton production in coral reefs has been addressed. Marsh (1977) assessed the effect of nutrient enrichment due to rain and ground water seepage in primary production in the fringing reefs of Guam. He observed that under bloom conditions, the nitrate concentrations dropped to 3.57 ± 3.12 μg at N l^{-1} (by a factor greater than two) from 8.04 ± 5.75 μg at N l^{-1} as observed in the non-bloom conditions, suggesting nitrate utilisation. The marked drop in the N:P ratio also suggested the possibility that the plankton bloom was nitrogen-limited. Lapointe and Clark (1991) studied the transformations of watershed nutrient input in the Florida Keys. They observed increase in the particulate N and P fractions (up to 48%) in canals and nearshore meadows, indicating rapid biological uptake of DIN and SRP (Soluble reactive phosphorous) into organic particles.

From the above references it is clear that nutrient uptake by phytoplankton in reef environments have been least studied. The basis for this is obvious from the following observations/assumptions on coral reefs:

- The phytoplankton biomass in coral reefs is a very low fraction in the productivity of a reef. Macrophytes contribute to a considerable part.

- The phytopankton in reefs may never be nutrient-limited. Given the high amount of regeneration in reefs, it is possible that the reef phytoplankton can easily sustain their productivity at their optimum levels. However, sporadic incidents of bloom are possible at the expense very rich nutrient inputs.

Despite the low importance assigned to phytoplankton metabolism in coral reefs, in the present study it was thought significant to study the contribution of phytoplankton communities in utilising the different compounds of nitrogen, their preferences and their relationship of uptake to nutrient availability. The reasoning for such a study is this:

In oceanic waters the low production was associated with the nitrogen-limiting conditions. Compared to oceanic conditions, the reef has more N and is not limiting in the real sense. This enhanced N, may sustain high phytoplankton productivity, however, thus has not been demonstrated. So, the difference in the uptake mechanism, if that is the reason, has to be understood. Secondly, coral reefs sustain high biological productivity in contrast to the very low primary productivity. The major biomass, corals and other organisms feed on zooplankton and other secondary producers which in turn, however, are dependant on primary producers. Hence, it is also important to understand the phytoplankton production which sustain, in part at least, the secondary production. Here again, the implication is with nitrogen nutrition.

In the present study, uptake of three major nitrogenous nutrients (ammonium, nitrate and urea) were studied in the atoll of Kalpeni island, Lakshadweep. The measurements were done at two stations, one in the lagoon and the other, in the open sea. The following chapters describe uptake patterns of each of these N compounds and the discuss the present results.

3.1.2.1 Nitrate uptake studies

Nitrate and N_2 are the two major sources of new nitrogen to phytoplankton. However, inspite of its abundance, the usefulness of N_2 as new nitrogen is restricted only to those organisms which can fix free nitrogen. Nitrate, on the other hand, supplied by the terrestrial and atmospheric inputs and through vertical advection from below the euphotic zone is readily taken by phytoplankton species. Consequently, N uptake, through this form of N should be representing most of new (nitrate)

phytoplankton production that determines the export of organic matter out of the euphotic zone in many productive regions of the ocean (Dugdale and Goering, 1967; Eppley and Peterson, 1979).

Dugdale and Wilkerson (1992) in his review on new production and nutrient limitation in the sea made the following observations from earlier studies of nitrogen uptakes.

- Eutrophic areas, as represented by coastal upwelling regions, exhibit high concentrations of nitrate, high values of biomass (as particulate nitrogen), high specific and absolute nitrate uptake rates (VNO_3 and ρNO_3), and high f values.
- Oligotrophic regions have low concentrations of nitrate, low VNO_3 values, low new production rates and low f values.
- The high-nutrient, low productivity areas are functionally similar to the oligotrophic low nutrient regimes, although there is abundant surface nitrate. These areas often have values of f that are intermediate between the truly oligotrophic and eutrophic regimes.

The implication from these studies is that in most productive, eutrophic regions of the ocean, the phytoplankton import a large proportion of new nitrogen as compared to the consumption of recycled nitrogen (Dugdale and Wilkerson, 1992). So, nutrient uptake studies invariably measured nitrate uptake by phytoplankton as a measure of new production and in turn as the measure of over all productivity of an ecosystem.

The factors which normally dealt with are listed below.

Effects of regenerated nutrient concentrations on nitrate uptake has been studied widely in laboratory cultures and under field conditions. Collos (1989) in a model explains the apparent inhibition of nitrate uptake by ammonium in many cases, but also the inhibition of ammonium uptake by nitrate, a phenomenon for which no physiological explanation has so far been offered. Dortch (1990) discussed the interactions of ammonium on nitrate uptake over the basic tenet that ammonium inhibits nitrate uptake. From the earlier literature on this topic, Dortch (1990) arrived at the conclusion that the presence of ammonium does not reduce nitrate uptake to the degree which is generally believed. It is primarily the indirect result of a preference for ammonium, manifest in higher V_{max} and a lower K_s for ammonium uptake than nitrate uptake (Dortch, 1990). In latter studies on interaction between nitrate/ammonium uptake on preconditioned cultures (*Thalassiosira psedonana*), Dortch *et al.*. (1991) clarified that there is preference for ammonium and inhibition of nitrate uptake by ammonium but not of ammonium uptake by nitrate. Urea also had inhibitory effects on nitrate uptake when presented with deprived light conditions (Molloy and Syrett 1988).

Douc' ette and Harrison (1991) observed extreme consequences of iron depletion on nitrate uptake experiments in red-tide dinoflagellate *Gymnodinium sanguineum*. Their data suggest an effect of iron deficiency on both the transport and reduction of nitrate, and a more rapid development of maximum NO_3 uptake and assimilatory capacity in NO_3^- grown than in NH_4-grown cells. Timmerman *et al.*.

(1994) measured the activity of the enzyme nitrate reductase with iron depletion. They observed that cells from iron depleted cultures had 15 to 50% lower enzyme activity than from iron -replete cultures.

Studies on the effect of physical parameters on nitrate uptake by phytoplankton show that light is a remarkable parameter in influencing NO_3^- uptake by phytoplankton (Martinez *et al.*., 1987; Kanda *et al.*., 1989; Berges and Harrison, 1993, 1995). Döhler (1992) also reported the same effects in phytoplankton consisting mainly of *P.puchetti* and in pure cultures of this algae. Other studies have also reported significant effects of temperature on new production. Lee-chen ; and Yuh-ling (1994) studied the effect of seawater temperature and nitrate concentration on the distribution of phytoplankton in the upwelling induced by the Kuroshio Current at the East China Sea, northeast of Taiwan. The significant observation was the high chlorophyll a concentration accompanying high surface temperatures during the cold season in the upwelling region while high nutrient and the low chlorophyll *a* are observed in the adjacent shelf waters. The authors also observed that during the warm season, the nitrate content was the only significant factor affecting surface chlorophyll *a* distribution, where in the cold season, both nitrate content and temperature played significant roles in determining chlorophyll *a* concentration. The inference is the enhancement of new production (utilization of nitrate) during high temperature or in the warm season.

Cell size and its relationship on nitrogen uptake has also been studied in many instances to demonstrate its influence on nitrate uptake. Though earlier studies on this aspect led to the notion that new production is associated with large phytoplankton

and regenerated production with small phytoplankton, later studies did not always support it. Daumas *et al.* (1981) observed with size fractionated phytoplankton that the relationship between nitrogen form and cell size is less clear-cut. Their monthly observations on nitrate uptake showed similar variations for the two size fractions (<5 μm and >5 μm), suggesting that both small and large phytoplankton used nitrate when available.

Le Bouteiller's (1986) observations are important where it was shown that nitrate uptake is strongly related to chlorophyll a abundance in equatorial Atlantic Pacific. He observed that the nitrate uptake is strongly related to the chlorophyll *a* abundance when NO_3^- concentration exceeded 0.1 μM. He did not find any correlation between specific uptake and nitrate concentrations which suggested no nitrate limitation when ambient concentrations were about 0.2 μM. Nitrate supply could satisfy 5 to 25% of the phytoplankton nitrogen needs as a function of the chlorophyll *a* abundance. Nitrate concentrations also did play a role in the nitrate uptake rates. Dugdale and Wilkerson (1992) stated that nitrate at a critical concentration (threshold concentration or critical concentration of nitrate of about 6 μM, appears in the field data from coastal upwelling areas) and light are required for induction of nitrate uptake and for transcription and synthesis of assimilatory enzymes.

Shiomoto *et al.* (1994) observed seasonal variations in the maximum uptake rates (ρ_{max}) of nitrate and ammonium in surface waters off Oyashio (JAPAN) in May (Spring) and September (Summer) 1990. They suggested that the average ρ_{max}/Chl*a* values, which was 3.5 times larger in summer than in spring, was associated with the

change in the water temperature and the size composition of the phytoplankton.

All these studies demonstrated that nitrate uptake in the marine environment is always dependent on various physical, chemical and biological parameters, which can bring distinct influences on new production at seasonal and temporal scales. The estimations of *f*- ratio in some of the above observations clearly attests to this statement.

In the present study, these observations, for the first time, are extended to coral reefs. Though all the interdependent parameters could not be addressed on an experimental basis, the current set of data hold information for a complete seasonal cycle which can be interpreted to understand the effect of environmental changes and also the dependence on other N compounds.

The specific and absolute uptake rates of nitrate, ammonium and urea for the lagoon and the eastern-side stations are presented in Tables 7 and 8.

The VNO_3 (Specific uptake rate of nitrate) ranged from 0.0009 to 0.019 (h^{-1}) in the lagoon waters and from 0.0009 to 0.0029 in the eastern side. They agree well with the rates reported from the oligotrophic areas (Table.6) in earlier studies (range: 0.0005 - 0.0029 h^{-1}). Almost 98% of the values (VNO_3) measured in the study were less than the lower limit (0.019 h^{-1}) reported from the eutrophic waters. Interestingly , the ρNO_3 values were higher (range: 0.001 - 0.1345 µg at N l^{-1} h^{-1}) and resembled the values reported from high nutrient low chlorophyll (HNLC) regions (range: 0.0016 - 0.0071). Dugdale and Wilkerson (1992) suggest that these HNLC areas fail to achieve

Table. 7 Uptake rates after trace additions in the lagoon waters.

DATE	NO_3 - μg at N l-1 h^{-1}		NH_4+ μg at N l-1 h^{-1}		Urea μg at N l-1 h^{-1}		f-ratio
	V	ρ	V	ρ	V	ρ	
8.1.93	0.0023	-	-	-	0.0108	-	-
15.1.93	0.0052	-	-	-	0.0009	-	-
5.2.93	0.0014	-	-	-	0.0029	-	-
6.3.93	0.0014	-	0.0176	-	0.0113	-	0.07368
1.4.93	-	-	-	-	-	-	-
2.5.93	0.0039	-	0.0593	-	-		0.06170
19.6.93	0.0132	-	-	-	0.0008		-
29.6.93	0.004	-	0.0320	-	0.0011		0.11111
13.7.93	-	-	0.0407	0.042	0.0516	0.0531	-
3.8.93	0.0073	0.0123	-	-	0.0647	0.1095	-
15.8.93	0.0067	0.0044	0.0087	0.0058	-	-	0.04350
27.8.93	-	-	0.1843	0.2464	0.0489	0.0655	-
6.9.93	0.038	0.1345	-	-	0.0026	0.0089	-
17.9.93	0.0017	0.0014	0.2832	0.2451	0.1262	0.1092	0.00596
28.9.93	0.0074	0.001	0.0704	0.0948	0.0377	0.0509	0.09511
8.10.93	0.019	0.0236	0.0594	0.0738	0.026	0.0319	0.24234
18.10.93	0.0133	0.0283	0.0766	0.1633	0.0249	0.0531	0.14794
29.10.93	0.0158	0.012	0.0653	0.0498	0.0174	0.0132	0.19482
11.11.93	0.0191	0.0275	0.1710	0.2465	0.1183	0.1705	0.10047
22.11.93	0.016	0.0256	0.1001	0.1605	0.0861	0.138	0.13781
6.12.93	-	-	0.0704	-	0.0016	-	-
16.12.93	0.0018	0.0021	0.0041	0.005	0.0101	0.0122	0.30508
26.1.94	0.0099	0.0199	0.1919	0.3869	-	-	0.04905
26.2.94	0.0065	0.0077	0.0937	0.1104	0.2945	0.347	0.06487
6.3.94	0.0009	0.0014	0.0855	0.1386	0.0743	0.1203	0.01041
18.3.94	0.0015	0.0023	0.0576	0.0892	0.2651	0.4103	0.02538
28.3.94	0.0034	-	0.0061	-	0.0547	-	0.35789
8.4.94	0.0011	0.0017	0.0487	0.7606	0.0697	0.1055	0.02208
19.4.94	-	-	-	-	-	-	-

Table 8. Uptake rates after trace additions in the eastern station (OS1) samples.

DATE	NO_3^- - µg at N l-1 h^{-1}		NH_4^+ µg at N l-1 h^{-1}		Urea µg at N l-1 h-1		f-ratio
	V	ρ	V	ρ	V	ρ	
17.1.93	0.0024	-	-	-	0.0112	-	-
27.1.93	0.004	-	-	-	0.0385	-	-
6.2.93	0.008	-	-	-	0.0697	-	-
18.2.93	0.0014	-	0.0014	-	0.0108	-	0.5
12.3.93	0.0009	-	0.0335	-	0.0048	-	0.0262
22.3.93	0.008	-	0.0489	-	0.0076	-	0.14059
19.6.93	0.0226	-	0.0022	-	-	-	0.91129
29.6.93	-	-	-	-	0.0008	-	-
10.7.93	0.0613	0.0407	0.0272	0.0181	0.0707	0.0469	0.69265
4.8.93	0.0065	0.0064	0.0288	0..0283	0.0239	0.0235	0.18413
14.8.93	0.0089	0.0132	0.0437	0.0649	-	-	0.16920
26.8.93	-	-	0.1098	0.6978	0.0387	0.246	-
7.9.93	0.0205	0.0196	0.1433	0.1372	0.0024	0.0023	0.12515
18.9.93	0.0015	0.0031	0.0604	0.1276	0.0373	0.0787	0.02423
27.9.93	0.0048	0.0051	0.1238	0.1307	0.0401	0.042	0.03732
9.10.93	0.0043	0.0031	0.0464	0.0338	0.0291	0.0212	0.08481
19.10.93	0.0129	0.0141	0.1236	0.1355	0.0193	0.0211	0.09450
30.10.93	0.0184	0.0265	0.0737	0.1484	0.0417	0.0602	0.19978
10.11.93	0.154	0.0297	0.0894	0.1728	0.0828	0.16	0.63270
23.11.93	0.0298	0.0396	0.1078	0.1433	0.0093	0.0124	0.21657
7.12.93	-	-	0.1075	-	0.0032	0.0051	-
17.12.93	0.0199	0.0462	0.0398	-	0.0088	0.0206	0.33333
25.1.94	0.0112	0.0194	0.1692	0.2686	0.1600	0.2769	0.06208
25.2.94	0.0048	0.0067	0.0637	0.0894	0.1943	0.2726	0.07007
7.3.94	0.0067	0.0046	0.094	0.0698	0.2588	0.1922	0.06653
17.3.94	0.0139	0.0192	0.0261	0.036	0.164	0.2266	0.3475
29.3.94	0.0067	0.0099	-	-	0.0579	0.0858	-
9.4.94	0.0092	0.0094	0.0696	0.0682	0.0374	0.0367	0.11675

high new production as a result of low values of VNO_3 ie., these regions fail to shift-up nitrate uptake to expected levels and have low particulate biomass. Coral reefs contrast with HNLC situation where the nutrient concentration itself places limitations on phytoplankton growth. The low VNO_3, in this study, therefore can be due to the low nutrient concentrations and is in agreement with most of the oligotrophic waters. Uptake rates versus concentration plots substantiate this view.

The high ρNO_3 rates can be explained as follows: In contrast to the general trend that the high VNO_3 supports high particulate biomass and the most productive regions import new nitrogen for their production, coral reefs harbour high particulate biomass, inspite of the low VNO_3. The particulate N concentrations estimated in the study ranged from 0.41 - 2.49 μg at N l^{-1}, which are similar in range known estimated from coastal waters, ie., much higher than the oligotrophic waters (see the section in PON). Such high PON concentration cannot be derived from uptake of nitrate alone, since the VNO_3 values are low and resemble very much those of the oligotrophic waters. So the bulk of the particulate N in this system must be of heterotrophic origin and other particulate nitrogen waste from the high secondary biomass of the coral reefs. This is especially true with the lagoon, as shown by the station-wise difference in ρNO_3 (Fig. 18.). Since the lagoon is a rich source of detrital N because of its large biomass, it can be said that the high ρNO_3 in this case is partly due the detrital N.

Fig. 18 a. Absolute uptake(r) of nitrate in the lagoon and estern stations.

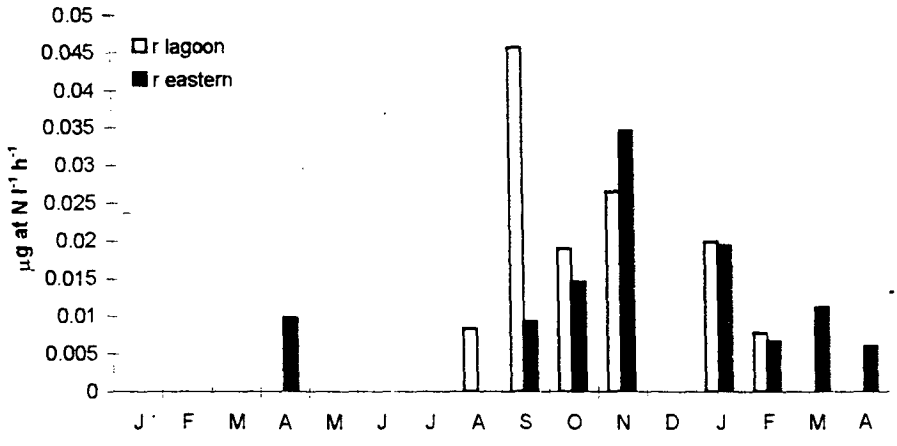
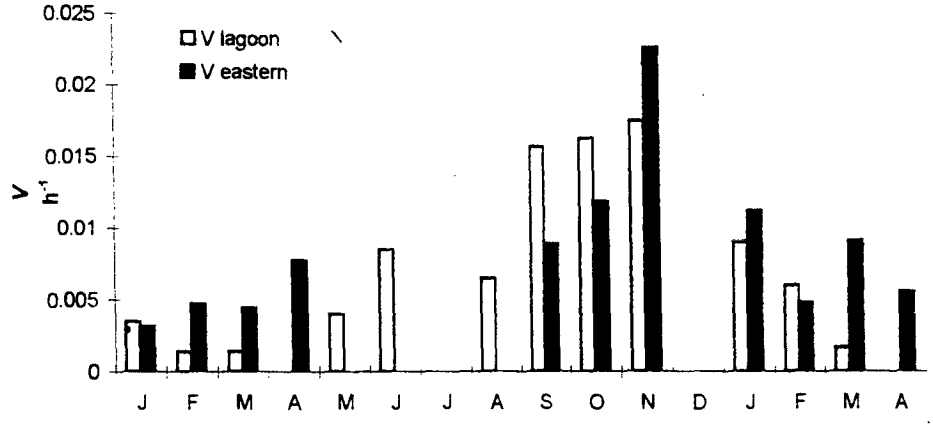


Fig.18 b. Specific uptake(*V*) of nitrate in the lagoon and eastern stn.



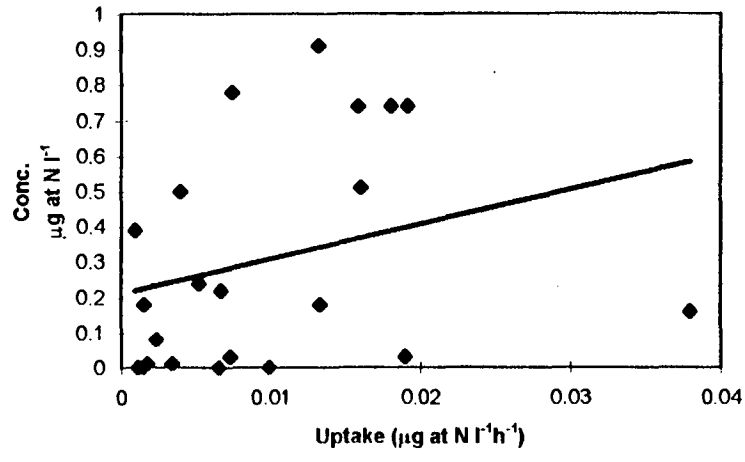
The specific uptake (VNO_3) rate also showed variations between the two stations but with a reverse trend to that of ρNO_3. The values reported for the eastern station (mean: 0.0117 ± 0.012 h^{-1}) were remarkably higher than the lagoon values (mean: 0.0081 ± 0.0086 h^{-1}). The general seasonal trend for both the stations showed a moderate increase in the post-monsoon period except for the peak observed in the monsoon months in the eastern station (Fig.18b). The post-monsoon season is a most favourable period for high phytoplankton production. The chlorophyll *a* in this season also showed increased values. Earlier studies have shown that the NO_3^- uptake increased with the chlorophyll *a* concentrations when the ambient concentrations were above 0.1 µg at N l^{-1}. Therefore the possible inference is that the chlorophyll abundance in this season influenced the $NO3^-$ uptake since the ambient concentrations were always above 0.1 µg at N l^{-1}.

The plots of VNO_3 *vs* ambient NO_3^- concentrations (Fig. 19) show that the uptake rates also increased with the ambient concentrations. The ambient NO_3 estimations show high values in the monsoon months(0.5 - 1.5 h^{-1}) followed by post-monsoon (0.5 - 0.6 h^{-1}) and pre-monsoon months (0.2 - 0.5 h^{-1}). Therefore high NO_3^- uptake is also due to enhanced NO_3^- concentrations and the favourable weather conditions in the post-monsoon months compared to the vey low values in the pre-monsoon months.

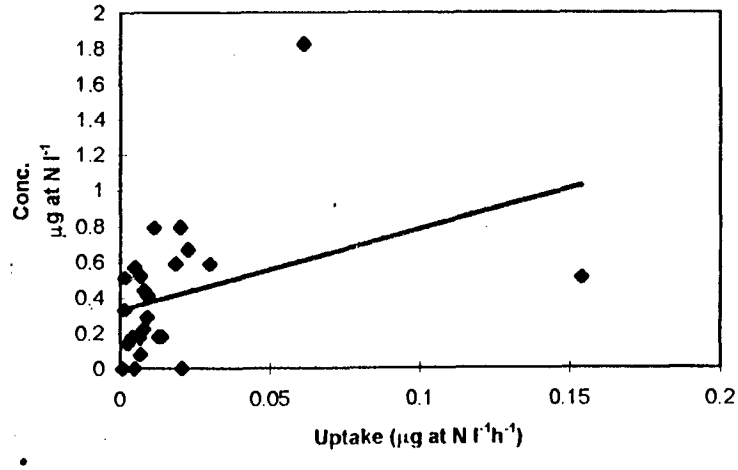
The peak observed in the monsooon months is again due to the high ambient NO_3^- concnetrations. The station-wise difference shows that the phytoplankton in the eastern station could utilize this new nitrogen where as the lagoon phytoplankton may

|. 19. Specific uptake *vs* ambient concentrations of nitrate in the lagoon and eastern stations.

Lagoon



Eastern



not. It is possible that light could be a limiting factor, since in the monsoon months the lagoon becomes highly turbid due to wave actions, and hence is less conducive for phytoplankton production. The peaks in the monsoon months show the ability for the phytoplankton to take up nitrate when it is available provided the uptake is not limited by other conditions. In contrast with the lagoon station, the eastern station may not experience a light-limitation in nirate uptake since this station is in the open ocean and the monsoonal disturbances may not amount much because of the high depths over this station. The most important observation of this study is whether it is situated in the leeward side protected by the island. (More information will be obtained in the discussion inclusive of NH3 uptake and concentrations)

The most important observation of this study is whether NO_3^- in this environment is limiting. The ratio Vsat/Vtrace in this study was always close to 1 which showed that the NO_3^- in this environment is not limiting. The moderately increased values of uptake under conditions of NO_3^- input ie., monsoon and post-monsoon period, shows that the phytoplankton metabolism changed with the change in ambient concentrations. However, the Vsat/Vtrace ratios suggest that the uptake is not seriously concentration-constrained. It can be that the phytoplankton in this environment adopt to environmentally controlled parameters where the nutrient concentrations also take part. It is also clear that the input of new nitrogen is used up only under favourable weather conditions where the chlorophyll also is in abundance.

3.1.2.2 Ammonium (NH_4^+)

Almost all the studies on nitrogen uptake by phytoplankton in marine waters, carried out until now have shown that, ammonium is the most preferred N form for phytoplankton uptake than urea and nitrate. Dortch (1990), in his review on the interactions of uptake between ammonium and nitrate, states that the preference for ammonium uptake is manifested in a heigher V_{max} and a lower K_s for ammonium uptake than for nitrate uptake. One of the physiological explanation for this is that the algae need to spend more energy for the utilization of nitrate, than ammonium, due to the additional number of electrons required to reduce nitrate to ammonium (nitrate has to be converted to ammonium through enzyamtic processes, before being assimilated) (Syrett, 1981). The second explanation lies in the differences in the transport mechanisms by which different N compounds enter the cell. According to Raven (1980), significant uptake of nitrogenous nutrients by non-mediated diffusion (passive diffusion, not enzymatically controlled) is feasible only for NH_3 and urea, since these two compounds are very soluble in the Lipid phase of membranes. Therefore linear uptake kinetics is shown in the case of ammonium and urea whereas nitrate and nitrite show substrate- saturable kinetics, characterized by mediated diffusion (enzyme-mediated). Wheeler and Hellebust (1981), quoting Walker *et al.*.(1979), assumed theoritically that passive accumulation of NH_3 by diffusion and acid trapping could result in $>10^3$ - fold internal accumulation in marine diatoms.

The following studies, under field conditions, have attempted to explain the phytoplankton preference for NH_4 against NO_3. Substrate concentrations, either of ammonium or nitrate, are known to influence the preference for them. Fisher *et al.*. (1988), considered ammonium utilization to be very important in ecosystems where nitrate concentrations are very low. In Lake Calado, Brazil, they estimated the nitrate uptake to be at ~10% of NH_4 uptkae (Fisher *et al.*., 1988). Probyn (1988) in his studies observed the preference for ammonium very clearly. In Namibian upwelling, during an austral spring, he (Probyn, 1988) observed that inspite of the high ambient NO_3^- concentrations, nitrogen was primarily taken up as NH_4^+ and urea. Probyn (1992) also demonstrated the reduction in f- ratio with the increase in the proportion of ammonium in the inorganic nitrogen pool. Goeyens *et al.* (1995), working with phytoplankton population of Southern Ocean and the Weddel Sea marginal ice zones, demonstrated that absolute as well as specific nitrate uptake rates decreased by an order of magnitude when ammonium stocks exceeded 1.7% of the total inorganic nitrogen. Besides the substrate concentration, physical and biological parameters also influence the preference for phytoplankton uptake. Such factors are light (Doehler and Stotler, 1986; Fisher *et al.*., 1988; Dodds and Priscu, 1989; Dortch, 1990; Kanda *et al.*., 1990; El-samra and Mahmood, 1990; Doehler, 1992), temperature (Le Bouteiller, 1986; Miyazaki, 1989; Shiomoto and Maita, 1990), chl*a* abundance (Le-Bouteiller, 1986; Suttle and Harrison, 1988; Harrison *et al.*., 1990; Presing *et al.*., 1996) and phytoplankton size distribution (Fisher *et al.*., 1988; Suttle and Harrison, 1988;

Sakamoto, 1989; Suttle *et al.*., 1991; Jiao-Niazhi and Wang-Rong, 1993; Shiomoto *et al.*., 1994)

Besides the uptake experiments, studies on the assimilation of ammonium in the phytoplankton cells have also been dealt in detail. Syrett (1953) and Hattori (1958) exposed N - starved cells to ammonium and observed a rapid increase of extractable nitrogenous compounds such as amino acids and oligopeptides within the cells. Later studies by Conover (1975), DeMonche *et al.* (1979), Dortch, (1982), Dortch *et al.* (1984) confirmed these earlier observations after pulse addition of N nutrients. Tupas and Koike (1991) observed the same phenomenon with the increase of ^{15}N concentrations in particulate matter with time, i.e. newly formed bacterial cells, signifying active assimilation of ammonium.

In recent years, ammonium uptake in pelagic marine systems and oligotrophic waters has also investigated with respect to the role of heterotrophy. The impetus for this research came with the realization of the importance of heterotrophic biomass in marine primary production. It has been estimated that 10 - 50% of primary production passes through the bacterioplankton (Andrews and Williams (1971), Sieburth (1977) and Furhman and Azam, 1980, 1982). Cole *et al.*. (1988) states that in the photic zone of lakes and ocean, bacterial production was significantly correlated with planktonic primary production, chlorophyll *a* or number of planktonic bacteria. The implications of this is that, in the marine nitrogen cycle, a significant fraction of inorganic nitrogen utilization is associated with heterotrophic bacteria.

The affinity for ammonium in particular than for the other DIN compounds led later on to the studies on the importance of ammonium uptake in the bacterial production. To cite a few: Hortsmann and Hoppe (1981), in the Baltic sea showed that bacteria could successfully compete with phytoplankton from the Baltic Sea for uptake of the ammonium analog methylamine. Wheeler and Kirchman (1986) suggested that a significant portion of ammonium uptake in the euphotic zone was by heterotrophic bacteria rather than solely by phytoplankton. The investigations of Suttle and Harrison (1988) add further evidence to this. They observed that 50 - 90 % of the saturated NH_4^+ uptake rates was in the <3um fraction and also that the saturated NH_4^+ uptake rates were maximum when chlorophyll (Chl) conentration was lowest (July), and minimum when Chl was greatest (May), whether expressed on a nutrient or volume-specific basis . Fisher *et al.*.,(1988) showed that smallest size fractions comprises of heterotrophic bacteria sized organisms and that they account for more than than 1/2 of the P uptake and 10-50% of the ammonium uptake, and for about 50% of the ammonium regeneration. Estimations (Tupas and Koike, 1991) have also show that ammonium supplied up to 80% of nitrogen in new bacterial cells. Hoch and Kirchman, (1995) observed that there is a preference for NH_4^+ uptake by bacteria in oligotrophic waters and low in eutrophic systems. All these studies attest to the importance of heterotrophy in ammonium utilization. Heterotrophy also plays a major role in the regeneration ammonium for utlization by phytoplankton and heterotrophic bacterioplankton. (See Chapter 3.1.1.3 Ambient concentrations - Ammonium).

The following studies are of particular interest, since they consider regeneration and uptake of ammonium together. Morrisey and Fisher (1988) observed that uptake of ammonium exceeded regeneration when ambient ammonium concentrations were high and were in near-balance when ammonium concentrations were <1 μM. A dial pattern was also evident in most of the studies, with higher uptake during the day and higher regeneration during the night (Wheeler *et al.*, 1989; Jiao,-Nianzhi and Wang,-Rong, 1993). Though the regenerated flux was lower than the uptake flux in some studies, a close coupling between these two processes was evident(Neuer and Franks, 1993). Fisher *et al.* (1987) observed that 1/2 of the ammonium regeneration appears to occur in the heterotrophic bacteria-sized fraction, the same fraction that is responsible for 10 - 50% of the NH_4 uptake. Tupas and Koike (1991) in natural assemblages of marine bacterium observed that there is active assimilation of ammonium simultaneous with the mineralization of DON to ammonium. Later estimations showed that regenerated ammonium met 87%, 42%-48% and 11% of the uptake demand in summer, spring/autumn, and winter respectively (Jiao,-Nianzhi and Wang,-Rong, 1993). Over all, these studies show that ammonium uptake is coupled with the regenerative processes so that both of them cater to each other.

The important feature recognised in the earlier studies on NH_4 uptake is the surge or non-linear time course uptake by N starved cells of phytoplankton. Its (surge uptake of NH4) significance is well recognised in the studies from oligotrophic,

nutrient-depleted waters. Since the external input and ambient concentrations are low, several investigations were concerned with the mechanism by which phytoplankton obtain their N requirement in these waters. In laboratory studies, nitrogen-depleted cultures, when supplied with ammonium, exhibited uptake rates that exceeded the amount required for their growth (Eppley and Renger, 1974; Conway and Harrison, 1977). This suggests that that the phytoplankton cells need only be exposed to intermittent pulses of nitrogen in order to acquire their daily ration of nitrogen (McCarthy and Goldman, 1979). Such situation in the seawater exist (McCarthy and Goldman, 1979) where cells randomly pass into microenvironments in which nitrogenous nutrient concentrations are elevated as a result of either metabolic waste excretion by animals or the degradation of organic matter by bacteria. Since ammonium is a primary end product of zooplankton metabolism, it forms the majority of the excretion product by zooplankton and, in oligotrophic waters a significant source of N. Therefore, as shown later in the studies of McCarthy and Goldman (1979), Jackson (1980) and Goldman and Glibert (1982) with ammonium, phytoplankton in oligotrophic oceans may obtain their nitrogen needs by rapid, transient uptake of ammonium. The studies which substantiate this under field conditons are those of Goldman *et al.*. (1981), Goldman and Glibert (1982), Wheeler *et al.*. (1982a) and Wheeler and McCarthy (1982) - all of them suggested the occurrence of nonlinear time courses for NH_4 uptake.

A compiled account of earlier estimations of NH_4 uptake from different ecosystems is given in Table. 4. The values show a region-wise characterization. The lowest values were reported for the oligotrophic waters (range: 0.0005 to 0.00026 μg at N l^{-1} h^{-1}), highest values for the shelf and coastal areas (range: 0.0232 to 0.39 μg at N l^{-1} h^{-1}) and intermediate values for the high nutrient low chlorophyll regions (range: 0.0019 to 0.0073 μg at N l^{-1} h^{-1}). The upwelling areas also had very high values, in the range resembling coastal areas (0.0557 to 0.129 μg at N l^{-1} h^{-1}). However, studies to understand regional patterns did not show a clear trend. Shiomoto (1990) measured nitrate and ammonium uptake rates in summer at several stations in subarctic, suptropical and transitional regions of the North Pacific Ocean. The region-wise difference among these regions for ammonium uptake rates (ρNH_4) were less marked though Chl *a* specific uptake activity (ρNH_4/Chl *a*) was high in the subtropical region and consistently low in other regions (Shiomoto, 1990). His results showed that ammonium was the main nitrogen source in the subtropical region.

In some of the temperate and sub-tropical regions, seasonal differences in NH_4 uptake were observed. Shiomoto *et al.*. (1994) measured the maximum uptake rate (ρ_{max}) and affinity constant (K_S) for nitrate and ammonium in the surface waters off Oyashio in May (spring) and September (summer). They related the water temperature and size composition of phytoplankton to the seasonal differences in the ρ_{max}/Chl a and showed that average values of ρ_{max}/Chl a for both nitrogen forms were 3.5 times higher in summer than in spring. Jiao-Nianzhi and Wang-rong (1993) found the

seasonal variations of the uptake and regeneration fluxes in the following order: summer > spring/autumn > winter, with the annual variations of regeneration more pronounced than those of uptake flux. Dickson and Wheeler (1995) observed highest ammonium uptake rates during the upwelling season (11 to 17 mmol $N/m^2/d$) and lowest during the non-upwelling season (3 mmol $N/m^2/d$).

Rates of ammonium uptake obtained in the present study are given below. These are from the two stations on either side of the Kalpeni island, representing lagoon and the leeward reef conditions.

The VNH_4 for the entire study period ranged from 0.0041 µg at l^{-1} to 0.2832 µg at l^{-1} in the lagoon station and 0.0022 µg at l^{-1} to 0.1692 µg at l^{-1} in the eastern station. The lagoon values (mean: 0.0686 ± 0.0459), were comparatively higher than the eastern station values(mean: 0.0807 ± 0.0694 µg at N l^{-1}) through out the study period. Though there is no clear seasonal pattern as that of NO_3, the monthly variations reported were similar for both the stations. The increased values for both the stations were found in the monsoon months except the peaks observed in the months of January and April in the pre-monsoon months. The highest values (>0.1 µg at N l^{-1}) reported were for August and September in the monsoon months and January in the pre-monsoon season (See table: 9a and 9b). Interestingly, post-monsoon months reported low values, contradictory to the high rates reported for nitrate. Though this trend agrees well for the avarage values calculated to the three seasons in the lagoon

ıle 9a. Uptake values for trace additions in the lagoon (Stn # 1) - mean values to show ısonal variations.

Seasons	NO^-_3		NH^+_4		Urea		*f*-ratio
	V	ρ	*V*	ρ	*V*	ρ	
Pre-monsoon	0.0025 ± 0.0019	0.0033 ± 0.0029	0.0526 ± 0.0322	0.2747 ± 0.3245	0.1103 ± 0.119	0.2457 ± 0.1556	0.088 ± 0.121
Monsoon	0.0112 ± 0.0123	0.0307 ± 0.0582	0.1076 ± 0.1076	0.1268 ± 0.1131	0.0417 ± 0.0426	0.0662 ± 0.0385	0.1617 ± 0.0879
Post-monsoon	0.0114 ± 0.0068	0.0198 ± 0.0096	0.0923 ± 0.0615	0.1551 ± 0.1306	0.0329 ± 0.041	0.0698 ± 0.0678	0.1682 ± 0.0866

le 9b Uptake values for trace aditions in the eastern side (Stn # OS1) - mean values to show seasonal Variations.

Seasons	NO^-_3		NH^+_4		Urea		*f*-ratio
	V	ρ	*V*	ρ	*V*	ρ	
Pre-monsoon	0.0066 ± 0.0039	0.0096 ± 0.0055	0.0482 ± 0.0308	0.1504 ± 0.0753	0.0895 ± 0.0931	0.1628 ± 0.0985	0.1809 ± 0.1755
Monsoon	0.018 ± 0.0206	0.0146 ± 0.0141	0.0674 ± 0.0516	0.172 ± 0.237	0.0305 ± 0.0243	0.0732 ± 0.0884	0.3062 ± 0.3496
Post-monsoon	0.013 ± 0.0089	0.0255 ± 0.0148	0.0946 ± 0.0423	0.0658 ± 0.0221	0.0403 ± 0.0482	0.0403 ± 0.0482	0.2319 ± 0.2006

station, at the eastern station, the high value is reported in the post-monsoon season followed by monsoon and pre-monsoon seasons (Table 9a and 9b). The reason is due to the exceptional peak in the month of January which enhance the average value of the post-monsoon season.

The ρNH_4 values ranged from 0.005 to 0.7606 μg at N l^{-1} h^{-1} in the lagoon stations and 0.0283 to 0.6978 μg at N l^{-1} h^{-1} in the eastern station. Like VNH_4^+, the ρNH_4 rates were higher in the lagoon station (mean: 0.1703 ± 0.182) than the eastern station values (mean: 0.1326 ± 0.155) during most of the observations. Both the stations did not report a clear seasonal trend. The monthly mean plots for the two stations show the highest peaks in the pre-monsoon season followed by comparatively smaller peaks in the post-monsoon season. However, the eastern station exhibited random high peaks in the monsoon months which is explicit in the integrated seasonal values. Accordingly the eastern station reported high integrated value in the monsoon (0.172 ± 0.237) followed by the premonsoon (0.1504 ± 0.0753) and the post-monsoon periods (0.0658 ± 0.0221) (Table 9b). Such random peaks are absent in the lagoon station, and the mean values showed the high to low order from the premonsoon (0.2427 ± 0.3245) followed by post-monsoon (0.1551 ± 0.1306) and to the monsoon period (0.1268 ± 0.1131) (Table 9a). As a general trend, the non-monsoon values were significantly higher compared to the monsoon months.

A comparative account of both VNH_4^+ and ρNH_4^+ in the present study with those from other marine systems(Table 6) showed that, the uptake rates in the present

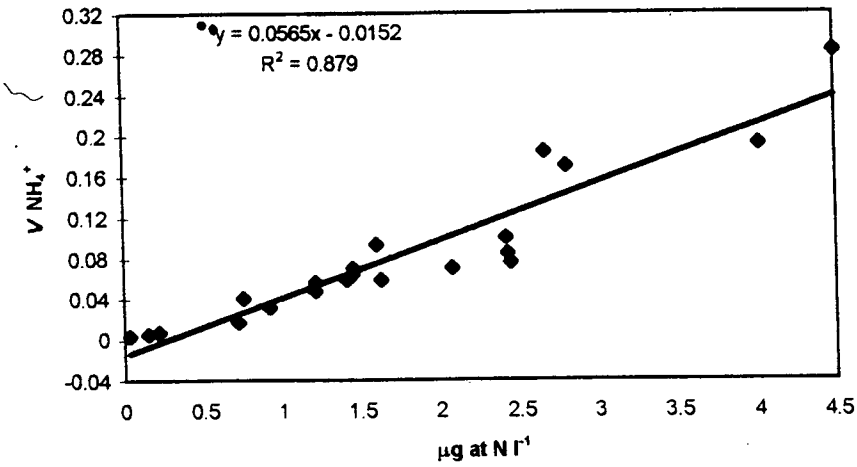
study occupy an intermediate position between those of oligotrophic and shelf waters. This shows that in terms of pelagic nitrogen flux, coral atolls are different from the oligotrphic waters in which they are found.

The uptake rates correlated well with the variations in ambient NH_4^+ concentrations suggesting a substrate dependency (Fig. 20).

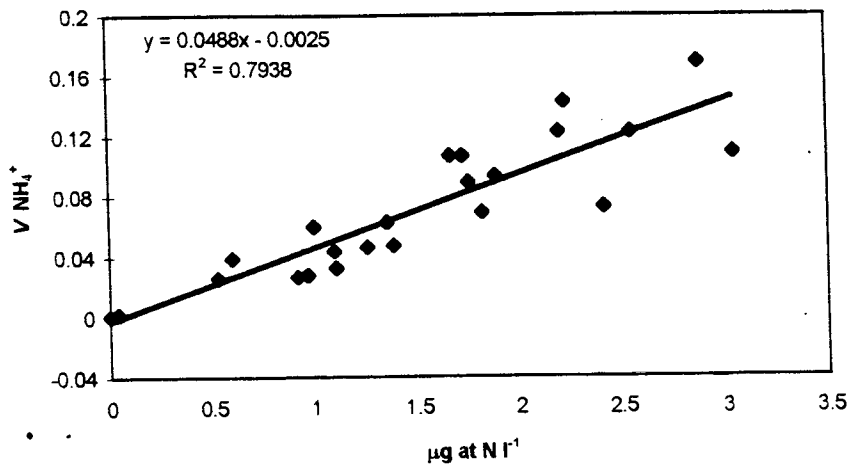
Ambient estimations of PON and phytoplankton biomass (Chlorophyll *a*) are not in coincidence. This proves that phytoplankton production alone does not contribute to the PON pool (See discussion, PON distributions). So, the PON specific uptake in this case is not clearly an index of ammonia uptake by phytoplankton. In the present observation, therefore, the high PON specific uptake were possibly by heterotrophic microorganisms, the abundance of that may not have similar seasonal trend as that of chlorophyll *a* but maintain a more or less constant biomass. The reason for this can be derived from the following points. 1) the more or less constant PON values. 2) the not so significantly correlated chlorophyll a abundance and NH_4^+ uptake values unlike NO_3^- uptke values in the present study and from the earlier observations. 3) the high PON specific uptake of NH_4^+ that is in contrast to the nitrate uptake values. 4) the utlization preference of heterotrophic microorganisms for the regenerated forms of nitrogen that can be obtained from the micropatches of animal remineralization than the new nitrogen which are occasionaly fluxed in from external sources (See para 3 and 4 on surge uptake and heterotrophy).

Fig. 20 Specific uptake(V) vs ambient concentrations of NH_4^+.

Lagoon



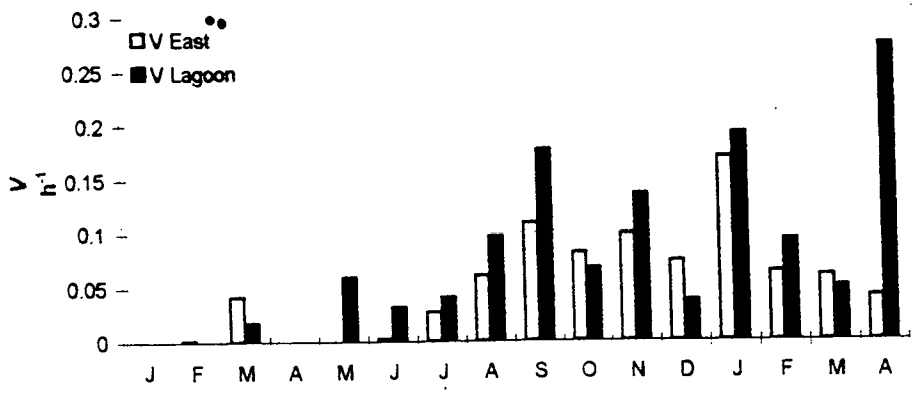
Eastern



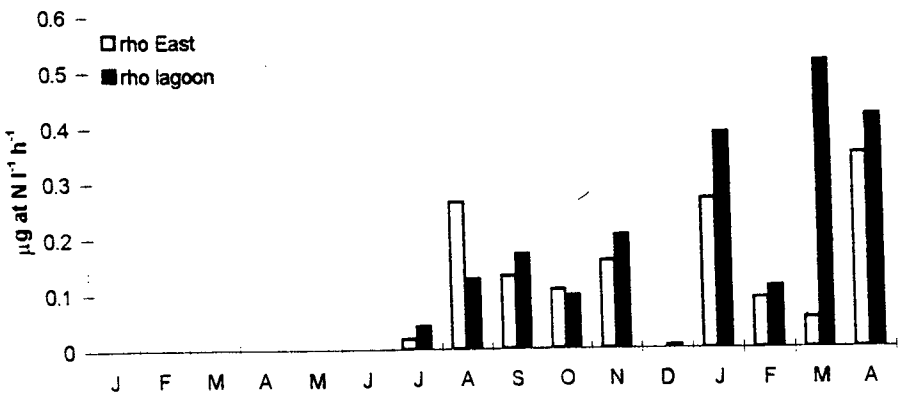
The uptake index (ρNH_4/chl *a*) [µg at N (µg chl *a*)$^{-1}$ l^{-1} h^{-1}] calculated showed the following trend. The average uptake index (mean: 0.470 ± 0.925) was higher in the lagoon station than the eastern station (mean: 0.3485 ± 0.551) through out the study period. The integrated values for the lagoon station showed higher values in the post-monsoon (0.8503 ± 1.485) followed by pre-monsoon (0.319 ± 0.232) with the lowest in the monsoon months (0.165 ± 0.185). Such a clear seasonality was not apparent with the data of the eastern station. The high value here is in the monsoon (0.463 ± 0.877), followed by more or less uniform values in the post and pre-monsoon months (0.274 ± 0.119 and 0.27 ± 0.238 respectively). This trend is also evident from the monthly average plots (Fig. 2a and 2b). The interesting observation is the the high uptake index in the most favourable months (post-monsoon) of phytoplankton production, that was not explained with the ρNH_4 and VNH_4 values. The post-monsoon months reported low VNH_4 and PNH4 values but with high chl a productivity. This shows that ammonium is not prefered when the chlorophyll production alone is high. The preference for ammonium is reported in the premonsoon months (low index and high ρNH_4 and VNH4 values), where the phytopalnkton biomass is low, should be domniated by the role of heterotrphic microorganisms.

The important conclusion is that the uptake favoured by phytoplankton had high index. Whereas periods assumed high heterotrophy, ie. ρNH_4 is high but with low chl values (pre-monsoon and monsoon) had low index. More clearly, ammonium is not a preferred compound when the phytopalnkton biomass is high.

Fig. 20a. Specific uptake rates(V NH_4^+) of ammonium.



20.b. Absolute uptake rates(ρ) of ammonium.



3.1.2.3. Urea

Though energy expenditure in the the assimilation of urea is of same order as that of nitrate, its preference next to that of ammonium has become evident from many studies on uptake with phytoplankton cultures. One of the important reasons, among others could be that the urea N may be assimilated into organic N without prior conversion to NH_3^+ (Kitoh and Hori, 1977), contrary to the belief that urea, like NO_3^- has to be converted to ammonium before being assimilated. A direct assimilation can enhance the significance of urea as an organic N source of phytoplankton.

At the cellular level, the distribution of urea is compartmentalized into two intracellualar pools, a large nonmetabolic (resulting from photosynthetically driven active transport) and a small metabolic pool (Dagestad *et al.*, 1981). This work suggests that ammonium inhibits transfer of urea from the nonmetabolic pool to the metabolic pool. Following points have to be discussed before to confirm this statement. Since photosynthesis is that cause urea uptake into the nonmetabolic pool, conversion to NH_3 should be effected here because the carbon from urea is assimilated only after its conversion to CO_2 (Allison *et al.*., 1954) on feeding [^{14}C]urea to *Nostoc* suggested this). Therefore, the urea N available for transfer into the metabolic pool may be ammonium after the carbon being assimilated in the nonmetabolic pool. In this case the inhibition of urea transfer to the metabolic pool may not be due to energetic preference of the cell but determined by the concentration of ammonium in the

metabolic pool. The external supply of ammonium in that case may have very little suppressing effect on urea uptake/transfer. Studies on the cellular aspect of ammonium inhibiton on urea uptake till now are not clear to explain this.

The metabolism of urea is described by the following reactions. The two enzyme systems which are known to metabolise urea are urease and ureaamidolyase (UAL-ase). Urease catalyses:

$$CO(NH_2)_2 + H_2O \rightarrow CO_2 + 2NH_3$$

In the ureaamidolyase reaction, the catalysis is by two specific enzymes known as urea carboxylase and allophanate hydrolase. This reaction is at the expense of a mole of ATP per mole of urea and is expressed as:

$$\text{urea} + \text{ATP} + HCO_3 \xrightarrow[\text{(urea carboxylase)}]{Mg_2^+\ K^+} \text{allophanate} + \text{ADP} + 2CO_2$$

$$\text{allophanate} \xrightarrow[\text{(allophanate hydroxylate)}]{} 2NH_3 + 2CO_2$$

(Roon *et al.*, 1972).

The reaction described here shows that, urea, upon decomposition releases two molecules of CO_2 with the two molecules of ammonium utilised. This formed the basis for the earlier uptake studies of urea, in which the CO_2 released was taken as measure of urea assimilated/metabolised. Remsen *et al.* (1972) measured $^{14}CO_2$ production in estuarine microbiota from [^{14}C]urea incubations. This method would seriously underestimates urea uptake, if the CO_2 released on the decomposition of urea is refixed by phytoplankton. This has been ambly demonstrated in the study of Remsen (1972)

when majority of urea decomposition occured in the >20 μm fraction that represented 15% of the phytoplankton and 39% of the chlorophyll *a*. This might explain the predominantly light dependant uptake of urea.

Later studies examined the significance of light and photosynthesis in the uptake of urea. Mitamura and Saijo (1975) found a parallel response to increasing light intensity between bicarbonate fixation and urea utilization in the coastal waters of Japan, with maximum rates of both occuring at 12,000 lx. The percent incorporation too was greater in the light, while dark uptake of [^{14}C]urea primarily resulted in $^{14}CO_2$ release (Mitamura and Saijo 1975). Webb and Hass (1976) measured both production of $^{14}CO_2$ and incorporation of ^{14}C into particualte fractions resulting from incubations with [^{14}C] urea, in an to elucidate the dependance of urea uptake on light. Their observations, were the first to show that the urea is a nitrogen source rather than acarbon source alone or can be independent of photosynthetic carbon assimilation, in the nitrogen cycle. The important observation from their study was that urea uptake/decomposition is light-dependent and is saturated at lower light intensities than required for photosynthesis, accounting for the C:N enrichment occurring in surface waters. Antia *et al.* (1977) demonstrated that urea is taken up only in light. Tamminen and Irmisch, (1996) observed differences in urea uptake rates with light and dark incubations. Their observations showed that light stimulated urea uptake; parallel dark incubations usually yielded uptakes rates 60 - 80% of those in the light.

Since [^{14}C]urea uptake studies considered mainly the photosynthetic assimilation of urea and $^{14}CO_2$ production (if the matabolic path way is UALase

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Since [^{14}C]urea uptake studies considered mainly the photosynthetic assimilation of urea and $^{14}CO_2$ production (if the matabolic path way is UALase decomposition to ammonium), it has been difficult from these studies to fully asses the importance of urea as a nitrogenous nutrient. According to Price and Harrison (1988) the fate of urea-N cannot be clearly elucidated based on [^{14}C]urea tracer uptake measurements alone. Studies of ^{15}N urea uptake were ideal in the latter case.

The following give the list of earlier studies on this aspect. McCarthy (1972) found in stations off the coast of Southern California that the percentage of total nitrogen productivity accounted for by urea averaged 28% and ranged from <1 to >60%. McCarthy and Eppley (1972) studied ^{15}N uptake on samples enriched with ammonium, nitrate and urea. They observed that urea uptake was totally suppressed in sea water enriched with ammonium. Rees and Syrett (1979) reported that nitrogen deprivation, increased the initial rate of urea uptake. Other studies have also reported preference for urea uptake. Kaufman *et al.*(1983) observed preference for urea uptake in coastal phytoplankton in Great South Bay, New York. Price and Harrison (1988) also observed this surpising trend of higher uptake of urea than NH_4^+ with Sargasso Sea phytoplankton.

The interference by other forms of N in urea N uptake has also been studied with phytoplankton cultures. Horrigan and McCarthy (1981) examined uptake of urea at saturating concentrations in short-term uptake experiments with batch cultures of marine diatoms, growing on NO_3 and NO_2, and at three different stages of nitrogen

depletion. They demonstrated that organisms in nutrient-depleted medium, for which Q (cell quota- total N content/cell)is less than Q_{max}, can maintain rapid uptake for upto an hour after which rate of uptake begins to slow, resulting in an assimilation of a mass of urea-N equivalent to 30% of its original cellular N in two hours. Horrigan and McCarthy (1981) concluded that the enhanced V'max capability may be common for urea uptake when cells are growing on NO_3 and NO_2. Their observation also showed that, the cell has the capability not only to take up urea but also to hydrolyse it as well, increasing its cellular N by nearly 2% in 20 minutes. This rapid uptake behaviour with urea is important in the phytoplankton uptake patterns, since it is turned over rapidly and the exposure of the cell to urea occurs only at brief, sporadic events (Jackson, 1980). Lund (1987), examining the inhibition effect of urea on nitrate uptake, observed in *Skeleteonema costatum* that the uptake of nitrate was not significantly changed with the addition of urea. Whereas, the uptake of urea decreased to 82 - 84% of the control value with the addition of either nitrate or ammonium. The nitrate + urea and the nitrate + ammonium uptake experiments showed that the uptake rate of nitrate was only suppressed when the uptake rates of reduced N sources was high enough to maintain the preconditioned growth rate (Lund, 1987).

The high turnover rates of urea (discussed in detail in the section on ambient concentrations) is another important aspect to be considered when interpreting seasonal changes in urea uptake. Steinman (1976) observed greatest numbers of urea hydrolysing bacteria when urea concentrations were high. The calculated turnover times of urea were also reasonably short and the urea-hydrolysing bacterial population was responsible for this rapid turnover rates (Steinman, 1976). Turnover of urea by

phytoplankton is also estimated to be fast in many coastal systems. The faster turnover times reported are: Herbland (1976)- 1.2 days in tropical South Atlantic waters, Kristiansen (1983) and Turley (1985)- turnover times of a few hours in Oslofjord and at a front in the weatern Irish Sea, respectively. So, urea turned over can underestimate the uptake is due to the release of labelled compounds ($^{14}C/^{15}N$) into the medium. However, the extend of the importance of the role of bacteria in the uptake of urea is still not very well known.

Values of urea uptake estimated under field conditions elsewhere are presented in Table 6. In shelf and coastal waters the specific uptake (V h^{-1}) values were between 0.0045 and 1.46 and the absolute uptake(ρ µg at N $l^{-1}h^{-1}$) ranged from 0.017 to 0.294. In the oligotrophic waters the values were very low. The V urea ranged from 0.0009 to 0.004 and the ρ values were between 0.0004 to 0.0021. No estimations of urea uptake are avilable from the high nutrient- low chlorophyll areas, except the one measurement of specific uptake (0.0137 h^{-1}) made by Wheeler and Kokkinakis (1990) in the North east Pacific. Probyn (1988) measured N uptake rates in the upwelling areas of Namibian upwelling. The V estimated was 0.0019 h^{-1} and the ρ was 0.0936 µg at N $l^{-1}h^{-1}$. Similar to the uptake of NO_3^- and NH_4^+, the urea uptake also was found to be higher in the coastal waters and were low in the oligotrophic waters. The values in the upwelling areas were intermediate from these two.

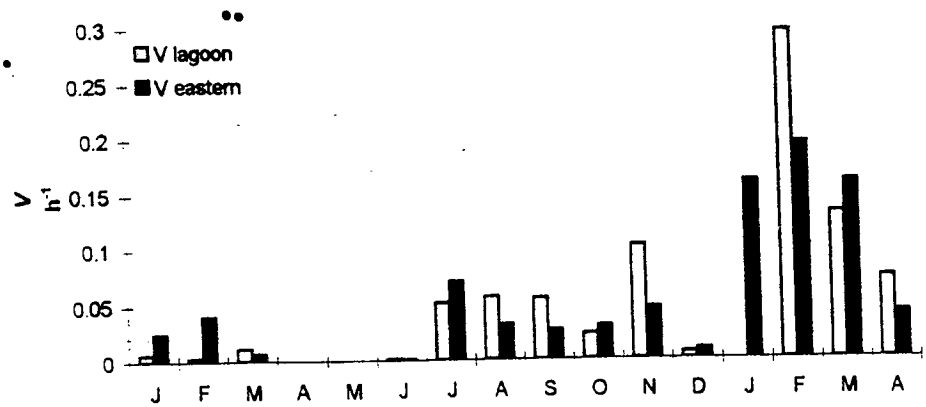
Compared to the data available on the uptake of nitrate or ammonium in the coral reefs, those on urea uptake are non-existent. Urea is generally considered less

significant in the oligotrophic waters, because of its very low ambient levels (below detection), but this is not the case with coral reefs. Measurements of the ambient concentration show that urea is most abundant than NO_3^- or NH_4^+ and, therefore, would be an important source of N for reef autotrophs.

The uptake rates measured in the present study are in the lower range reported for the shelf and coastal waters but higher than those of the oligotrophic areas. Very few reports on urea uptake are available from other ecosystems and this makes a comparative account very difficult.

The *V*urea(h^{-1}) values estimated from *in situ* incubations (trace additions of urea) in lagoon and eastern station are presented in Table 7 and 8 respectivly. In the lagoon station, the rates (V urea) ranged from 0.0009 to 0.2945 h^{-1} and in the eastern station they were from 0.0008 to 0.2588 h^{-1}. The seasonal trend was well-defined, with high values in the pre-monsoon months and the low, more or less uniform, values in the monsoon and post-monsoon months (Table 9a & b). The highest value for both the stations, measured in the month of February, lies within the range known for the coastal oceans. The seasonal trend was similar at both the stations (Fig.22a&b). The specific uptake rates correlated significantly with the ambient urea concentrations ($r = 0.69$, $P<0.001$ for the lagoon station and $r=0.52$, $P<0.01$ for the eastern station) (Fig.23) but not with Chl *a* concentrations (Fig.24). Observations that are of interest are, the high urea uptake in the low productive season (pre-monsoon), as seen from Chlorophyll *a* concentrations and the linear relation of the rates with the ambient concentrations. While the former shows that urea uptake was not totally associated

Fig. 22. a. Specific uptake rates(V) of urea.



22.b. Absolute uptake rates(ρ) of urea.

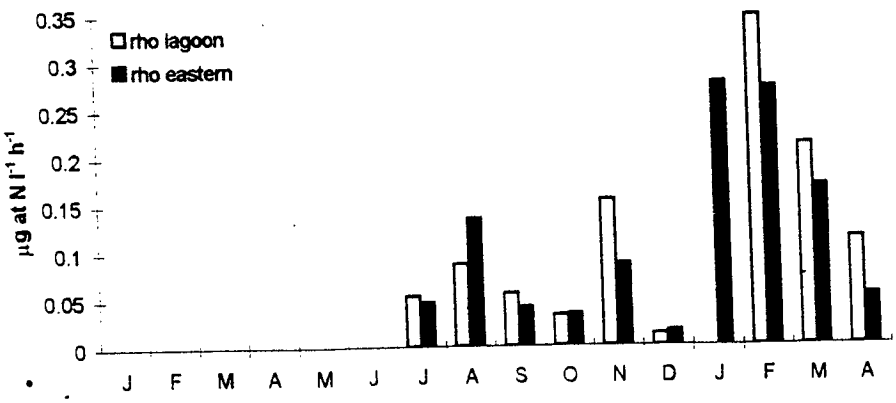
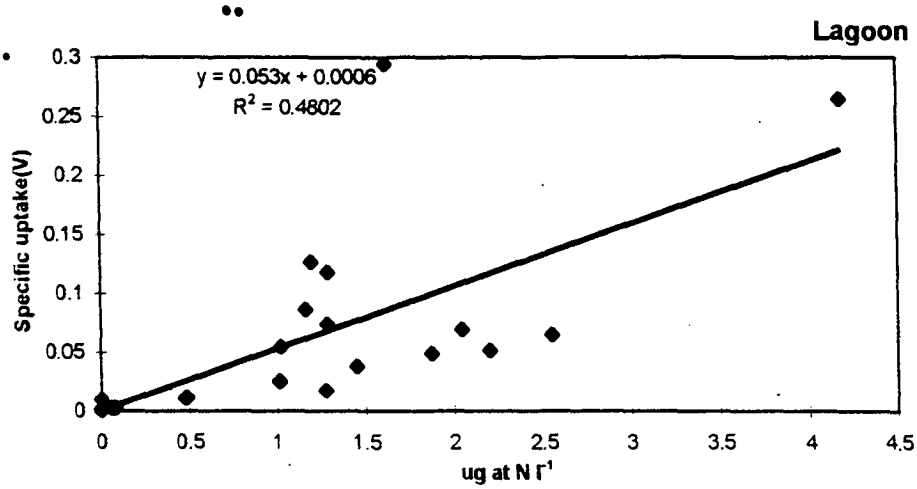


Fig. 23. Specific uptake(V) vs ambient concentrations of urea for lagoon and eastern stations.



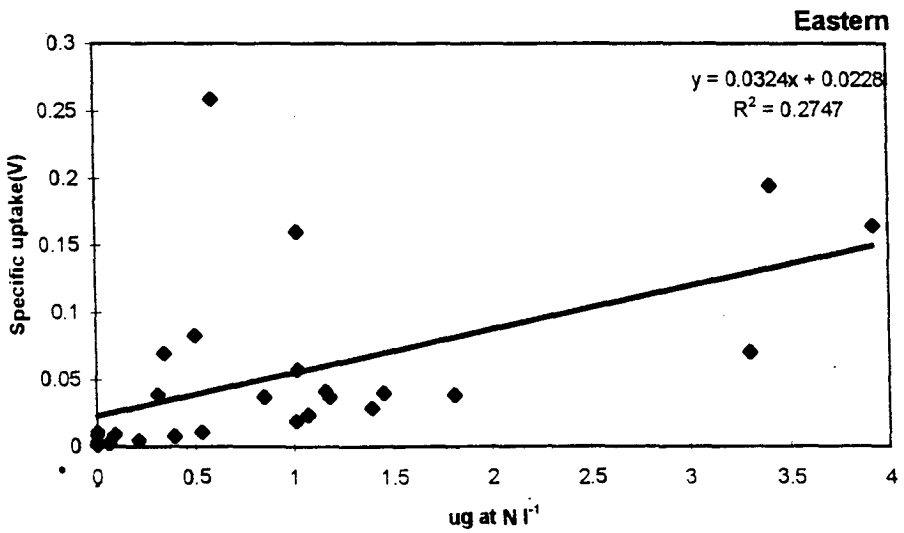


Fig. 24. Specific uptake(V) of urea vs chl.a. concentrations for lagoon and eastern stations.

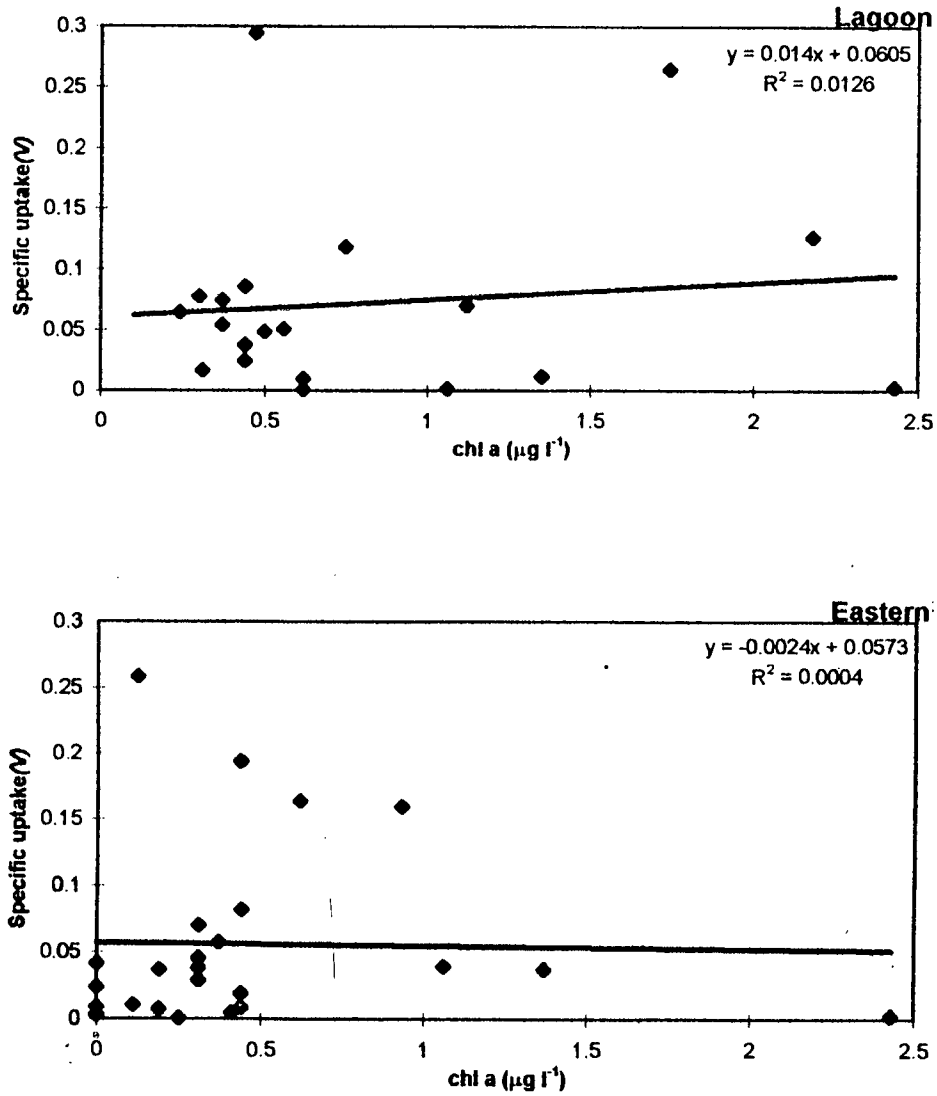
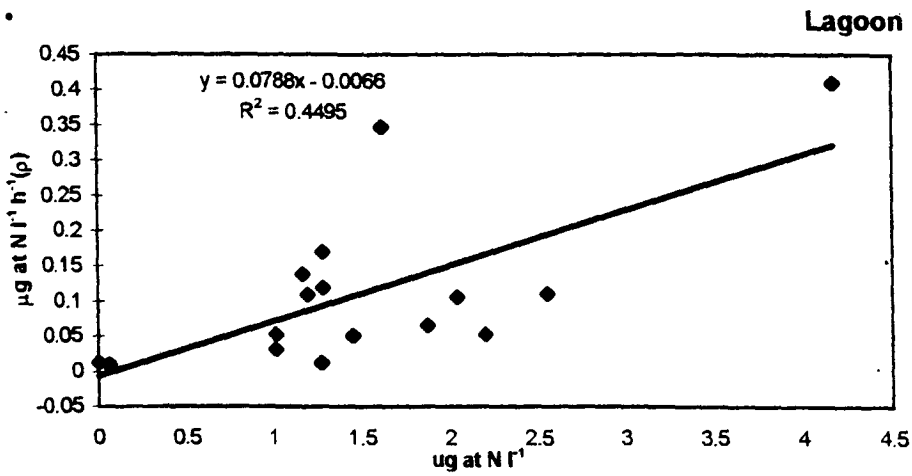


Fig. 25. Rho urea vs ambient concentrations - lagoon and eastern stations.



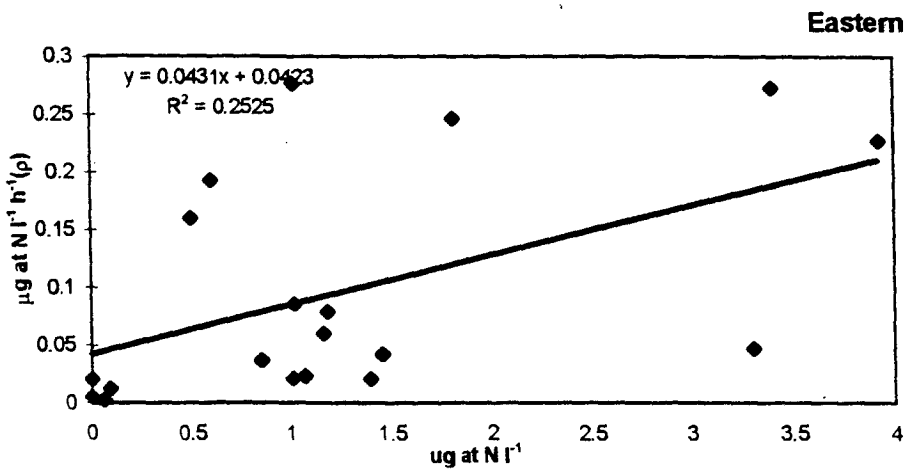
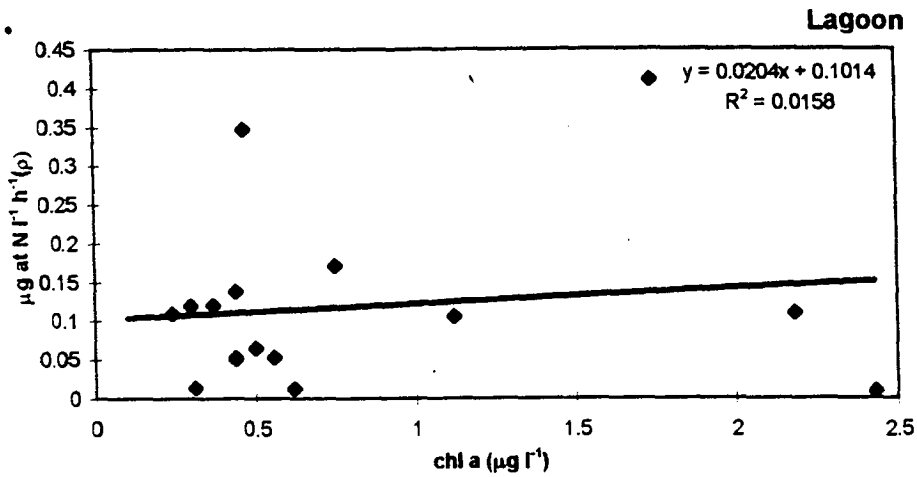
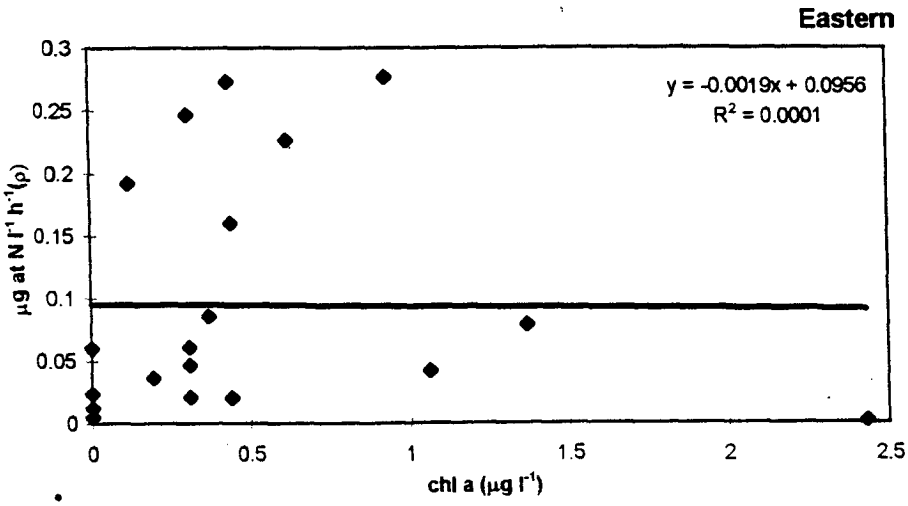


Fig. 26. Rho urea vs ambient concentrations of chlorophyll a for lagoon and eastern stations.





in this case does not deviate much from the uptake index. The present values are several orders less compared to the $V\ NO_3^{Chl}$ estimated by Dickson and Wheeler (1995). Yet, the present estimations of PON specific values never exceeded the uptake index values and are comparable to the coastal ocean waters. However, in coral reefs, given the contrasting situation that the phytoplankton productivity is akin to any oligotrophic system, the comparativly high uptake index may be discussed as below. Since the uptake index is the ratio of the absolute uptake (ρ) to the chlorophyll, the less the chlorophyll, higher will be the index or values higher than PON specific. This led to the conclusion that phytoplankton in the present samples make up only a small percentage of the planktonic biomass, as it is already reported in many other occassions (Holligan *et al.*., 1984; Kokkinakis and Wheeler, 1987).

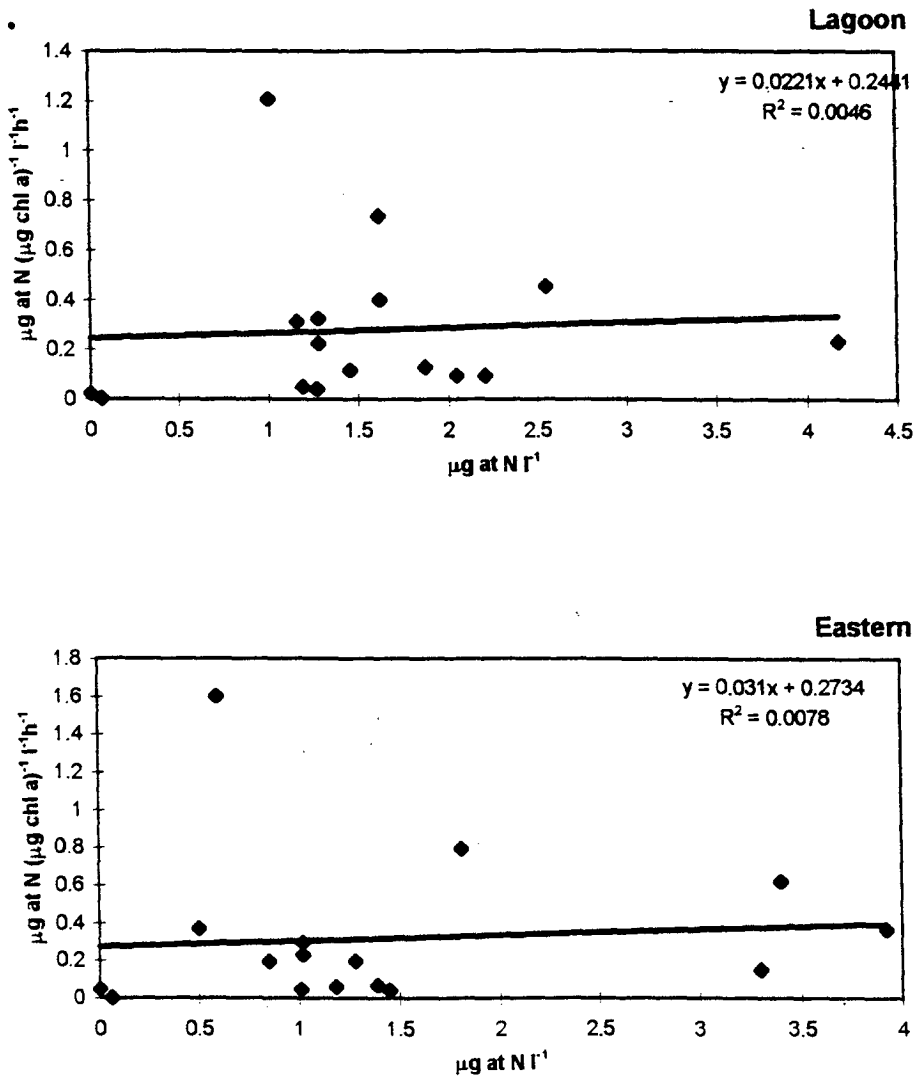
Helguen *et al.*, observed that unlike ammonium, urea uptake was dependent on its availability. This is true in the present study also, as shown by the linear relationship between V and ρ and the ambient concentrations. So, the arguement is, the uptake contributed by the heterotrophic biomass in the PON is concentration dependent (linear functions of PON specific uptake to the urea availbility), and the phytoplankton are not so - i.e. the phytoplankton uptake is saturated at concentrations much lower than the existing levels or phytoplankton are either efficient to utlize urea at any given level. It seems, the two assumptions are applicable. The following paragraphs lend a better understanding on this.

The assumption that the phytoplankton uptake is saturated at concentrations much lower than the existing levels can be substantiated by the lack of a correlation

between the uptake index and the urea concentrations (Fig.27) - this shows that the efficiency of the phytoplankton to take up urea did not increase with the increase in urea availability. The second assumption can be substantiated by the following points. McCarthy and Goldman (1979) hypostheisised that phytoplankton, grow well in the nutrient-depleted waters by efficiently taking up nutrients at very low concentrations. Further, ambient concentrations at most of the ecosystems were not limiting in the real sense is due to efficient regeneration. Coral reef ecosystems are best examples. So, phytoplankton utilise these N efficiently for growth is shown here with the uptake index showing high values (even when the availbility is less) through out the year when other conditions are not limiting (eg. light, temperature).

The RPI (Relative Preference Index) values of urea for most of the season were generally at unity or more than unity (Table in Appendix 8.1 & 8.2). The seasonal trend shows that RPI values in the Post and Pre-monsoon months were greater than one, whereas the monsoon values were either at unity, or at times less. McCarthy (1981) stated that the RPI values for NO_3, NH_4, Urea and NO_2 all converged at values of unity when availability of the more preferred forms was insufficient to meet the nutitional needs of the organisms. This could be have been been the cause of the RPI values in the monsoon period, which were less than or equal to one. It has been demonstrated (McCarthy, 1981) that urea may or may not be utilized when the prefered forms (ammonium and in some cases nitrate) are available in adequate quantities to meet the entire N demand. Therefore the high RPI values of the non-monsoon season in this study is an important observation since the ammonium

Fig. 27. Uptake index vs ambient concentrations of urea for lagoon and eastern stations.



and nitrate levels in this season are high. The lack of a relationship between RPI and Chlorophyll *a* ambient concentrations suggests that the high RPI could be due to due to heterotrophy, and not due to phytoplankton uptake.

Although the *V*urea and absolute uptake (ρurea) values were seasonally similar for the two stations, the lagoon station values were higher than those of the the eastern station at most of the observations (Fig. 22 a & b). Interestingly, however, the uptake index and the relative preference index were low in the lagoon station compared to the eastern station values. These observations of spatial variability in urea uptake are discussed below with reference to the role of heterotrophy and the availabity of urea through rapid turnover rates and higher regeneration.

The low uptake index (Chl *a* specific) in the lagoon station suggests that the uptake here is due to heterotrophy because the total uptake (ρurea) and PON specific rates (*V*urea) were high - which otherwise would have been low, corresponding to the low uptake index. The comparatively higher uptake index in the eastern station explains that the uptake is mostly by phytoplankton. This is persumably due to the low heterotrophic planktonic biomass than in the oceanic waters. The reason is that the eastern station explains the oceanic conditions, different from the lagoon that is reasonably shallow and not thoroughly flushed with oceanic waters. Studies prove this with the highest heterotrophic activity in the shallow waters than the deep waters (Chandramohan and Ramaiah, 1987). Other possibility is that the eastern station has more favourable conditions for phytoplankton uptake than the lagoon waters. Since the seasonal trend is same for the two stations this possibility is ruled out.

The low RPI (Relative Preference Index) for the lagoon station, in spite of high absolute uptake (ρurea) is due to the availability of urea in very high quantities that relatively give a lower preference index (Fig. 28). This also suggests that in the lagoon, urea is available in surplus quantities and all that is not preferentially taken up, like for ammonium, to have a higher index. The production of regenerated N forms is mainly due to heterotrophy explains the high levels of regenerated N in the lagoon. In the eastern station however, the RPI values were higher is due to low avilability of urea that increases the preference for urea.

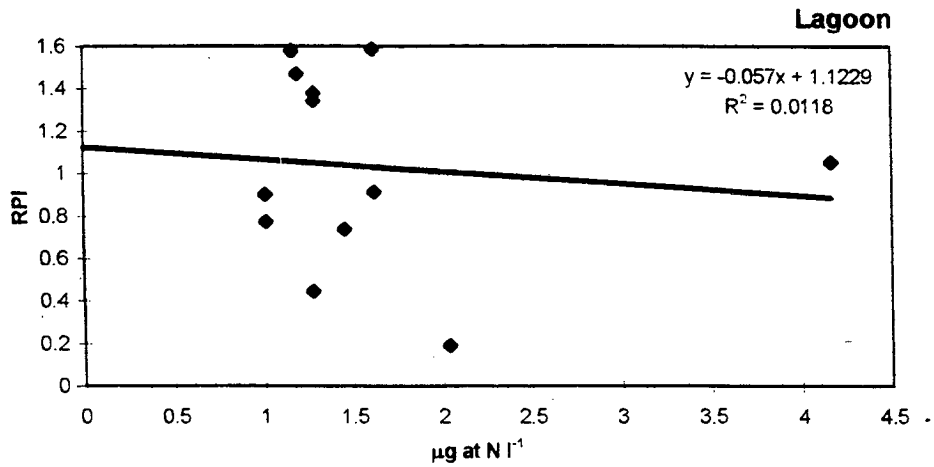
The conclusion, therefore, from the station-wise study are: In the lagoon, the uptake rates are high is mainly due to heterotrophy. The availbility of urea is more that makes the preference for urea less. In the eastern station, the uptake is mainly by chlorophyll bearing phytoplankton since the heterotrophic planktonic biomass is supposed to be low. Here, the low heterotrophy may be the reason for the low levels of regenerated N (NH_4 and urea)that resulted in high preference index.

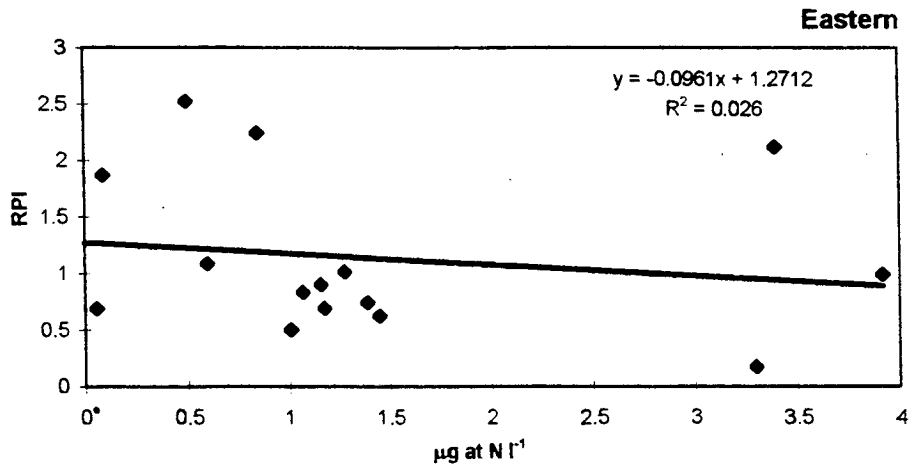
Overall, the study gives the following conclusions.

1) Urea uptake by phytoplankton is not constrained by urea ambient concentrations. That means urea concentrations are nor limiting for the phytoplankton neither it is preferred by them.

2) The main utilization is by heterotrophy -The total uptake (ρ urea) and PON specific uptake are linear with the ambient concentrations. That can mean high turnover rates too.

Relative preference index(RPI) vs ambient concentrations of urea for lagoon and eastern





3.1.3 Nitrification studies

N_2 is the most abundant species of nitrogen, present as a dissolved gas in the sea water. However, this is biochemically inert and needs to be transformed into other assimilable forms (by far, there are five oxidation states of nitrogen) for biological utilization. Nitrate is the most abundant of these biologically active compounds, and has been studied extensively in relation with primary productivity. Dugdale and Goering (1967) hypothesised a two-layer system, where nitrate is produced in the deep water by re-mineralization of organic matter and is returned to the euphotic zone. This re-mineralization is the sequential oxidation of reduced inorganic nitrogen to nitrite and nitrate (Kaplan, 1983) by micro-organisms that are collectively called as nitrifiers.

Nevertheless, Falkowski (1997) present an analysis that states, it is fixed nitrogen, not phosphorous, that limits primary productivity on geological time scales in the Ocean. He argues on the basis of denitrification, through which the fixed nitrogen from the oceans is removed as N_2. On the basis of the above argument it is very essential that the process which is intermediary of nitrogen fixation and denitrification (nitrification) - the rate at which it presents the utilisable form of N in the ocean (ie NO_3), is to be quantified in terms of marine nitrogen primary productivity. Falkowski (1997) suggested the importance of nitrification from a geological perspective, the conversion of ammonium to nitrate probably proceeded rapidly and provided a substrate (namely, NO_3), that eventually could serve both as a source of nitrogen for photoautotrophs and as an electron acceptor for a diverse group of heterotrophic, anaerobic bacteria, the denitrifiers. The importance on nitrification

is also evident from the secondary nitrite maximum at the base of the photic zone in most of the oceans (Vaccaro and Ryther, 1960; Carlucci et al, 1970; Hattori and Wada, 1971; Olson, 1981). Kaplan (1983) concludes that, given the preponderance of NO_3 relative to NH_4^+ and NO_2^- in oceanic waters below the thermocline, nitrification must be complete and very efficient indeed, even at the low levels of NH_4^+ and NO_2^- found in the sea.

Several environmental parameters have been shown to influence the nitrification rates in marine ecosystems. These are: light, oxygen, temperature, NH_4 concentration, organic matter etc.

Oxygen - Chemoautotrophic nitrifying bacteria are strictly aerobic and require free O_2 for the oxidation of NH_4^+ and NO_2^- (Rees and Nason, 1966; Aleem *et al.*, 1965; Painter 1970). However, Kaplan (1983), in his review has shown that marine nitrifiers can grow and oxidize their substrate at very low oxygen tensions. Low oxygen conditions (down to 10 μM O_2) induced a marked decrease in the rate of production of nitrite, from 3.6×10^{-10} to 0.5×10^{-10} mM NO_2-.cell^{-1}.day^{-1}, and at the same time increased the yield of N_2O (Kaplan, 1983). Rysgaard *et al.*(1994) observed stimulation of nitrification in sediment cores with increased oxygen concentrations (0-100% saturation) in the overlying water. Only a slight stimulation was observed above 100% saturation, and at concentrations >300 μM O_2, it was NH_4^+ rather than oxygen that regulated nitrification (Rysgaard *et al.*, 1994). The same inhibitory effects were observed with high O_2 concentrations in the estuarine sediments (Henriksen and Kemp, 1988; Jorgensen *et al.*, 1984). So, oxygen plays a major role in the processes of nitrification.

The optimum temperature for all the nitrifying bacteria isolated from northern Pacific Ocean was found to be 28°C (Carlucci and Strickland, 1968). Studies in pure cultures (in sewage studies) also showed optimal activity in a similar temperature range of 25 - 35°C (Focht and Verstraete, 1977). Watson and Waterbury (1971) observed optimum growth for cultures *Nitrospira* and *Nitrococcus* at temperatures ranging from 25 - 35°C, but found no growth below 14°C. Most of the available literature show that below 4 - 5°C nitrifiers do not grow (Kaplan, 1983). However, nitrifying activity is seen even at temperatures as low as <-2°C (Horrigan, 1981). These studies help to assess the activity in deep waters, which is substantial as shown by the NO_3 concentrations - where the temperature ranges between 4 - 5°C. Benounsky and Nixon (1990) observed that temperature is a major factor in influencing the annual cycle of pelagic nitrification in Narragansett Bay, Rhode island.

Organic matter- Efforts to grow nitrifying bacteria in organic media did not show good results (Watson and Waterbury, 1971). They (Watson and Waterbury, 1971) examined *N.gracilis* and *N.mobilis*, neither of which could oxidize significant quantities of organic matter. The biochemical basis for an apparent lack of heterotrophic ability in nitrifying bacteria is due, in part, to the lack of Krebs cycle enzymes, particularly α-ketoglutarate dehydrogenase (Kaplan, 1983). Williams and Watson (1968), however, identified the presence of Krebs cycle enzymes, which suggest that that in certain environments, nitrifiers may act as mixotrophs and combine utilization of inorganic carbon/energy sources with that of organic matter (Kaplan, 1983). He concludes that interactions between nitrifiers and heterotrophs

and possible mixotrophic nutrition of marine nitrifiers may be of ecological importance and should be investigated further.

Kinetic experiments proved that marine nitrifiers in natural environments utilize their substrate at much lower levels than those observed in culture studies (Kaplan, 1983). Hashiomoto *et al.* (1983) estimated nitrification rates in Cariaco Trench waters, with substrate levels ranging from 0.1 to 5 μM NH_4^+ and demonstrated that the rates increased sharply as the substrate concentrations increased from 0 to 0.1 μM NH_4^+. Benounsky and Nixon (1993) demonstrated that ammonium concentrations were most likely responsible for the large differences in rates among three sites along an estuarine gradient in Narragansett Bay. A strong positive relationship ($r^2 = 0.81$) was observed between the nitrification rates and ammonium concentrations when all the values at temperatures >20°C were plotted separately (Benounsky and Nixon 1993). Qiu and McComb (1996) in a novel experiment observed that air drying of intact sediment cores released substantial amount of ammonia following re-flooding - probably from the biota killed in the process, which eventually stimulated nitrification rates at rates 10 times higher than in original water-logged sediments under aerated conditions.

Kaplan (1983) presented a review of nitrification studies in pelagic systems. Most of them show a relationship with the secondary nitrite maximum. Several mechanisms have been proposed to account for this. The first is the nitrite excretion by phytoplankton (Vaccaro and Ryther, 1960) and the second, nitrate reduction by nitrate reducers (Payne, 1973). Wada and Hattori (1971) and Miyazaki *et al.*(1973) supported the nitrification hypothesis. The conceptual model by Olson (1980) gives

an allowance for a shift from nitrite excretion by phytoplankton to ammonium oxidation that explains a 'continuum' of nitrite production potential with depth. Olson (1981) hypothesised a differential photoinhibition, shown from the inhibitory effect of light on nitrite oxidizers to explain the secondary nitrite maximum. NH_4^+ oxidizing activity is high in the upper water column, while NO_2^- oxidizing activity is inhibited - NO_2^- oxidizers, responsible for the nitrate produced in deep waters showed activity only in the dark (Olson, 1981). Later Wood (1986) demonstrated that nitrifying bacteria are sensitive to solar radiation at wavelengths less than 480.

Rates of nitrification that have been measured in aquatic marine environments range from 0.01 - 100 ηmol N l^{-1} h^{-1} over a wide range of NH_4^+ concentrations, locations and depths (Kaplan, 1983). The rates reported from estuarine and coastal areas range generally between 0 and 166.6 ηmol N l^{-1} h^{-1}, except for some very high values: a maximum of 1083 ηmol N l^{-1} h^{-1} in estuary Scheldt estuary (Somville, 1978); a maximum of 466.6 ηmol N l^{-1} h^{-1}, in the Providence river (Benounsky and Nixon, 1993) and the maximum values of 916 ηmol N l^{-1} h^{-1} (McCarthy *et al.*, 1984) and 1333 ηmol N l^{-1} h^{-1} (Horrigan *et al.*, 1990), in Chesapeake Bay (Table.10). The open ocean rates were comparativly very low (range: 0.01 - 12.5 ηmol N l^{-1} h^{-1}) (Table.10). Vincent and Downes (1989) presented values (range: 1.62 - 4.92 ηmol N l^{-1} h^{-1}) from the upwelling region off the west coast of the South Island. The higher rates for the coastal areas reported may be related with high organic production, since the ultimate source of regenerated nitrate is decomposing organic matter (Kaplan, 1983).

Table 10-: Watercolumn nitrification rates in marine systems - studies so far.

Location	Rates (ηmol l^{-1} h^{-1})	Reference
Estuaries,Coastal bays		
Alaska, Skan Bay	0.66-6.25(15N assay)	Hattori *et al.* (1978)
	0.83-9.16(Chemical assay)	Hattori,*et al.* (1978)
Japan, Sagami Bay	0.62 - 1.12	Miyazaki,*et al.*(1973)
York River, Virginia	10 - 28.7	McCarthy,*et al.*(1983)
Chesapeake Bay	30 - 100	McCarthy,*et al.* (1983)
Chesapeake Bay	0 - 916	McCarthy,*et al.* (1984)
Chesapeake Bay	0 - 375 (spring) 20.83 - 1333(fall)	Horrigan,*et al.*(1990)
Scheldt estuary	0 - 1083	Somville, 1978
Tamar estuary	0 - 166.6	Owens, 1986
Providence R. estuary	0.4166 - 1.666	Nixon and Berounsky, 1984
Lower Narragansett Bay	0.833 - 40.98	Berunsky and Nixon, 1993
Providence R. estuary	1.666 - 466.6	Berounsky and Nixon, 1993
Delaware River	0 - 50	Lipschultz,*et al.*1986
Blackstone River	1.666 - 70.83	Berounsky and Nixon, 1993

able 11-: Nitrification rates in marine sediments.

ocation	Rates (ηmol g^{-1} h^{-1})	Reference
nshore		
laska, eelgrass bed	0.1125	Iizumi *et al.* (1980)
assachusetts, salt arsh	0 - 0.833	Kaplan *et al.* (1979)
apan, coastal bays	0.833 - 2.08	Koike and Hattori (1978)
orth Sea	0.150 - 1.17	Vanderborght and Billen (1975)
orth Sea	0.0125 - 8.75	Billen (1978)
orth Sea	0 - 0.833	Billen (1976)
anish coast	0 - 1.042	Henriksen (1980)
ew Zealand, ntertidal	0.916	Belser and Mays (1980)

ffshore, open ocean		
laska, shelf waters	2.9 - 5.42	Schell (1974)
outhern California	0.19 - 2.5	Olson (1981a)
	0.79	Ward et al. (1982)
	0.63 - 3.1	Olson (1981a)
ariaco Trench	0.09 - 0.63	Hashimoto *et al.* (1983)
argasso Sea	0.01 - 1	Vaccaro (1962)
ast China Sea	0.16 - 0.27	Miyazaki (1975)
hillipine Sea	0.21 - 0.3	Miyazaki (1975)
orth Pacific	2.8	Hattori and Wada (1971)
orth Pacific	0.38 - 0.67	Wada and Hattori (1971)
est Pacific	0.37 - 1.17	Miyazaki*et al* (1975)
altic Sea	0 - 12.5	Enoksson, 1986

In sediments, nitrification may occur primarily at the oxygenated sediment/water interface - the nitrate diffuses away from its zone of production to be released into the water or reduced to nitrogenous gases or ammonium in deeper sediments (Kaplan, 1983). The nitrate values that are often higher than that present in the overlying water indicates high nitrifying activity in the sediments. It is supported by several mechanisms that enhance the nitrate production in the sediments. Grundmanis and Murray (1977) postulated that O_2 was supplied from surface waters by irrigation through burrows of benthic organisms, thus enhancing the nitrification rates. In a different mechanism, Chaterpaul *et al.* (1980), suggested that the tubificid worms accelerated the upward flux of ammonium into the aerobic surface layers in stream sediments, thus providing substrate for nitrifying bacteria. Henriksen et al. (1980) found that the presence benthic infauna also increased nitrification rates in marine sediments.

Earlier estimates of nitrification in marine sediments have been listed in the review by Kaplan (1983). The values estimated so far range from 0 to 8.75 ηmol g^{-1} h^{-1} (Table.11). Relatively more studies have been made on sediments than with water column in marine environments. However, a comparison of values from different areas is still difficult because of the differences in the expression of the rates, such as m^{-2}, cm^{-3} and g^{-1}. The values in Table.11 are converted from a cm^{-3} representation, assuming the density of sediment as 1 g cm^{-3}.

Despite the importance assigned to nitrification in marine systems, only few estimates of nitrification are available in coral reefs. Nutrient flux studies prove that there is considerable output of nitrate, ammonium and DON from corals and uptake

by algal communities (Webb *et al.*, 1975). The source of nitrate in this case may be from nitrifiers (Webb *et al.*, 1975; Webb and Wiebe, 1975; Wafar *et al.*, 1986). The following account lists the studies in which nitrification activity in several nirifying sites of a reef was estimated. Webb and Wiebe (1975), estimated nitrification rates of 1.3 ηmol cm^{-2} h^{-1} during night time and 3.9 ηmol cm^{-2} h^{-1} during the day in tide pools of Enewetak atoll. Corredor and Capone (1985), estimated values ranging from 0 to 1.95 ηmol (g dry sediment)$^{-1}$ h^{-1} in the suface, and 27 ηmol cm^2 h^{-1} when depth-integrated (down to 30 cm) in reef sands. Corredor *et al.* (1988), observed high rates of nitrification (~ 400 nmol cm-2 h-1) in a sponge (*Chondrilla nucula*) harbouring symbiotic cyanobacteria, and lower rates (~ 2 ηmol cm^2 h^{-1}) in the case of *Anthosigmella varians* having symbiotic zooxanthellae. The study of Wafar *et al.*, (1990) demonstrated that living corals themselves are active sites of nitrification in a reef. Their comparisons of NN_4^+ produced with N-serve addition and $NH_4^+ + NO_3^-$ produced without N-serve addition in many corals showed that almost all the NO_3^- production is at the expense of NH_4^+ arising from coral excretion. Excluding the very low values measured in *Fungia*, they estimated a mean NO_3 production rate of 9.4 ± 6.0 nmol (mg coral tissue N)$^{-1}$ h^{-1}.

The present estimates of nitrification are based on the following facts. Though rate measurements are available for several active sites of nitrification in a reef, compared to other ecosystems, measurement of nitrifying activity in the sediments and water column of a coral reef are still scarce. Secondly, similar to the situation in coastal systems, where there is a dearth of seasonal assessment, no estimates are made so far in coral reefs on a seasonal basis. A comparative study of nitrification

rates in different sites of a reef is also a necessity. The data in the present study fills up the lacunae.

The rates of water column nitrification ranged from 0.78 to 23.84 ηmol N l^{-1} h^{-1} (mean: 5.15 ± 5.48 ηmol N l^{-1} h^{-1}) in the lagoon and from 0.24 to 13.41 (mean: 3.05 ± 3.72 ηmol N l^{-1} h^{-1}) in the eastern side. Earlier estimations on coral reefs (Webb and Wiebe, 1975) fall in the lower end of this range (1.3 and 3.9 ηmol cm^{-2} h^{-1}). Though the values are comparable to the estimates of most of the open ocean and offshore waters (Table.10), the values varied considerably within the seasons and were often higher than those of open ocean conditions.

Fig.29a shows nitrification rates for the entire set of observations. A distinctive seasonality in the nitrification rates in the water column as well as in the sediment becomes evident. In the lagoon waters, the observations show that highest activity was in the post-monsoon season (mean: 5.94 ± 4.51 ηmol N l^{-1} h^{-1}, followed by slightly lower rates (mean:5.44 ± 1.41 ηmol N l^{-1} h^{-1}) in the pre-monsoon and remarkably reduced rates (2.81 ± 2.49 ηmol N l^{-1} h^{-1}) in monsoon months. Similar trend can be seen with the data of the eastern station also. While the average value for the post-monsoon months was 4.78 ± 4.09 ηmol N l^{-1} h^{-1}, that of the pre-monsoon was 3.64 ± 3.24 ηmol N l^{-1} h^{-1} and that of the monsoon was 2.55 ± 2.11 ηmol N l^{-1} h^{-}.

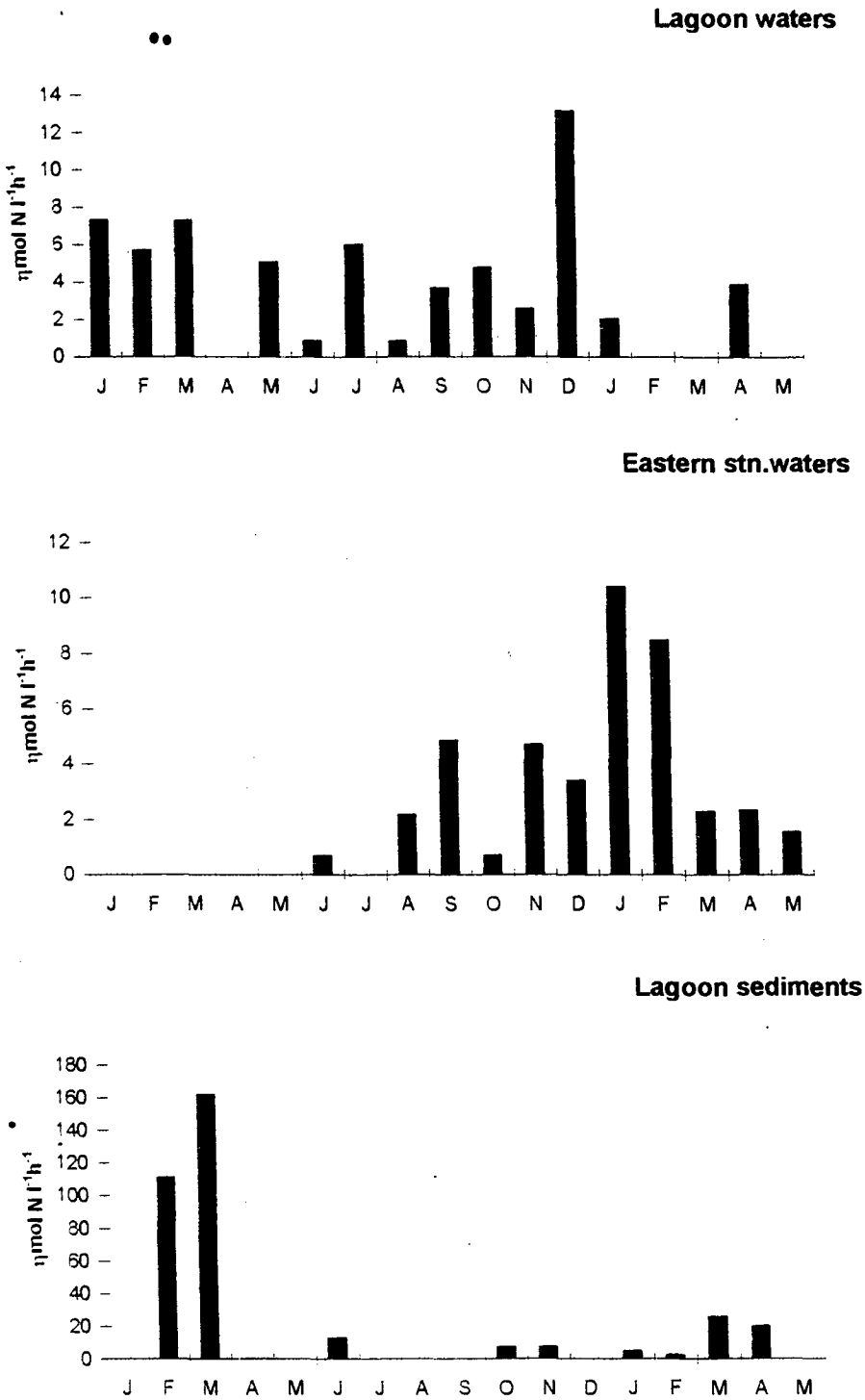
The amplitude of nitrification rates in beach sediments (0.172 - 172.337), unlike in previous studies from other ecosystems that showed a narrow range (Kaplan, 1983), was quite large. The rates were remarkably higher (mean: 33.56 ± 54.37 ηmol N g^{-1} h^{-1}) than even the earlier estimations in coral reefs (0 - 1.95 ηmol g^{-1} h^{-1}, (Corredor and Capone, (1985) The column integrated rates in the study of

Corredor and Capone (1985), (27 ηmol cm^{-2} h^{-1}), however, is close to the present estimates. As mentioned earlier, very few measurements are available for comparison from other marine systems, since several authors used different units. Nevertheless, the nitrification rates in the present study appear to be several orders higher than those from other ecosystems listed in Table.11.

The seasonal changes in the sediment nitrification rates differed from those of the water column. Some measurements in the post monsoon months showed some high rates but the values generally remained constantly low during the rest of the year (Fig. 29a). The integrated values for the three seasons showed a very high value for the pre monsoon season (53.0 ± 66.7 ηmol g-1 h-1) with the considerably low values in the post monsoon (5.62 ± 1.83 ηmol g-1 h-1) and monsoon (9.65 ± 3.86 ηmol g-1 h-1) periods.

The remarkable features emerge from these results. First, is the distinct seasonality and second, the very high rates of nitrification in the sediments. Seasonal patterns of nitrification have been demonstrated in salt marsh sediments (Thompson et al. 1995). An apparent relationship between temperature and nitrification rates indicated a seasonal trend. Henriksen and Kemp (1988) suggested that competition for NH_4^+ with photoautotrophs may limit the growth of nitrifiers in the surface sediments. Both these cannot account the variations in the present study because, 1) temperature is not a highly variable parameter in tropical atolls and, 2) the high values of nitrification in the present case are associated with the seasons where the phytoplankton productivity is also high.

Fig. 29a. Average nitrification rates

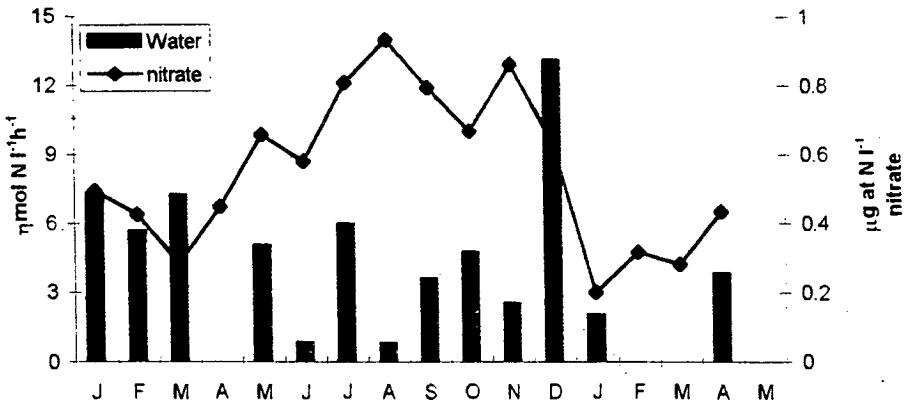


The possible relationship can be observed with the increased abundance of nitrogenous substrates in the non-monsoon months compared to the monsoon months. Fig.29b & c show the relationship between water column and sediment nitrification rates with ambient DIN concentrations. The rates showed a characteristic increase with increase in ammonium concentrations. The same relationship is explained in the earlier studies also. Benounsky and Nixon (1993) found a positive (r^2 = 0.71) relationship between rates of nitrification and ammonium concentrations. Interestingly, with NO_3^- and NO_2^-, however the trend is reversed. In spite of the lower rates, ambient concentrations remained higher especially monsoon. The high NO_3 concentration is contributed to reduced consumption by primary producers since the uptake is always linear (see uptake). Therefore the high NO_3 concentrations are not contributed to by nitrification but, as discussed earlier (in the Chapt.3.1.1.1), this may be due to monsoonal input. The lack of accumulation of NO_3 when of nitrification rates are high is due to utilization, of NO_3 because this (high nitrification rates) happens during periods of high productivity. Denitrification cannot be a major sink of NO_3, given the highly oxygenated conditions.

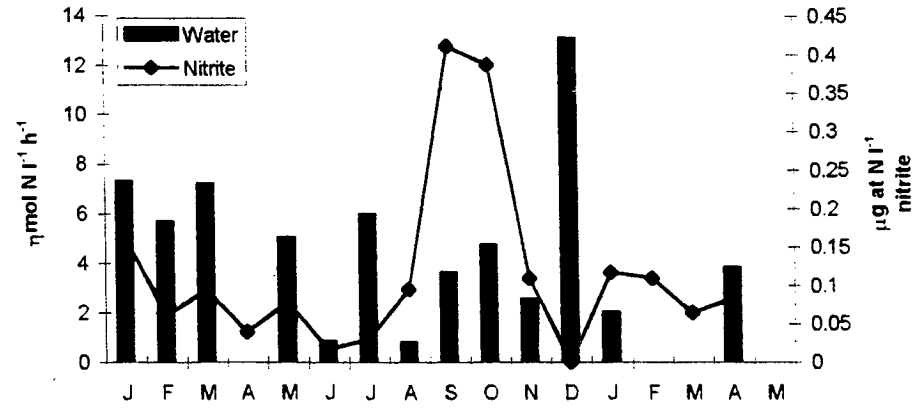
Another reason for the high rates during the most favourable months can be traced from the high organic matter production, since ammonification through organic matter degradation can supply enough substrate for the nitrifiers. This explanation is also supported by the differences observed between the lagoon rates and the eastern station; higher rates in the lagoon (mean: 5.15 ± 5.48 $\eta mol\ l^{-1}\ h^{-1}$) than in the eastern station (mean: 3.05 ± 3.72 $\eta mol\ l^{-1}\ h^{-1}$). The explanation for this resides in the fact that the lagoon supports a higher organic matter production

Water column nitrification rates and ambient DIN concentrations in the lagoon.

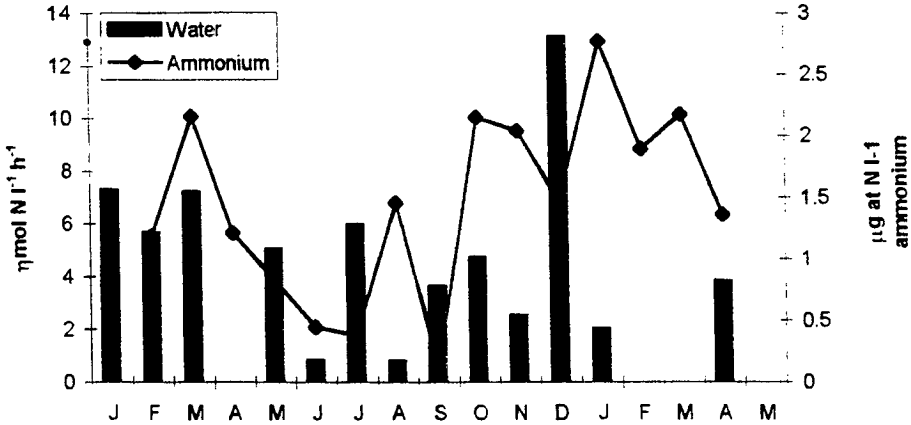
a) with nitrate



b) with nitrite

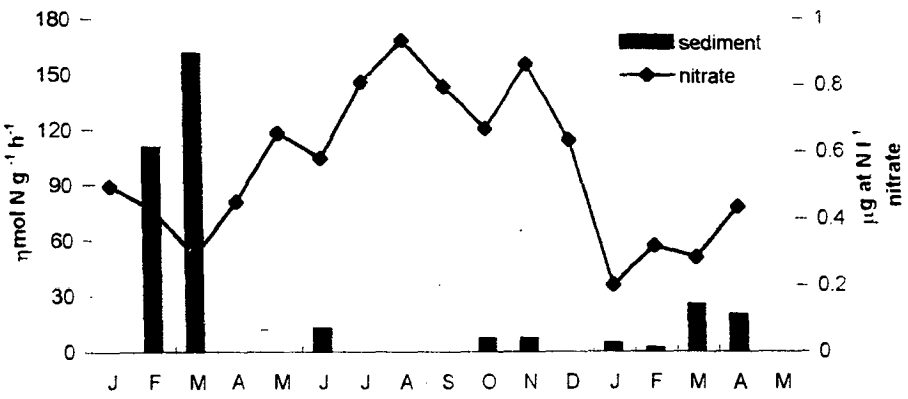


c) with ammonium

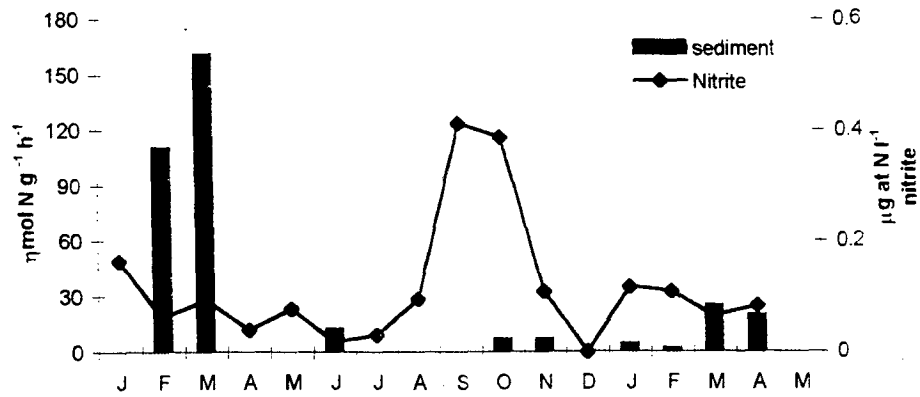


Sediment nitrification rates and ambient DIN concentrations in the lagoon.

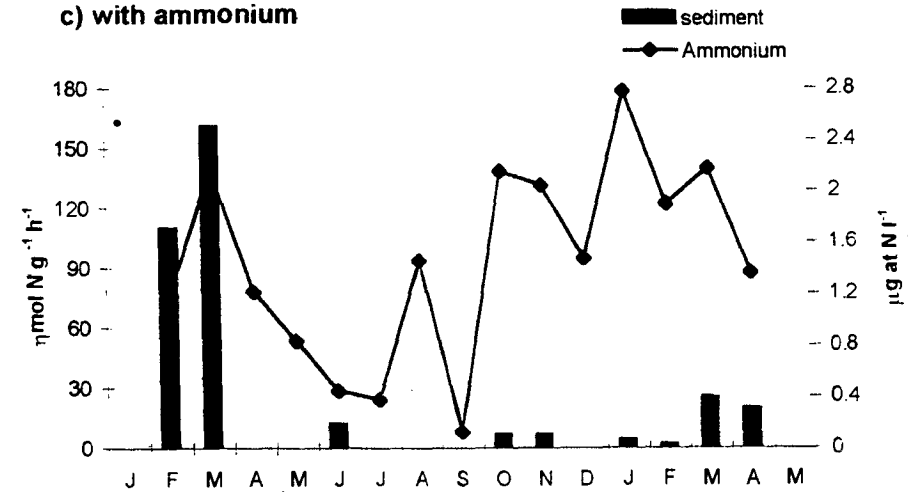
a) with nitrate



b) with nitrite



c) with ammonium



through its large biomass which can through excretion, supplement the substrate pool for nitrification. The eastern station, on the contrary, represents open ocean conditions, with relatively lower biomass, and have lower rates of nitrification. This observation emphasizes the need for estimating NO_3 production rates in different niches of an ecosystem, that support different levels of productivity. The high rates of nitrification observed in the corals (Wafar et al. 1990) and sponges (Corredor et al. 1988) can be cited as best examples to support this line of reasoning. Wafar et al.(1990)'s observation that all the NO_3 produced is at the expense of NH_4 arising from coral excretion, further lend support to these arguments.

The second important observation is the very high nitrification rates reported in the lagoon sediments. The following conditions in the lagoon might have favoured this: 1) the highly oxygenated waters which enriches the sediment, 2) the high organic matter in the lagoon sediments, that upon degradation can supply large quantity substrate for nitrification (discussed earlier), and 3) NH_4^+ excretion through the high numbers of benthic in fauna.

The following conclusions are possible:

1) Nitrification rates in the coral atoll are regulated by substrate concentrations. The factors that control the ammonium production are important in this case.

2) Physical conditions seem to play an indirect role through controlling organic matter production.

3) There is a strong coupling between nitrification and NO_3^- utilization, since the NO_3^- produced does not accumulate in the environment.

3.2. Nitrogen uptake in the oceanic waters off the Lakshadweep atolls.

Coral atolls have primary production rates typically in the order of several g C m^{-2} d^{-1} in spite of the fact that they are located in the middle of low productive oceanic waters (< few hundred mg C m-2 d-1) with often undectable levels of nitrogen and phosphorous nutrients in the euphotic zone. They sustain such high productivities by effectively recycling the nutrient elements and by conserving them within the ecosystem (Crossland, 1983; Wafar *et al.*, 1986). Nevertheless, reefs cannot remain totally 'leak- proof' and must export a fraction of the nutrient elements, in particulate and dissolved form, if only to remain in balance with their import into the reef ecosystem (e.g. advection, N_2 fixation).

Coral reefs have indeed been found to be net exporters of particulate N and consequently become important in fuelling the planktonic food chain in the surrounding waters. Export of "particulate organic aggregates" by the reef has been demonstrated more than two decades ago (Johannes, 1967), and thus could equal as much as 20% of the gross production of the reef (Qasim & Sankaranarayanan, 1970), an order or more of magnitude greater than the measured phytoplankton production near the reefs (Wafar, 1977). The organic aggregates constitute a significant source to the particulate carbon and nitrogen pools in reef waters, and are readily ingested by a variety of heterotrophs, including species that are important components of reef zooplankton communities (Johannes, 1967; Gottfried and Roman, 1983). These observations, viewed from the perspective of low phytoplankton to zooplankton ratios in reef waters, provide a clear evidence of the importance of energy flux from

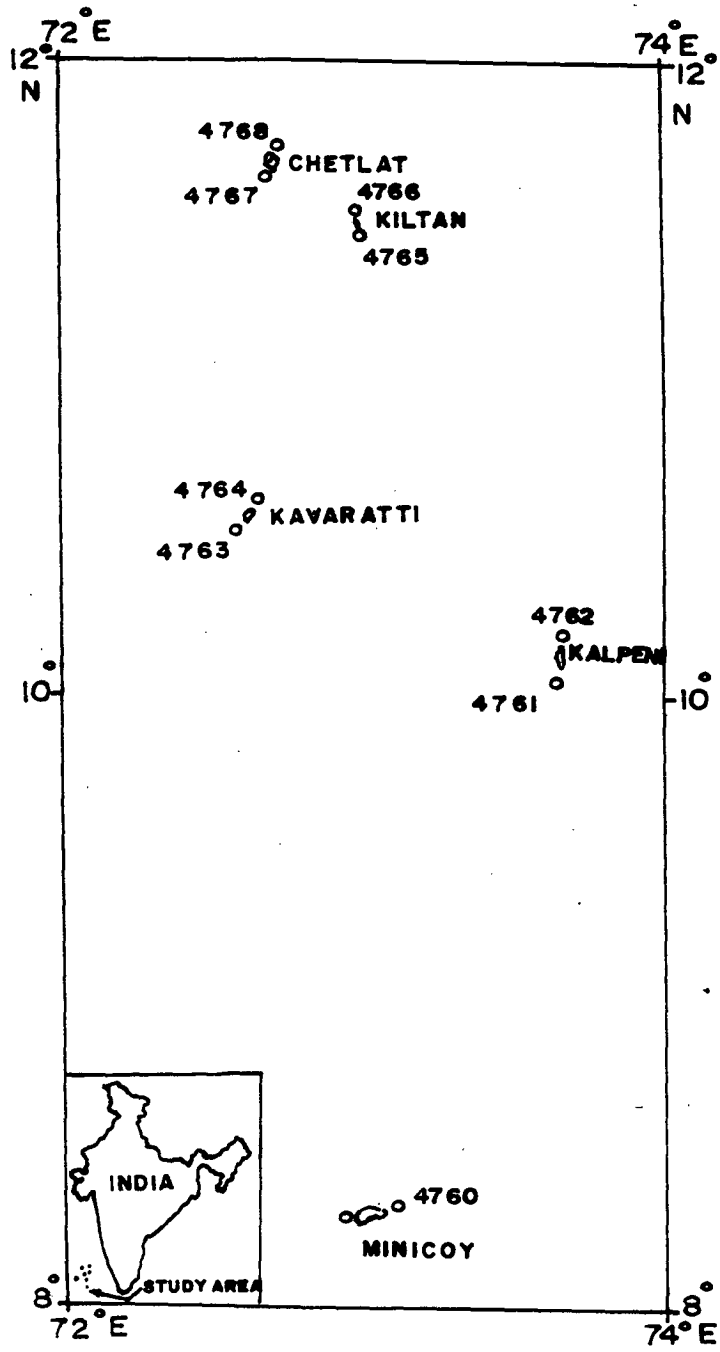
nutrient-rich benthic production regime to nutrient-poor planktonic regime. It is only natural, therefore, to expect that the dissolved nutrients must flux in a similar way and hence influence the phytoplankton production near the reef; in fact, nitrate export from the reef regions dominated jointly by algae and corals is known (Webb *et al.*, 1975), but whether other nitrogen compounds, which are far more readily taken up by phytoplankton (e.g. ammonium and urea) are also exported in a similar way, and if so, how far they influence the planktonic productivity near the reefs, still remains to be resolved. The present study addresses these two questions.

3.2.1 Materials and methods

During the 196th cruise of R.V Gaveshani (April 1988) to the Lakshadweep Sea, 10 stations near 5 coral atolls (two for each atoll) were occupied (Fig.30). The stations were within 1 Km from the reef, and the depth at the stations was around 500 m.

Water samples were obtained from 5 light-depths (0, 8, 16, 27 and 54 m corresponding approximately to 100, 50, 25, 10 and 1% light penetration) within the euphotic zone and at 7 depths (75, 100, 125, 150, 200, 300 and 400m) below. Parameters measured and the methods adopted were: NO_3^-, NO_2^-, $NH_4^+$and PO_4^{3-}, by colorimetry, dissolved organic nitrogen (DON) by persulphate digestion and colorimetry and chlorophyll a by fluorimetry (Strickland and Parsons, 1972); urea by the diacetyl-monoxime method (Newell ,1967), and particulate organic carbon (POC) and nitrogen (PON) in a Perkin Elmer model 240 elemental analyser. Determination

Fig. 30. Station locations.



of POC, PON, and *Chl a* concentrations were made only on samples from the euphotic zone.

Measurement of NH_4^+, NO_3^-, and urea uptake rates were made on all water samples collected from the 5 light depths at all stations. Samples were always collected 1 h before before dawn or noon, so that the incubations could be initiated precisely at dawn or noon, and run for half-day periods; this was done to minimize the effects of diel variations in photosynthetic activity on N uptake. After collection, samples were pre-filtered on 200 μm nytex mesh, dispensed in to 2 l glass bottle, and added with tracer (99 atom % ^{15}N ; Kor isotopes, USA) at 0.05 μmol l^{-1}. Incubations were under simulated *in vivo* conditions on the deck, and the particulate matter at the end of the incubations was recovered on pre-combusted GF/F filters and dried at 40°C. ^{14}N:^{15}N isotope ratio of this fraction was determined by emission spectrometry in a Spectro-optique GSI nitrogen analyser.

Nitrogen uptake rate were calculated from the equation (Dugdale and Goering, 1967)

$$Pa = p/t * \Delta I_p/I_s (O) - I_o$$

where P is the amount of PON, t is the incubation duration, ΔI_p is the increase in isotopic content (atom %) in the particulate fraction, $I_s(O)$ is ^{15}N atom % of the substrate at the begining of the experiment, and I_o is the natural level of ^{15}N atom %. Conservtive uptake rates (Eppley *et al.*, 1977) were calculated with the same equation by replacing $I_s(0)$ with I_t where I_t is the ^{15}N atom % in the tracer; this sets the ambient concentration of the substrate at zero.

Apparent consumption of substrate was calculated as

$b = \rho a\ T/S$

where ρa is the conservative uptake rate and S is the concentration of the added

tracer. Ratio of actual to apparent uptake rates (x or ρ/ρa) was calculated as

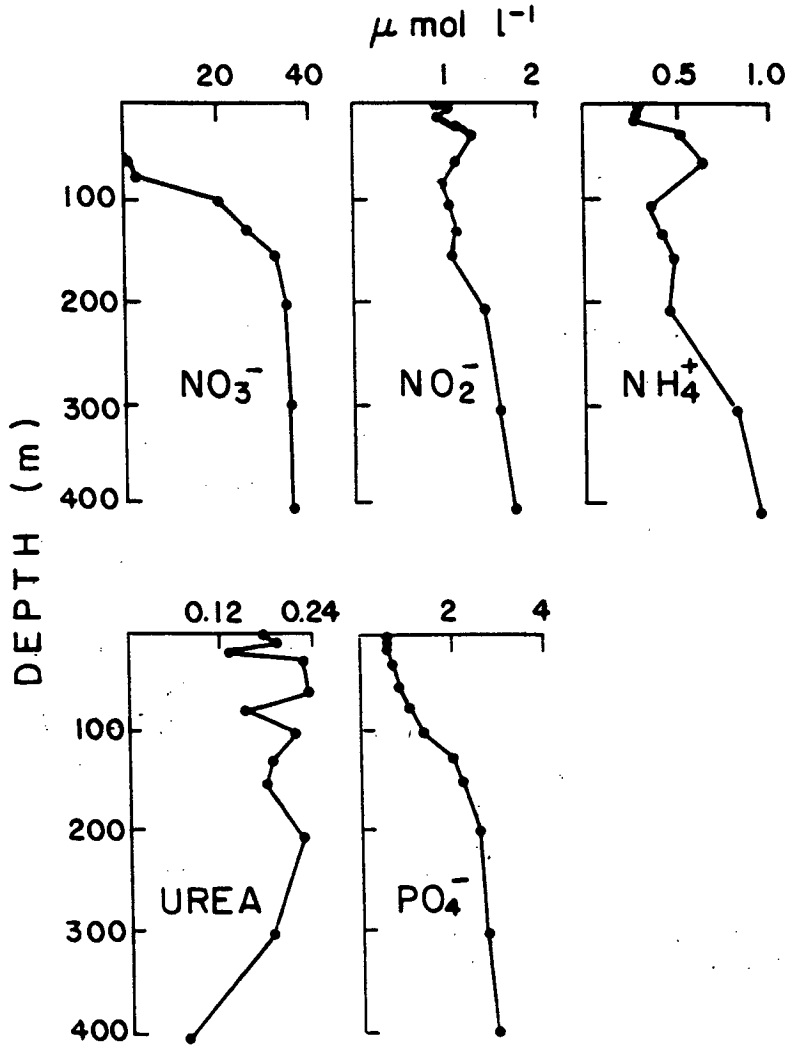
$x = -1+(1-b)^{1-a}/(a-1)b$

where a is the ratio of rate of regeneration of the substrate to true uptake rate. The last two equations, proposed by Kanda *et al.* (1987) are useful in correcting for the isotope dilution effect, which is not provided for in the equations of Dugdale and Goering (1967).

3.2.2 Results

Representative profiles of the distribution of N nutrients are shown in Fig.31. NO_3^- was generally <0.5 μmol l^{-1} in the euphotic zone, increasing rapidly below. NO_2^- was below the limits of detection at stns 4759 - 4763 and at 4768; at other stations it was, in measurable concentrations. NH_4^+distribution was random with a tendency for a sub-surface maximum at about 100 m. Urea concentrations were generally higher in the euphotic zone than below. DON was the largest fraction of N compounds within the euphotic zone, but decreased rapidly in deeper waters. Total dissolved N was < 10 μmol l^{-1} in the euphotic zone, increasing to >30 μmol l^{-1} below 200 m. PO_4 concentrations within the euphotic zone were generally 0.5 - 1 μmol l^{-1}, increasing to >2μmol l_{-1} in the deeper waters (Fig.31). DOP and total dissolved P concentrations were high (5-9 μmol l^{-1}) without a clear description pattern in the

Fig. 31. Representative profiles of N nutrients and phosphate near the reefs.



euphotic zone but decreased below. The slope of the regression line relating NO_3^- and PO_4 from all depths at the 10 stations was 19.9 ($p<0.01$), but it was less than unity ($p<0.05$) when either NO_3^- alone, or $N0_3$ and NH_4^+ together, were regressed against PO_4 for only the euphotic zone depths (Fig.32) Average POC and PON concentrations were 132.4 ± 49.6 μg C l^{-1} and 11.7 ± 5.7 μg N l^{-1} with a C:N ratio of 12.3 ± 4.6. Regression analysis of POC on PON gave a slope of 5.6 ± 1.99 ($p< 0.001$), with an intercept of 73 ± 13 μg l^{-1} of POC. Neither POC nor PON related significantly with *Chl a*.

Ammonium uptake rates (ρNH_4) were highly variable (range: 5-97 nmol l^{-1} h^{-1}; mean:37.3 nmol l^{-1} h^{-1}) and light dependent (Fig.33). Average conservative estimate of ρNH_4 was 7.8 nmol l-1 h-1. When some unusually high values were excluded, ρNH_4 correlated significantly with ambient NH_4^+ ($P< 0.05$), but not with *Chl a*. Average NH_4^+ uptake index (mol N (g *chl a*)$^{-1}$ h^{-1}) ranged from 0.31 at 50% light depth to 0.74 at 10% light depth, and like absolute uptake rates, was not light - dependent.

Urea uptake rates (ρUrea) were also variable (range: 1-20 nmol l^{-1} h_1; mean: 8.5 nmol l^{-1} h^{-1}) but light-dependent (Fig.33). These did not correlate well with either ambient urea concentration or phytoplankton biomass. Average urea uptake index ranged from 0.42 at the surface to 0.09 at 1% light depth.

Nitrate uptake rates (ρNO_3), were also variable (range: 0.2-6.5 nmol l^{-1} h^{-1}; mean: 1.8 nmol l^{-1} h^{-1}) and light- dependent (Fig.33). Like ρNH_4, ρNO_3 also correlated significantly with the ambient concentrations ($P<0.001$), and not with *Chl*

Fig. 32 Regression between NO_3^- and PO_4^-
a) all depths upto 400 m
b) euphotic zone

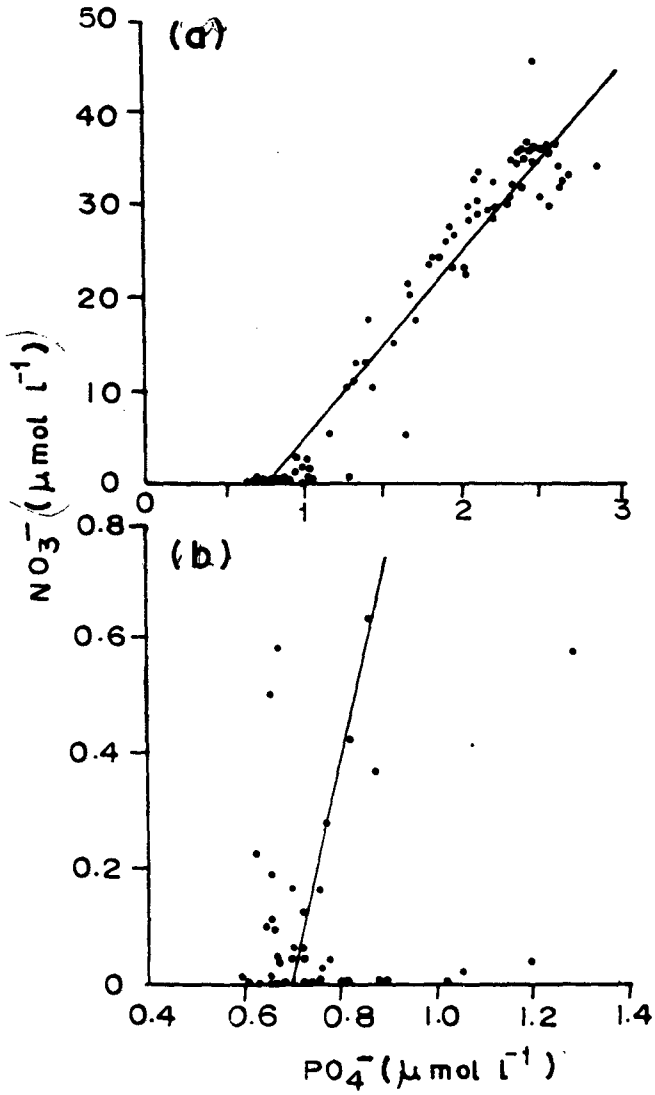
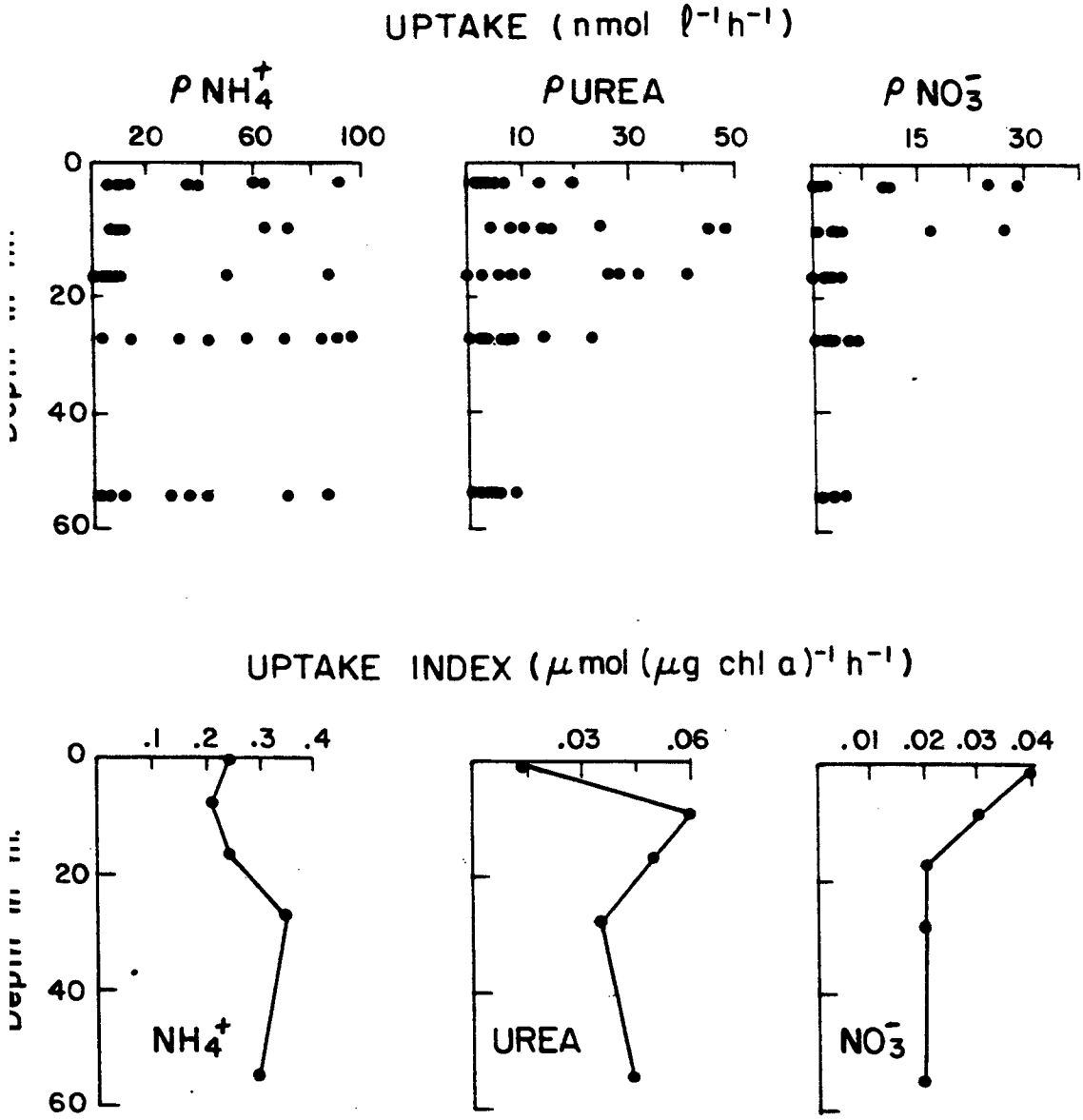


Fig. 33 Uptake rates relationship with light availability



a. Average NO_3^- uptake index ranged from 0.23 at the surface to 0.02-0.03 at depths at and below 25% light penetration.

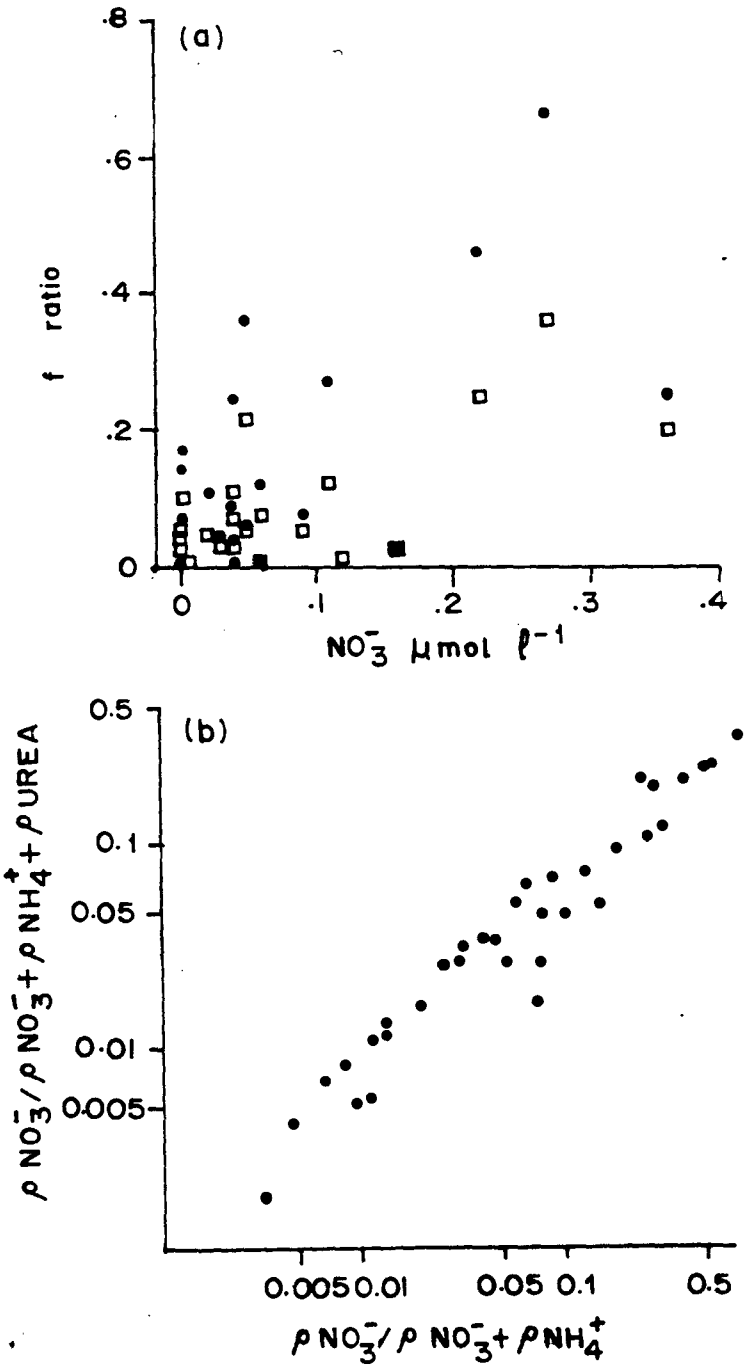
NH_4^+ was the most preferred form of N for uptake by phytoplankton, with relative preference indices >1, followed by urea and NO_3^-. Regenerated production ($\rho NH_4^+ \rho Urea$), contributed to >90% of the measured N uptake. *F* ratios [ρNO_3 ($\rho NO_3 + (\rho NH_4^+ \rho Urea)^{-1}$] were except for a few values, very low (<0.1), correlated linearly with ambient NO_3^- ($P<0.001$), and were light-dependent (0.07 on an average at 100% and 50% light depths and 0.03 below). F- ratios calculated by excluding ρUrea from total N uptake were about 44% higher than those where ρUrea was inlcuded. This set of ratios also correlated significantly with NO_3^-. Correlation between the two sets of values was highly significant (Fig .34).

3.2.3.Discussion

3.2.3.1. Nutrient export from the reef

Export of particulate by the reef and its flux in planktonic herbivory are easily demonstrable than those of nutrients. In the case of the former, their longer residence time and a concentration gradient, high carbon or nitrogen ratio to *Chl a* than in phytoplankton, presence in gut contents of herbivores and feeding experiments are good indices with respect to dissolved nutrients derived from the reef such tracers do not exist; neither are they distinguishable from those regenrated locally or advected/upwelled, nor they remain unutilized long enough to form a concentration gradient. Hence their export can only be deduced from indirect evidences, and their

Fig. 34. Correlation between a) f-ratios with ambient NO_3^-
b) t - values with and without ρ urea in total uptake



influence on phytoplankton productivity by comparison with data from elsewhere in nutrient - limited oceanic waters.

Four different observations in our studies provide evidence for an export of nutrients by the reef. The first is a comparison of concentrations of some measured properties close to the reefs and elsewhere in the oceanic waters of the Lakshadweep Sea. Of particular interest in these are the concentrations of NH_4^+ and PO_4 which are distinctly higher near the reef. These two are typically heterotrophic excretion products, and the source for these would be the large heterotrophic biomass on the reef. the second evidence lies in the difference in NO_2^- levels in the euphotic zone among the 10 stations. At stations 4759-4763 and 4768, NO_2^- was in traces (av.=0.02 mmol m^{-2}), whereas at stns 4764-4767, it was in significantly higher concentrations (av.=61.65 mmol m^{-2}). The later profiles (Fig.31) are typical of oceanic waters, and coupled with the fact that these stations were occupied during the ebb tide, as against the others which were occupied during the ebb tide, as against the others which were occupied at the flood tide, imply an export of NO_2^- from the reef. This indeed is possible as nitrification is a quite important process in a coral reef and occurs not only at the level of abiotic substrata, but also at the level of organisms, including corals and sponges, with a release of NO_2^- and NO_3^- into the surrounding waters (Wafar *et al.*, 1990). the third evidence is from the distribution of NO_3^- and NH_4^+ at several transects across the Kalpeni lagoon (Fig.35). In all these, $N0_3^-$ and NH_4^+ increase distinctly over live coral patches. The last evidence is from the diel changes of N nutrients out side the reef at 30 m depth at Kadamat atoll (11°15'N; 78°46'E) (Fig.36). Low concentrations of NO_2^- and NO_3^- measured at flood tide increase

Fig. 35 Distribution of NH_4^+ and NO_3^- in the Kaipeni lagoon.

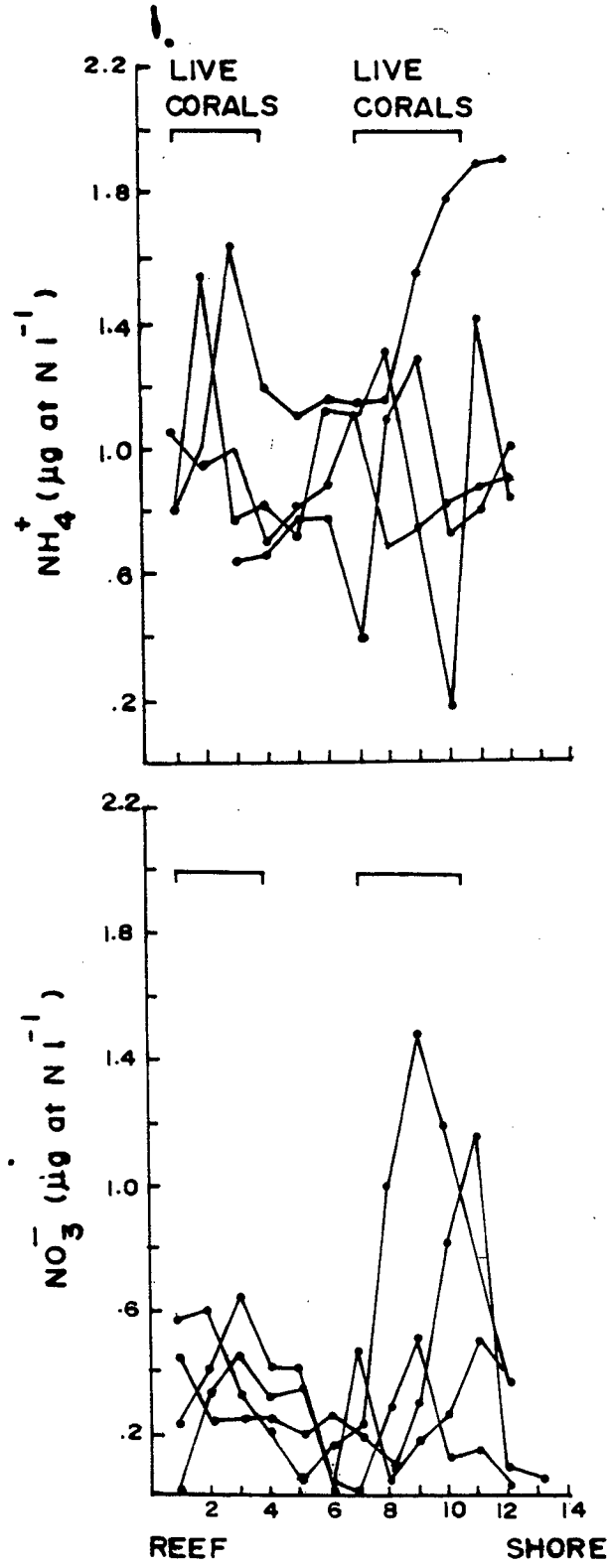
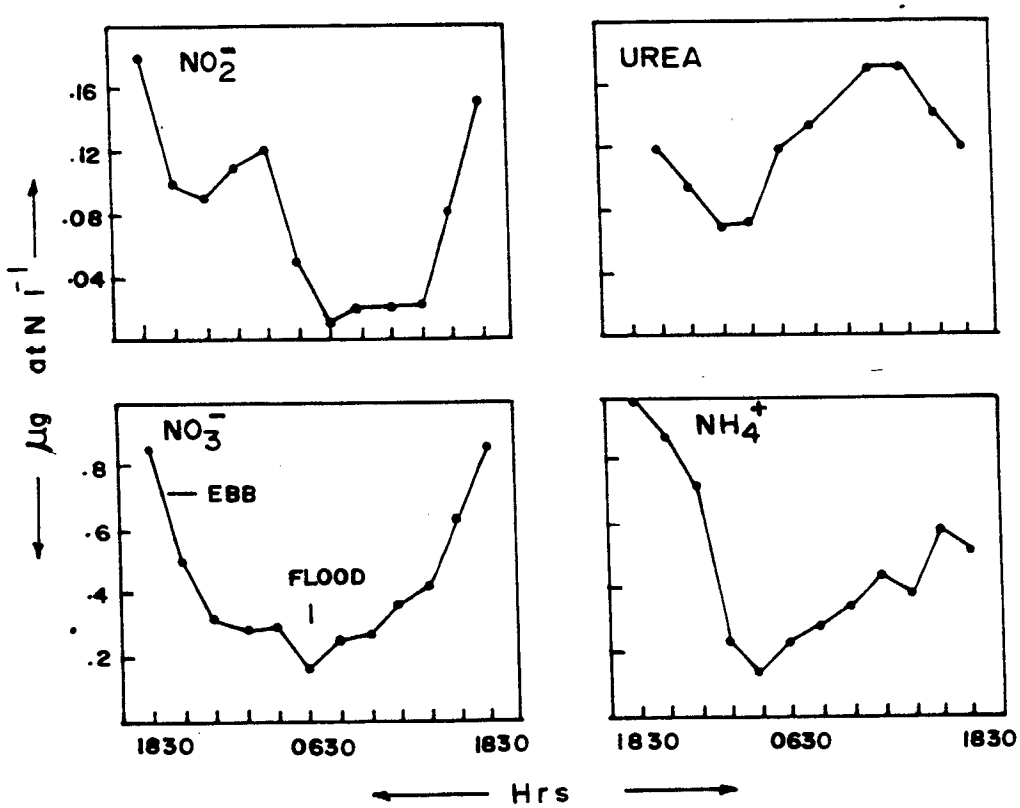


Fig. 36. Diel changes of N nutrients outside the reef at 30 mts depth.



distinctly during the ebb tide implying an import from the reef. In this case, it is not only NO_2^- or NO_3^-, but also NH_4^+ and urea show similar changes, albeit to lesser degree probably because the removal of these two nutrients photosynthetic assimilation would be much more rapid than with NO_3^- and also because these two can be lost to other microbial pathways. Collectively all these observations present a strong arguement in favour of a nutrient flux from the reef to the oceanic waters.

3.2.3.2 . Nitrogen uptake

Notwithstanding the greater variability, ρNH_4 measured near the coral reefs are distinctly higher than those reported elsewhere for oceanic waters [0.08-1.6 nmol l-1 h-1 in the north Pacific Ocean (Eppley *et al.*, 1977); 2-20 nmol l-1 h-1 in the Sargasso Sea (Glibert and McCarthy, 1984); a·ρmax of 6.47 nmol l-1 h-1 for the Pacific Ocean (Kanda 1985); upto 9 nmol l-1 h-1 in the surface waters of the western Pacific Ocean (Kanda *et al.*, 1988); up to 9 n mol l^{-1} h^{-1} in the surface waters of the western Pacicific Ocean (Kanda *et al.*, 1988); 287.1 μmol m^{-2} h^{-1} for the euphotic zone of the central Pacific ([illegible])]. In an earlier study also at Kavaratti atoll Wafar *et al.*. (1985) measured a mean ρNH_4 of 264 nmol l^{-1} h^{-1} in the waters near the reef. The average `conservative estimate' of ρNH_4 (7.8 nmol $l^{-1}h^{-1}$) is also higher than those (0.06 – 0.9 nmol $l^{-1}h^{-1}$) calculated by Eppley *et al.* (1977) for the North Pacific Ocean phytoplankton assemblages. As the atom % excess and the PON are determined with a greater degree of accuracy than ambient NH_4^+ concentrations by conventional colorimetry, the high `conservative' estimates alone would be sufficient

o justify our conclusion that NH_4^+ uptake near the reefs is significantly higher than elsewhere in the open ocean.

Ammonium uptake rate and the uptake index were light-dependent. These results agree with those for oceanic (Sahlsten, 1987) and near shore (Fisher *et al.*, 1982) waters. Fisher *et al* (1982) observed the light – independence of NH_4 uptake at low NH_4 concentrations and concluded that this was a response to N stress. In that event a good correlation between ρNH_4 and its ambient concentration, as obtained in this study can be expected .

Average ρurea (8.5 nmol $l^{-1}h^{-1}$) was remarkably the same as the one (8.5 ±0.12 nm $l^{-1}h^{-1}$) measured at Kavaratti atoll in an earlier study (Wafar *et al* ,1985). As with NH_4 ρ urea are also about an order of magnitude greater than those reported for other oceanic waters (0-15.5 nm $l^{-1}\cdot d^{-1}$ and 0.44-1.15 μm m^2 d^{-1} (Eppley *et al.* 1973); 1.7-11 nm $l^{-1}\cdot d^{-1}$ and 1.7-11 nm $l^{-1}\cdot d^{-1}$ with a conservative estimate 0.25-3.25 nm $l^{-1}\cdot d^{-1}$ (Eppley *et al.* 1977); 2-3 nm $l^{-1}\cdot d^{-1}$ (Sahlsten, 1987); ρ max of 0.21-2nm $l^{-1}\cdot h^{-1}$ (Kanda *et al.* 1985). Urea uptake indices were also high compared with those for central north Pacific gyre (Sahlsten, 1987).

The rate and characteristics of NO_3^- uptake had many similarities with those in other studies (Harrison *et al*, 1987; Eppley *et al.* 1990). NO_3^- uptake ranks an order behind urea and ammonia, with an average ρ NO_3 (1.8 nm $l^{-1}\cdot h^{-1}$) in the same range of those reported for other oceanic waters (1-2 nm $l^{-1}\cdot h^{-1}$) (Charlseton, 1987: 0.34-1.67 nm

$l^{-1}\cdot h^{-1}$ Glibert and Mc Carthey, 1984: ρ max of 0.23 – 1.44 nm $l^{-1}\cdot h^{-1}$ (Kanda *et al.* 1985).

Substrate concentration and light dependence , inverse relations of specific and absolute uptake rates with those NH_4^+ in the low f ratios are other characteristics that are common with those reported for nitrate uptake in oceanic waters.

3.2.3.4 Nitrogen utilization:

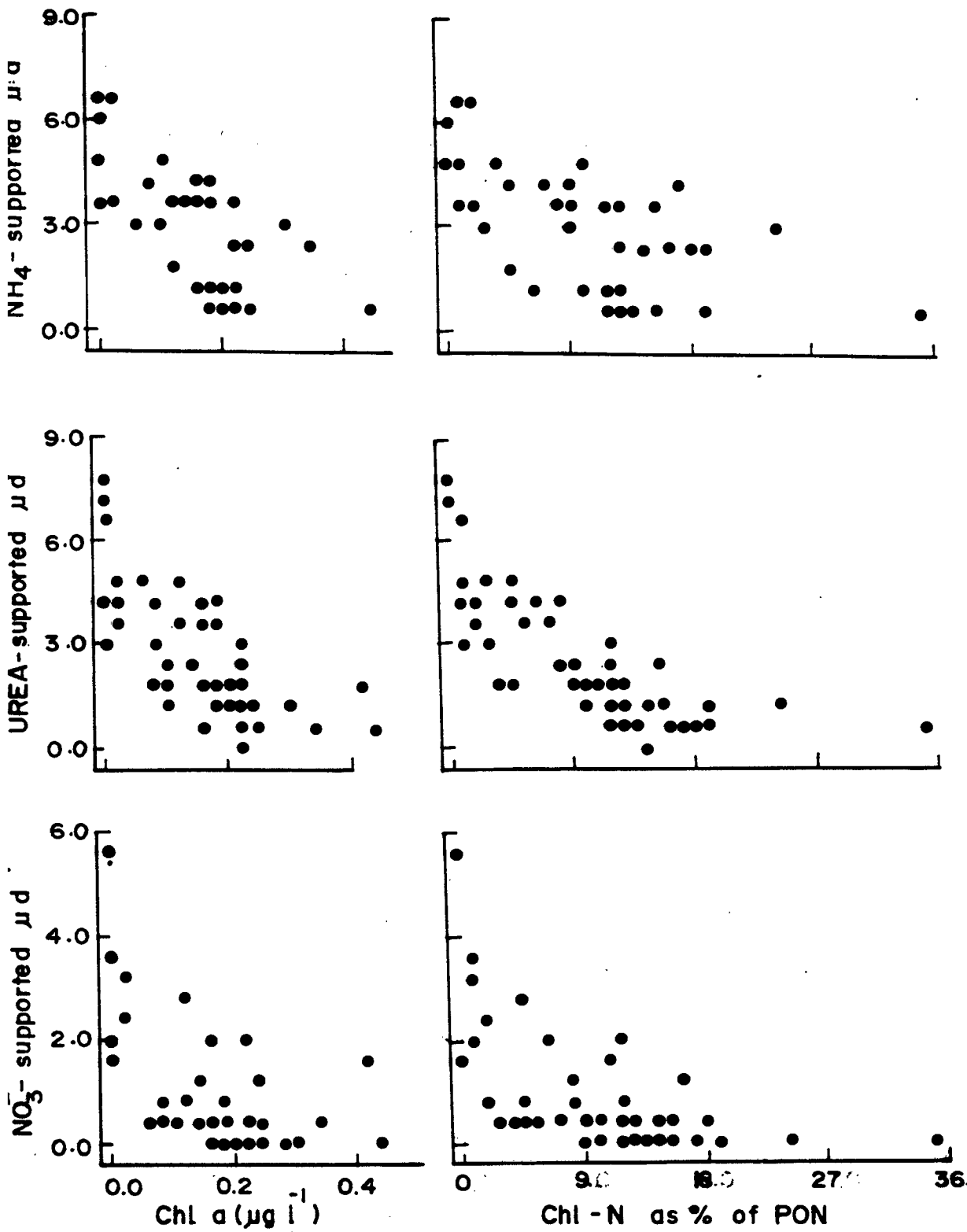
The high N uptake rates, especially of ammonium and urea unrelated to chlorophyll a are suggestive of a significant influx through heterotrophy parallel to autotrophy. Extent of N flux through these two pathways can be differentiated by calculating N specific growth rates and comparing them with known growth rates of phytoplankton communities. The former (as doublings per day) was calculated by the following equation

$\mu = 3.32 \log_{10} [(pp -N + \Delta N)/ pp\text{-}N)]$

where pp –N is phytoplankton N calculated with a ratio of 2.25 μg *chl a* : 1 μmol cell nitrogen (Darley, 1980). and ΔN is the absolute uptake rate of a given N nutrient. For the latter we have take n two sets of values; the first are the potential community growth rates of Arabian sea phytoplankton – more relevant to the study area (slightly .2 v doublings per day – Banse, 1988), and the second are the maximal diel-averaged growth rates of natural phytoplankton communities reviewed from literature. (3 - 3.6 doublings per day – Furnas, 1990),

The results (Fig. 37) show that 64% of ammonium specific growth rates exceeds 2, and 44 percent of them exceed 3.6 doublings per day. These proportions were 30 and 11% with urea specific growth rates but were smaller (10 and 5%) with NO_3 – specific growth rates. If the uptake rates were pooled together, then at least

Fig. 37. Specific growth rates of phytoplankton, chl a and PON.



46% of the measured N flux is through heterotrophy, but this can become as high as 74%, depending on the upper limit chosen (3.6 or 2 doubling per day). This , and the consistent negative relations of N-specific growth rates both phytoplankton biomass and its N content expressed as % of PON ($p < 0.001$) on Fig.37 are convincing evidences to conclude that heterotrophy is as much responsible as if not more than, autrophy in dissolved N utilisation near the reef.

The conclusion is that a substantial fraction of ammonium_N and urea –N fluxes through heterotrophy is also supported by measurements of biomass and activity of NH_4^+ oxidising and urea decomposing bacteria in other studies on Lakshadweep atolls. A year- long study on water column bacterial nitrification rates at Kalpeni atoll gave an average NH_4^+ oxidation rate of 34.3 nmol $l^{-1}h^{-1}$ (see nitrification). Average MPN (most probable number) of urea hydrolysers at Kavaratti atoll (209 ml $^{-1}$ outside the reef and 243 ml $^{-1}$ in lagoon) were 2-3 orders of magnitude greater than in the open ocean (Chandramohan and Ramaiah, 1987), with a urea decomposing rate of 7 nmol l^{-1} h^{-1} (Wafar *et al.*, 1985). Both NH_4 – oxidising and urea-decomposing rates are only slightly lower than the average ρNH_4 ρUrea measured in this study and thus led credence to the conclusion that heterotrophy assumes a high significance in NH_4 and urea flux in reef waters.

About 80% of the NO_3-specific growth rates were <1 day^{-1}, yet they correlated negatively with *chl a* and PP-N as % of PON. Like NH_4^+ and urea a significant fraction of NO_3^- may flux through heterotrophy; though heterotrophs cannot use NO_3^- as an energy source, they might still deriving N from it.

3.2.3.5 Implications for phytoplankton productivity.

Nutrient export from reef certainly enhances phytoplankton productivity near the reefs to levels higher than measurable in typically oligotrophic waters, as the difference in *chl a* levels in waters near the reef (4-14 mg m^{-2}) and elsewhere in the oceanic waters of Lakshadweep Sea (2-5mg m^{-2}; Wafar *et al.*, 1986) indicate. Nevertheless, this enhancement is not as much as one would expect if N uptake rates alone are considered. The latter are of the order that are normally measured in near shore waters yet *chl a* levels are not compatibly high, and account for no more than 8 % of POC and PON. Besides, the high POC/PON ratios of discrete samples, the high POC intercept of POC-PON regression and the less than unity ΔNO_3: ΔPO_4 ratio in the euphotic zone imply a nitrogen insufficiency, which is inconsistent with high N uptake rates. This, and the inverse relations of N-specific growth with chlorophyll a and PP-N as % of PON are clear indices to the fact that in these waters the phytoplankton are unable to utilize the N efficiently. In fact, the competition between autotrophy and heterotrophy for available NH_4^+ is not unknown in open ocean waters (Eppley *et al.*, 1977), or even in microenvironments in reefs themselves such as coral colonies (Wafar *et al.*, 1990), but what is remarkable in the reef waters is the overwhelming evidence for heterotrophic flux of dissolved flux of dissolved N in reef waters.

4. Summary and Conclusions

The aim of this study was to assess the relative importance of the biological processes that intervene in nitrogen recycling within a coral reef ecosystem and quantify the rates of nitrogen flux through these pathways in space and time.

The specific objectives were:

1) To study spatial and temporal variations of ambient nitrogenous nutrient concentrations.

2) To assess the relative importance of each of these nutrients to reef primary producers and seasonal changes in it - assimilation by phytoplankton.

3) To measure nitrogen flux through some bacterial pathways (e.g. nitrification) over seasonal

scales and relate it with the availability of each nitrogenous nutrient.

The study was carried out at the Kalpeni atoll (10° N and 73° E) in the Lakshdweep group of islands. A total of 12 stations in the lagoon and two stations in the open sea were chosen for seasonal studies. The study period extended from January 1993 to March 1995.

Salient observations

Ambient nitrogen concentrations

1. The dissolved inorganic and organic nitrogen concentrations, tested with ANOVA, showed significant variations among all the three seasons and between monsoonal

and non-monsoonal months. PON concentrations showed significant variations only between monsoon and non-monsoon months.

2. Range and average concentrations of nitrate in the three seasons showed a decreasing trend, from relatively higher values in the monsoon months through low values in the post-monsoon to the lowest values in the pre-monsoon period.

3. The nitrite values did not show such a trend as with nitrate. In monsoon months (July and August) the levels often fell below the limits of detection, in contrast to the higher values of NO_3 in this season.

4. Changes of ammonium and urea showed same seasonal patterns. Higher concentrations of these two nutrients were observed in the post-monsoon season followed by the pre-monsoon and remarkably low concentrations in the monsoon months.

5. Urea concentrations were higher than those of ammonium throughout the study period.

6. The dissolved organic nitrogen (DON) values were several orders of magnitude higher than those of dissolved inorganic nitrogen (DIN). The DON was the largest fraction, accounting for 74% of the total dissolved nitrogen. Seasonal changes of DON were interesting in that they contrasted with most of the DIN nutrients, except nitrate.

7. Changes of the concentrations of particulate organic nitrogen (PON) showed a close similarity to those of ammonium and urea. However, ANOVA tests showed that

the variations between the three seasons were not significant. Variations significant at 95% level were observed only between the monsoon and non-monsoon months.

8. Chlorophyll values also changed in a trend similar to that of ammonium and urea. The variations between the three seasons and in the nonmonsoon months were highly significant (99% level) as against the small variations in the PON values.

Uptake studies

1. The seasonal changes in the uptake rates of NO_3, NH_4 and urea show clearly lower values in monsoon months, higher values in post-monsoon and intermediate values in pre-monsoon.

2. The correlation co-efficients between ambient concentrations and specific and absolute uptake rates were significant (95% and 99% levels) in all instances except in the case of absolute uptake of urea in relation to it's concentration in the lagoon.

3. Ammonium was the prefered form for uptake followed by urea and nitrate.

4. Regenerated production (ammonium and urea uptake) was responsible for more than 90% of the total N uptake.

5. In the lagoon, ammonium is the form clearly prefered over urea and nitrate at any time, with urea ranking next in importance. While, this order is generally valid for the eastern station, in the post monsoon months nitrate is taken up at more or less equal rates along with ammonium and urea.

Nitrification studies

1. There is a definite seasonality in the rates, with high values in pre-monsoon months, followed by a sharp decrease in monsoon, and a subsequent increase in post-monsoon season.

2. The rates were generally high compared to those from the other ecosystems (Kaplan,1983).

3. The rates measured in this study for surface sediments (33.6 nmol g^{-1} h^{-1}) are higher than those of Corredor and Capone (1985).

Oceanic uptake studies

1. Nutrient concentrations were remarkably high in the euphotic zone near the reef in comparison with the surrounding oligotrophic waters.

2. Diel changes of N nutrients at stations outside the reef showed low concentrations at flood tide and increased levels during ebb tide.

3. Average nitrogen uptake rates were 37.3, 8.5 and 1.8 nmol l^{-1} h^{-1} respectively for ammonium, urea and nitrate. Among these ammonia and urea rates are an order of magnitude greater than those reported for other oceanic waters.

4. The distribution of nitrate and ammonium at several transect stations across the Kalpani lagoon showed a distinct increase in the values over live coral patches.

Conclusions

1. The findings suggest that there is sufficient new nitrogen input (NO_3)in the monsoon months. While the post-monsoon season is supported mainly by regenerative

flux (Ammonium and Urea), there is no indication of either new or regenerative fluxes in the pre-monsoon season.

2. The heterotrophic biomass build-up is not interfered even at low concentrations of available nitrogen. The more or less equal values of PON in the pre and post-monsoon are indicative of this.

3. It is concluded that the nitrogen uptake is dependent not only on the substrate availability but also on the prevailing weather conditions.

4. Nitrification studies in the water column and sediment lead to conclude that, the production of N in one form and its transformation to another, proceeds at appreciable rates in the coral reef ecosystems.

5. The nutrient flux studies provide evidence for the fact that reefs export particulate organic matter and dissolved inorganics in measurable quantities.

6. Comparison of phytoplankton growth rates calculated as N-supported with those from literature (Wafar et al. , 1986) showed that most of the ammonium and urea uptake would rather be due to heterotrophic utilization. This along with high microbial biomass and heterotrophic activity observed in other studies in the Lakshadweep atolls (Chandramohan & Ramaiah, 1987) suggest a predominance of heterotrophy over autotrophy in nitrogen flux in reef waters.

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6. Appendix

1. Nitrate concentrations estimated in the lagoon stations (ug at N /l)

	1	2	3	4	5	6	7	8	9	10	11	12
	0.64	0.33	0.21	0.34	0.22	0.18	0.52	0.25	0.11	0.62	0.31	0.41
3	0.98	0.8	0.61	0.69	0.38	1.15	1.09	0.34	0.53	0.38	0.28	0.53
3	0.16	0.27	0.18	0.38	0.4	0.5	0.52	0.42	1.01	0.52	0.4	0.35
		0.074	0.95	0.138	0.105	0.173	0.22		0.147	0.323	0.195	0.068
3	0.449	1.1	0.49	0.396	0.379	0.696	0.062	0.19	0.111	0.252	0.217	0.357
3	0.154	0.035	0.27	0.322	0.309	0.07	0.979	0.999	0.387	1.02	0.739	0.105
	0.186	0.442	0.372	0.518	0.208	0.284						
	0.015	1.66	0.334	0.311								
		0.255	0.714	0.558	0.99	1.64	0.958	0.909	0.702	0.494	1.48	
3		0.282	0.65	0.314	0.029							
3	0.499	0.348	0.641	2.25								
		1.22	1.99	1.59		0.182	1.61	1.12	1.23		1.39	1.75
3				0.99	1.03	0.657	0.142	0.657	0.657	0	0.99	0.99
3	0.182	0.221	0.142	0.142	0.475	0.515	1.11	0.475	1.7	0.515	0.515	0.515
93	0.681	0.681	0.475	0.475	0.166	0.166	1.67	0.886	0.807			
93	0.61	0.9	0.229	1.28	1.28	0.61	0.229	1.31	1.31	0.634	1.31	0.634
3	0.99					0.871			0.04			
4	0	0	0.144	0.226	0.095	0.311						
4	0.037	0.196	0.772	0.105	0.076	0	0.671	0.442	0.012	0	0.212	0.128
4		0.751	0.146	0.223	0.36	0.358	0.111	0.31	0.023	0.317	0.479	0.411
	0.508	0.28	0.262	0.1115	0.56	1.3	0.494	0.477	0.38	0.644	0.051	0.161
4	0.062	0.031	0.093	0.089	0.023	0.122	0.036	0.144	0.327	0.393	0.177	0.064
4		0.754	0.889	0.358	0.227	0.08	0.262	0.314	0.019	0.477	0.28	0.395
4	0.214	0.162	0.179	1.03	0.442	0.245	1.052	0.706	0.658	0.441	0.836	0.159

2. Nitrite concentrations estimated in the lagoon stations (ug at N/l)

	1	2	3	4	5	6	7	8	9	10	11	12
3	0	0.11	0.18	0.15	0.22	0.26	0.22		0.18	0.26	0.18	0.18
93	0.15	0.18	0.18	0.15	0.11	0.18	0.29	0.15	0.11	0.11	0.11	0.26
93	0.04	0.07	0.07	0.11	0.04	0.04	0.07	0.07	0.07	0.07	0.04	0.04
3	0.108	0.172	0.086	0.108		0.08	0.237	0.086	0.064	0.064	0.086	0.108
93	0.043	0.129	0.108	0.237	0.043	0.108	0.043	0.022	0.065	0.065	0.065	0.065
93	0.021		0.043	0.065	0.043			0.021				
3	0.024	0.048	0.048	0.072	0.072	0.096						
3							0.167	0.072	0.072	0.072	0.096	0.096
3	0.017	0.035	0.017	0	0.017							
3			0.052	0.017	0	0.052	0	0.017	0	0.017	0.017	
93		0.069	0.052	0.069	0.035							
93	0.095	0.167	0.071	0.048								
3	1.57	1	0.309	0.309		0.571	1	0.309	0.309	1.21	0.309	0.309
93	0.309	0.309	0.309	0	0.024	0						
93	0	0	0	0	0.333	0.333	0.033	0.033	0.667	0	0	
93	0.333	0.333	0.333		0	0	0	0	0	0	0	0
.93	0.309	0.309	0	0	0.309	0.309	0.309	0.619	0.619	0.619	0.619	0.619
.93	0.024	0.405	0.405	0.024	0.024	0.024	0.405	0	0	0	0	0
93	0	0	0	0	0	0	0	0	0	0	0	0
94	0.297	0.087	0.087	0.105	0.07	0.087						
94	0.07	0.035	0.087	0.192	0.122	0.035	0.122	0.087	0.087	0.35	0.052	0.07
94		0.175	0.052	0.139	0.07	0.105	0.087	0.087	0.175	0.245	0.017	0.052
4	0.087	0.017	0.035	0.017	0.035	0.052	0.035	0.052	0.017	0.017	0.052	0.017
94	0.07	0.087	0.105	0.175	0.175	0.175	0.07	0.087	0.07			
94	0.069	0.069	0.105	0.192	0.087	0.175	0.175	0.175	0.069	0.105	0.069	0.52
94	0	0.105	0.07	0.105	0.07	0.052	0.035	0.017	0.052	0.035	0.017	0.035

Table 3. Ammonium concentrations estimated in the lagoon stations (ug at N /l)

DATE	1	2	3	4	5	6	7	8	9	10	11	12
19.2.93	1.11	1.51	1.1	1.1	1.1	1.88	1.23	1.02	0.97	1.18	1.04	0.97
1.3.93	5.918	2.623	1.462	7.427	1.648	2.437	3.087	1.648	1.764	1.903	3.644	1.601
14.3.93	1.697	1.393	1.044	1.23	1.462	2.042	1.23	1.237	1.88	1.207	1.068	1.23
25.3.93	1.485	1.857	1.694	1.09	1.323	0.835	1.021	0.882	0.952	1.206	0.905	1.299
5.5.93	1.07	0.409	0.597	0.975	1.07	0.91						
5.5.93							1.26	0.629	1.1	0.692	0.597	0.692
7.7.93	0.314	0.629	0.535	0.314	0.44							
7.7.93		0.503	0.314	0.22	0.535	0.252	0.22	0.188	0.157	1.26	0.22	
4.7.93		0.126	0.56	0.75	0.031							
4.8.93	0.44	0.566	2.11	2.7								
9.93		0.126	0.126	0.126								
1.10.93	1.258	0.566	1.761	1.038	1.667	1.226	1.447	1.226	1.258	1.478	1.258	1.73
8.10.93	4.497	2.988	1.887	1.887	1.667	2.233	2.233	3.365	2.767	3.051	3.648	5.472
0.11.93	5.378	2.107	2.107	1.541	1.541	0.723	1.793	2.076	3.019	1.793	1.358	1.006
.12.93	1.635	1.321	1.604	1.635	1.635	1.635	1.635	0.66	1.635	1.635	0.975	1.635
4.1.94	4.245	3.563	4.245	2.805	2.122	1.289	4.096	2.805	1.668	1.212	1.365	3.86
4.2.94		2.577	2.046	3.259	2.122	1.663	1.061	1.231	1.061	2.577	1.212	2.047
.3.94		0.682	2.275	2.274	2.047	2.122	1.743	1.971	1.819	1.592	1.971	1.819
0.3.94	3.714	2.88	2.577	1.819	2.805	2.426	2.198	2.198	2.274	2.35	1.743	1.21
0.4.94	0.227	2.274	1.289	2.047	1.44	0.227	2.274		0.834	0.379	0.227	0.379
0.4.94	0.91	0.83	1.14	8.56	1.29	1.97	0.45		2.956	3.259	1.895	1.36

e 4. Ambient urea concentrations estimated in the lagoon stations (ug at N /l)

E	1	2	3	4	5	6	7	8	9	10	11	12
3	0.26	0.31	0.52	0.23	0.29	0.29	0.34	0.052	0.26	0.18	0.6	
93												
93	1.15	1.17	1.07	0.414	1.15	1.35	0.909	0.16	0.187	0.307	0.267	0.08
93	1.05	0.307	0.227	0.381	0.381	0.241	0.321	0.16	0.181	0.307	0.267	0.227
3	0.134	0.388	0.294	0.147	0.254	0.455	0.08	0.227	0.281	0.17	0.267	0.094
93	0.387	0.254		0.107								
3							0.386	0.772	0.208	0.119	0.267	
3		2.7	3.12	3.44	3.36							
93	1.01	0.267	1.39	1.1								
93	0.059	0.416	0.505	0.03	0.03	0.501	0.98	0.148	0.148	0.624		
3	1.188	0.386	0.861	0.386	0.386	0.988	0.505	0.505	0.505	0.505	0.505	
93	1.455	2.435	0.98	0.564	0.653	0.238						
93	0.238	0.356	0.861		0.386		0.891		1.04	0.386	1.426	0.475
.93	0.238					0.238			2.732		1.01	0.238
.93	1.84	2.73		0.238	0.238							
93	2.3	6.55	6.13	4.43	2.21	4.51						
94	2.3	3.23	6.89	4.6	5.28	3.49	3.06	7.23	4.08	2.81	4.68	2.64
94		0.85	4.51	2.21	2.47	3.32	2.04	2.98	2.89	2.21	2.64	1.71
94		1.11	3.74	1.79	0.511	2.13	2.21	2.72	5.02	3.57	2.38	2.55
1	0.766	1.53	0.851	0.93	0.255	1.45	1.28	0.34	0.851	0.255	0.851	0.17
94	3.49		3.23	0.511	1.79	1.19	0.936	1.19	3.83	2.13	1.71	2.89
94	0.851	1.79	2.72	1.7	2.98	1.87	5.36	1.53	2.3	1.28	1.96	1.53
94	1.87	1.96	1.87	0.596	0.851	1.7	3.06	2.47	2.55	2.13	4.25	2.8

e 5. Dissolved organic nitrogen (DON) estimations in the lagoon stations (ug at N /l)

E	1	2	3	4	5	6	7	8	9	10	11	12
3	15.97	13.896	18.82	14.127								
3		27.31	40.97	48.15	25.39	6.102	19.54	24.27	18.39	34.28	12.94	
3												
93		5.176	3.435									
93		1.099	2.762	3.677								
93	1.697	1.174										
.93	6.068	14.488	15.159	14.105	11.88	12.47	14.52	10.45	9.491	11.39	11.152	12.18
.93	15.525					4.89			4.095			
94		0.296		0.303	3.4	1.932	3.516	8.338	3.23	1.463	0.864	
94								1.23	0.763			
94		0.701										
4		17.38		2.88	1.73	0.147						
94			0.622	1.09	1.203	1.851		2.739	1.64	1.82		1.44

Table 6. Particulate organic nitrogen(PON) estimations in the lagoon stations (ug at N /l/h)

Date	1	2	3	4	5	6	7	8	9	10	11	12
4.7.93		1.325	0.799	0.947	0.615							
.9.93		0.409	0.41			0.896		0.922		0.91		1.124
7,9,93	1.071		1.019		0.996		1.247		0.804		0.804	
0.9.93		0.902		1.034		1.17		0.877		1.09		
0.10.93	1.809		1.318	1.096		0.345		0.914	0.978			1.566
8.10.93	1.23		1.732		2.177		1.359		2.236		0.827	
0.11.93		0.246		1.366		0.62		0.699		0.9814		0.512
.12.93	1.132		0.943		0.86		2.49		1.05		0.566	
4.1.94		1.006		2.035		0.598		1.974		1.302		1.01
.3.94	1.98		1.95		1.47		0.365		1.76		0.959	
0.3.94		1.336		0.872		1.829		1.076		1.041		1.36
0.4.94	0.766		0.965		1.265		0.854		0.854		0.71	
0.4.94		1.16		0.915		1.862		0.712		1.18		0.944
0.4.94	0.639		1.168		1.106			—	1.057		1.12	

Table 7. Chlorophyll a estimations in the lagoon stations (ug /l)

DATE	1	2	3	4	5	6	7	8	9	10	11	12
4.2.93	0.534		0.178					0.134	0.045			2.67
9.2.93	1.215		0.748		0.505			0.224				
.3.93	0.654		0.654			0.093	0.374		0.748			0.187
4.3.93		0.498		0.498		0.872		0		0.125		0.187
5.3.93	0.093		0.935		1.682							
.5.93							0.561		0.654		0.467	
.5.93	0.561	0	0	0	0							
.7.93		0.187	0.125	0	0.187	0.062	0.125	0.187	0	0	0.187	
.7.93												
4.7.93	0.125	0.249	0.187	0.125								
4.8.93												
9.9.93		0.311			0.311		0			0.062	0.311	
8.10.93	0.561		0.654		0		1.215		0		1.215	
0.11.93		0.498		0.498				0		0	0	0.498
.12.93	2.305	0	0.249	0.561	0.374	0						
3.1.94	0.748		0.654		0.747		0.467		0.748		0.467	
4.1.94												
4.2.94		0.28		0.187		0.093	0	0		0.187		
3.94	0.872		0.623		0.498		0.187		0		0.374	
0.3.94		0.311		0.498		0.498		0.062		0.249		0
0.4.94	0.187		0.126		0.436		0.125		0.249		0.374	
0.4.94		0		0		0.062		0.374		0.249		0.436

Table 8. Phaeo pigment estimations in the lagoon stations (ug /l)

Date	1	2	3	4	5	6	7	8	9	10	11	12
19.2.93	0.169		0.566					0.698	0.022	0	0	0
4.3.93	4.672		0.887		0		0		0.224			
14.3.93	0.117		0.457			0.949	0.818		0.187			0.304
25.3.94		0.249		0		0		0		0.016		0
5.5.93	0.119		0		0.07							
3.5.93							0.14		0		0.094	
3.7.93	0	0	0	0	0							
5.7.93		0	0.078		0.047	0.078	0	0		0	0	
24.8.93	0.294	0	0	0.156								
3.9.93	0			0	0		0		0		0	
11.10.93		0			0.311		0			0	0	
20.11.93	0		0		0		0		0	0	0	
4.12.93		0		0				0		0		0
23.1.94	3.489	0	1.386	1.542	1.215	0						
24.1.94	2.617		2.92		2.336		3.738		4.649		3.037	
3.3.94		0.56		0.374		0.257		0		0.304		
30.3.94	0.062		0.265		0.109		0.794		0.567		0.514	
0.4.94		0.202		0.483		0.109		0.638		0.031		0.42
20.4.94	0.327		0.265		0.265		0.809		0.265		0.184	
30.4.94		0		0		0		0		0.031		0.358

Table. 8.1. Uptake index (□NO3/Chla) and Relative Preference Index (RPI) calculated for NO3-, NH4+ and Urea after trace addtions in the lagoon station.

Date	NO3-		NH4+		Urea	
	upt. index	RPI	upt.index	RPI	upt.index	RPI
13.7.93	-	-	0.075	-	0.09482	-
3.8.93	0.5125	-	-	-	0.4562	-
15.8.93	0.0363	-	0.0483	-	-	-
27.8.93	-	-	0.4929	-	0.131	-
6.9.93	0.05534	-	-	-	0.0036	-
17.9.93	0.00064	0.08	0.1124	0.876	0.05009	1.47
28.9.93	0.00227	0.127	0.0948	1.375	0.11568	0.737
8.10.93	-	0.779	-	1.279	-	0.773
18.10.93	0.06432	0.657	0.3711	1.144	1.2068	0.904
29.10.93	0.0387	1.019	0.1606	1.48	0.0425	0.447
11.11.93	0.03667	0.557	0.3286	0.909	0.2273	1.379
22.11.93	0.05818	0.462	0.3647	0.884	0.3136	1.58
6.12.93	-	-	-	-	-	-
16.12.93	0.00338	-	0.0081	0.2591	0.0196	-
26.1.94	0.199	-	3.869	-	-	-
26.2.94	0.01638	0.314	0.2348	0.5051	0.73829	1.587
6.3.94	0.00378	2.016	0.3746	0.815	0.3251	1.344
18.3.94	0.00132	-	0.0513	0.7902	0.2358	1.0551
28.3.94	-	-	-	-	-	-
8.4.94	0.0015	-	0.679	2.69	0.09419	0.1939
19.4.94	0.01	2.5	0.2553	1.14	0.39933	0.917

Table. 8.2 Uptake index (□NO3/Chla) and Relative Preference Index (RPI) calculated for NO3-, NH4+ and Urea after trace addtions in the eastern station.

Date	NO3		NH4		Urea	
	upt. index	RPI	upt.index	RPI	upt.index	RPI
10.7.93	0.1313	0.286	0.0603	0.252	0.15129	0.178
4.8.93	-	1.415	-	1.107	-	0.834
14.8.93	0.04	-	0.1966	-	-	-
26.8.93	-	-	2.251	-	0.7935	-
7.9.93	0.0082	0.676	0.0564	1.083	0.00095	0.686
18.9.93	0.02263	-	0.0931	1.327	0.05744	0.695
27.9.93	0.0048	0.6085	0.1233	1.28	0.03962	0.625
9.10.93	0.01	0.833	0.109	1.307	0.06838	0.743
19.10.93	0.032	0.584	0.3079	1.293	0.04795	0.508
30.10.93	-	0.902	-	1.066	-	0.902
10.11.93	0.0675	0.396	0.3927	0.773	0.3636	2.522
23.11.93	-	0.672	-	1.106	-	1.867
17.2.93	0.105	-	-	-	0.04682	-
25.1.94	0.0208	0.291	0.288	0.73	0.29774	-
25.2.94	0.0154	0.505	0.205	0.882	0.6252	2.12
7.3.94	0.0383	0.708	0.5816	0.463	1.6016	1.087
17.3.94	0.0309	0.809	0.058	1.171	0.3655	0.997
29.3.94	-	-	-	-	0.23189	-
9.4.94	0.0495	1.624	0.4546	1.95	0.19315	2.245
20.4.94	0.0084	1.587	0.0513	0.897	0.19645	1.016

Table 9. Watercolumn nitrification rates in the lagoon

Dates	Rates (ηmol N/l/h)
9.1.93	3.5
21.1.93	17.6
31.1.93	0.837
15.2.93	5.67
1.3.93	5.27
11.3.93	11.45
23.3.93	4.94
31.5.93	5.05
21.6.93	0.78
29.6.93	0.91
13.7.93	5.98
5.8.93	
15.8.93	0.8
27.8.93	
6.9.93	6.203
16.9.93	0.603
28.9.93	4.068
7.10.93	1.143
20.10.93	8.507
30.10.93	4.567
12.11.93	0.273
22.11.93	4.79
1.12.93	2.35
12.12.93	23.84
23.1.94	2.016
2.2.94	
27.2.94	
27.3.94	
6.4.94	
16.4.92	2.262
26.4.92	5.398
6.5.92	
16.5.92	

Table 10. Watercolumn nitrification rates in the Eastern station

Dates	Rates (ηmol N/l/h)
29.6.93	0.67
16.8.93	3.53
26.8.93	0.783
7.9.93	0.137
18.9.93	0.963
28.9.93	13.413
8.10.93	1.707
20.10.93	0.186
30.10.93	0.24
12.10.93	0.58
22.11.93	4.687
1.12.93	1.45
12.12.93	5.317
23.1.94	10.385
2.2.94	
27.2.94	8.461
8.3.94	2.183
27.3.94	2.328
6.4.94	3.362
16.4.94	
26.4.94	1.241
6.5.94	1.526

Table 11. Nitrification rates in the sediments (lagoon station)

Dates	Rates (ηmol N/g/h
15.2.93	110.153
11.3.93	172.337
2.3.93	149.86
21.6.93	16.313
30.6.93	8.467
13.7.93	
5.8.93	
16.8.93	
27.8.93	
7.9.93	
16.9.93	
30.9.93	
8.10.93	8.7391
20.10.93	1.7236
30.10.93	10.3252
12.11.93	4.233
22.11.93	9.588
1.12.93	
12.12.93	
23.1.94	4.32
2.2.94	1.861
27.2.94	
27.3.94	25.11
6.4.94	24.542
16.4.94	14.819
26.4.94	
6.5.94	0.172
16.5.94	8.114