Chapter 1
Introduction

Although Nitrogen (N) is one of the highly depleted elements on solid earth, it plays a tremendously important role in the environment, which encompasses regulating the oxygen in the atmosphere (Holland 1970) to carbonate compensation depth in the deep ocean (Ben-Yaakov et al. 1974). The cycling of nitrogen in our ecosystem is also one of the most important environmental issues. The primary production of food by photosynthesis is directly related to the nitrogen cycle and the productivity of many ecosystems is known to be controlled by nitrogen availability (Vitousek et al. 2002). Approximately 78% of the atmosphere is diatomic nitrogen (N_2) but nitrogen in this form is normally unavailable for consumption by organisms due to the strong triple bond between two nitrogen atoms (N≡N). The limitation of the availability of nitrogen in reactive or biologically active forms (NO_3^-, NH_4^+, NH_3, HNO_3 etc.) to grow more food due to demand from the growing human population has lead to a very significant alteration of the nitrogen cycle in air, land and water at local, regional, and global scales (Galloway et al. 2004).

Nitrogen was formally named the 7th element of the periodic table (atomic number: 7) by Jean Antoine Claude Chaptal (1756-1832). Nitrogen has an atomic weight of 14.0067 and mass number 14. The whole earth abundance of N is only 0.03%, out of which 97.76% is stored in rocks, 2.01% in the atmosphere and the remaining in hydrosphere and biosphere (Hubner 1986). Nitrogen has five valence electrons and can take on oxidation states between +5 (NO_3^-) and -3 (NH_4^+). Most of the nitrogen compounds are soluble in water or are gaseous and do not form minerals except under special conditions. Most abundant minerals are $NaNO_3$ (sodaniter) and α-KNO_3 (niter) that occur in non-marine evaporate deposits in the arid regions of the earth. The most common species of marine nitrogen are listed in Table 1.1.

Table 1.1 Common species of marine nitrogen.

Species	Molecular Formula	Oxidation Number of Nitrogen
Nitrate ion	NO_3^-	+V
Nitrite ion	NO_2^-	+III
Nitrous Oxide gas	N_2O	+I
Nitric Oxide gas	NO	+II
Nitrogen gas	N_2	0
Ammonia gas	NH_3	-III
Ammonium ion	NH_4^+	-III
Organic amine	RNH_2	-III

Nitrogen has two stable isotopes: ^{14}N and ^{15}N whose abundances in nature are 99.634 and 0.366% respectively. Nitrogen isotopic composition is generally reported in permil (‰) using the standard definition of δ (delta):

$$\delta^{15}N\ (‰) = [\{(^{15}N/^{14}N)_{sample} / (^{15}N/^{14}N)_{standard}\} - 1] * 1000$$

The standard for nitrogen is N_2 in atmospheric air whose average abundance of ^{15}N is constant with $^{15}N/^{14}N = 1/272$ (Junk and Svec 1958).

1.1 Isotopic Fractionation of Nitrogen

Isotopic fractionation of light elements like N is a characteristic phenomenon in chemical, physical and biological processes that can be either reversible equilibrium or irreversible unidirectional kinetic reactions. Equilibrium controlled isotopic fractionation can be predicted theoretically (Urey 1947), whereas kinetically controlled fractionation (most biochemical processes) is determined empirically. The isotope effect of N is expressed in terms of fractionation factor (α). The fractionation factor for equilibrium exchange reaction A↔B is defined as: $\alpha^{B}_{A} = (^{15}N/^{14}N)_{B} /(^{15}N/^{14}N)_{A}$. Nitrogen is cycled in the marine environment in a complex manner mainly through metabolic nitrogen transformations that involves irreversible kinetic fractionation. The kinetic fractionation factors in such cases are highly variable depending on the kinetic mode of individual metabolic reactions, concentration of products and reactants, environmental conditions, and species of the organism. In general, the lighter isotope reacts faster resulting in a product isotopically lighter than the reactant, in contrast to reversible equilibrium reactions where products can be heavier or lighter than the original reactant. Kinetic fractionation factors can be defined as:

$$\alpha = (^{15}N/^{14}N)_{product} / (^{15}N/^{14}N)_{reactant}$$

Isotopic enrichment factor (ε) is defined as: $\varepsilon = (\alpha - 1) * 1000$ ‰

The Rayleigh equation is used to describe the evolution of isotopic composition of the reactant (substrate) during both kinetic and equilibrium processes. The commonly used formulation for Rayleigh equation for a system with constant fractionation factor is given as:

$$R = R_0 f^{(\alpha-1)}$$

Where, R = $^{15}N/^{14}N$ of the substrate at any time,

R_0 = initial $^{15}N/^{14}N$ of the substrate,

f = fraction of the remaining substrate, and

α = the fractionation factor between the product and the substrate.

In terms of isotopic composition the same can be expressed as:

$$\delta = \delta_0 + (\alpha\text{-}1)*1000* \ln f = \delta_0 + \varepsilon * \ln f$$

Where, δ and δ_0 are the isotopic compositions of the substrate at any later time and the initial isotopic composition of the substrate.

In metabolic reactions, organisms prefer lighter (^{14}N) over the heavier isotope (^{15}N) resulting in an isotopically lighter product than the remaining substrate. For example, during the process of denitrification the microbes convert nitrate into final product N_2 ($NO_3^- \rightarrow N_2$) whose $\delta^{15}N$ is always lighter than that of the residual NO_3^-. However, the isotopic composition of product is highly dependent on the value of the isotopic fractionation factor and fraction of reservoir left. Figure 1.1 shows a typical example of denitrification for different fractionation factors where N_2 is the cumulative product $\delta^{15}N = [-(f/(1\text{-}f))* (\delta_0 + \varepsilon * \ln f)]$ and NO_3^- is the residual substrate ($\delta^{15}NO_3^-{}_{initial} = 0‰$).

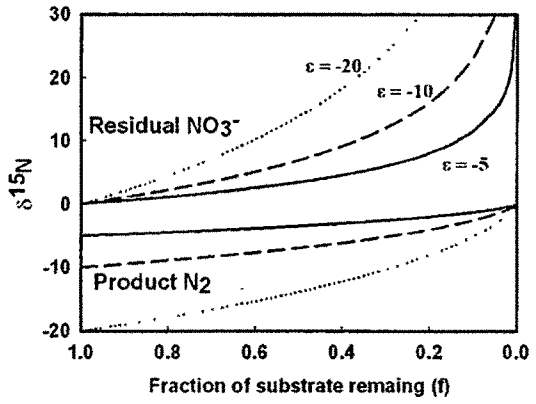

Figure 1.1 Evolution of isotopic composition of substrate (NO_3^-) and product (N_2) for different fractionation factors as denitrification progresses.

The biological processes like nitrification (organic-N$\rightarrow$ $NH_4^+ \rightarrow$ $NO_2^- \rightarrow$ NO_3^-) or denitrification ($NO_3^- \rightarrow NO_2^- \rightarrow N_2$) consists of number of steps with each step having a potential for isotopic fractionation. The overall isotopic fractionation for such reactions is highly dependent on environmental conditions, the number and types of intermediate steps, sizes of reservoirs of various compounds involved in the reactions and species of the organisms etc., making the estimation of isotopic fractionation in natural systems

very complex. Generally most of the isotopic fractionation is caused by the slowest step called "rate determining step" which is commonly associated with a large pool of substrate, with a small amount of material used (Kendall 1998).

1.2 Natural distribution of $^{15}N/^{14}N$

The overall range of reported $\delta^{15}N$ values in natural systems covers 100‰, from about -50‰ to +50‰; however, most values fall within the much narrower spread from -10‰ to +20‰ (Heaton 1986; Owens 1987; Peterson and Fry 1987). The nitrogen isotopic variation in biological material was reported by Schoenheimer and Rittenberg (1939) for the first time whereas Miyake and Wada (1967) were first to report the $^{15}N/^{14}N$ ratios of nitrogenous compounds occurring in marine environment. In general, marine organic material has higher $^{15}N/^{14}N$ ratio than the terrestrial organic material mainly due to the different isotopic compositions of source materials. The major source of nutrient nitrogen for land plants is molecular nitrogen ($\delta^{15}N$ = 0‰) in the atmosphere (Sweeney et al. 1978) which is depleted with respect to nutrient sources available for marine phytoplankton ($\delta^{15}N$ of nitrate ~3-7‰ and $\delta^{15}N$ of ammonium ~

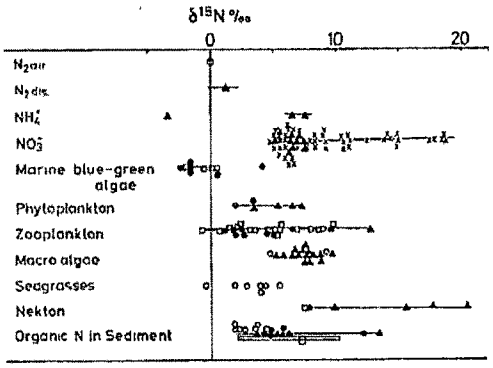

Figure 1.2 Summary of $\delta^{15}N$ in biogenic nitrogen containing substances in the marine environment (Miyake and Wada 1967; Cline and Kaplan 1975; Wada and Hattori 1976; Wada 1980).

6-8‰; Miyake and Wada 1967). On an average, $\delta^{15}N$ of marine biogenic nitrogen relative to the atmospheric nitrogen is +7‰ (Wada 1980) and it increases along the food chain with each trophic step (DeNiro and Epstein 1981). ^{15}N abundance in pelagic plankton is strongly related with the form and isotopic composition of inorganic nitrogen used for their growth (Wada and Hattori 1976). Figure 1.2 presents the summary of biogenic nitrogen bearing substances (Wada 1980) in the marine environment.

1.3 Biogeochemical transformation of nitrogen in the marine environment

Nitrogen is redistributed and recombined continuously by biochemical, physical and geological processes. The most important biochemical reactions and their interrelationship is shown in Figure 1.3:

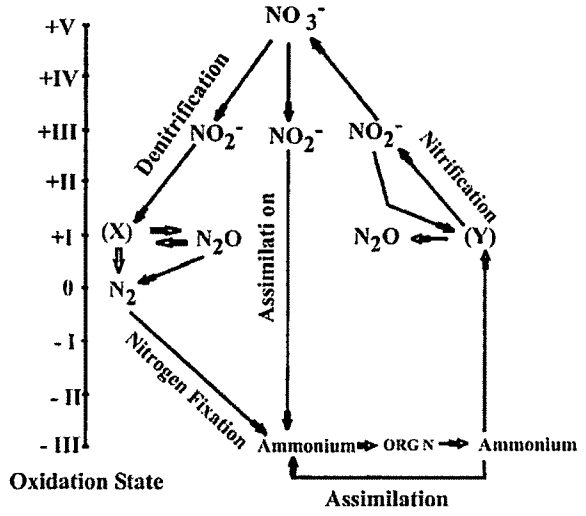

Figure 1.3 Important biogeochemical transformations involving nitrogen and their relationships.

1.3.1 Nitrogen Fixation

Nitrogen fixation is a process where unreactive atmospheric N_2 is converted into different forms of reactive nitrogen (NO_x, NH_y, and organic N) by a variety of algae and bacteria, both symbiotic and free living. The N_2 fixation in the oceanic environment takes place mainly by nonheterocystous cyanobacteria *Trichodesmium* and is understood to be a process of great importance in the oceanic nitrogen cycle and the biological sequestration of carbon (Capone 2001; Capone et al. 1997). Fixation of atmospheric N_2 by blue-green algae and other bacteria by the enzyme nitrogenase commonly produces organic material with $\delta^{15}N$ comparable to or slightly lower than 0‰ (e.g., ~ 0.6‰; Emerson et. al. 1991). Fogel and Cifuentes (1993) have shown fractionations (ε) ranging from -3 to +1‰ in concurrence with -2 to 0‰ reported by Minagawa and Wada (1986). Due to these lower values of $\delta^{15}N$ of organic materials compared to those produced by other mechanisms, low $\delta^{15}N$ in organic matter is often cited as evidence for N_2 fixation. The most simplified equation describing the nitrogen fixation reaction is (Sweeney et al. 1978):

$$N_2\,(g) + 3H_2O(g) \text{ ----nitrogenase} \rightarrow 2NH_3(g) + 3/2\ O_2\,(g) \quad \Delta G^0 = 155\text{kcal/mole } N_2$$

There are two major limitations to biological nitrogen fixation:

(I) The requirement for high amount of input energy to overcome the high activation energy of N≡N. Therefore organisms with highly developed catalytic system alone are able to fix nitrogen.

(II) Nitrogen fixation is a reductive process and is highly sensitive to the presence of oxygen.

1.3.2 Assimilation

Assimilation refers to incorporation or uptake of N-bearing compounds like nitrate, ammonium and nitrite by organisms. Under normal oceanic conditions, nitrate is the most stable and therefore, the most common form of combined nitrogen (Delwiche 1981); however, ammonium may become significant where rate of degradation is greater than assimilation or nitrification. For those organisms that can directly utilise ammonium (termed as ammonium assimilation), this can be a significant nitrogen source. Direct ammonium assimilation results in a significant energy saving to provide the organisms a competitive advantage. During the assimilation process, oxidized forms of nitrogen are first reduced to ammonium by nitrate or nitrite reductases to be eventually assimilated into organic matter. The assimilation of N-bearing compounds by marine organisms is associated with isotopic fractionation where organisms prefer ^{14}N to ^{15}N forming one of the most important isotopic fractionation processes in the biogeochemical cycle of N in the ocean. However, the mechanism that controls this fractionation is poorly understood (e.g., Handley and Raven 1992). The fractionation for nitrate and ammonium assimilation by marine microorganisms measured in laboratory and field experiments show a wide variation (-27 to 0‰; Wada and Hattori 1978; Montoya and McCarthy 1995; Fogel and Cifuentes 1993; Waser et al. 1998). Assimilations by microorganisms in soils show a range of -1.6 to +1‰ (Hubner 1986) whereas by vascular plants show a range of -2.2 to +0.5‰ relative to soil organic matter (Mariotti et. al. 1980). The much larger range of fractionations observed in aquatic vs. soil environments reflects the interplay of several kinetic and equilibrium isotope effects as a function of environmental conditions.

1.3.3 Nitrification

Nitrification is a multi-step oxidation process mediated by several different autotrophic organisms for deriving metabolic energy (Delwiche 1981). Nitrate is the end product of nitrification with various nitrogen oxides (NO_2^-, NO, N_2O) as intermediate products along with hydroxylamine (NH_2OH) and other less stable compounds (Jaffe 2000). Because of intermediates like N_2O, a green house gas, nitrification has a significant role in the earth's radiation balance. Nitrification can be expressed in two energy yielding steps:

First, oxidation of ammonium to nitrite principally done by bacteria of genus *Nitrosamonas*

$$NH_4^+ + 3/2\ O_2 \rightarrow NO_2^- + H_2O + 2H^+ \qquad \Delta G^0 = -290 \text{ kJ/mole}$$

Second, oxidation of nitrite to nitrate by *Nitrobacter*

$$NO_2^- + 1/2O_2 \rightarrow NO_3^- \qquad \Delta G^0 = -82 \text{ kJ/mole}$$

Heterotrophic bacteria utilising organic compounds can also perform nitrification but this is much less significant than autotrophs (Bremner and Blackmer 1981). The overall isotopic fractionation involved during nitrification depends upon the rate determining step, i.e., slow oxidation of ammonium by *Nitrosamonas* rather than the oxidation of nitrite to nitrate, which is a rapid process. Miyake and Wada (1971) have reported an enrichment of remaining ammonium pool in the range of 0 to 21‰ in the marine environment whereas 12-29‰ has been reported for soils (Shearer and Kohl 1986) during nitrification.

1.3.4 Denitrification

Denitrification is a multi-step process where nitrate is reduced to N_2 due to chemical or biologically mediated reduction with various nitrogen oxides (e.g. N_2O, NO) as intermediate products. Depending on the redox condition the organisms use different oxidized entities as electron acceptor during the degradation of organic matter in the general order: O_2, NO_3^-, SO_4^{2-}. When the conditions become anoxic (< 4μM in ocean water column; Devol 1978) the facultative bacteria (approximately 17 genera of anaerobic bacteria can utilise NO_3^-) switch over to nitrate ions, which are the next most abundant source of free energy available for the oxidation of organic matter. Denitrification is of vital geochemical significance as N_2 refluxed (80-100% of the

nitrogen release; Delwiche 1981) to the atmosphere makes it the only process where the major end product is removed from the biological nitrogen cycle. Under certain environmental conditions (low pH and higher O_2) N_2O can become a major product but the overall rate of denitrification decreases under such conditions. Denitrification also balances the natural fixation of nitrogen but the increasing industrial nitrogen fixation has the potential to change this balance (Delwiche 1970). Denitrification causes the $\delta^{15}N$ of the residual nitrate to increase exponentially as nitrate concentration decreases. Different enrichment levels of residual nitrate have been reported: 0 to 21‰ (Miyake and Wada 1971); 14-23‰ (Blackmer and Bremner 1977). The highest enrichment of 40‰ has been reported for the oxygen depleted layer of eastern tropical North Pacific by Cline and Kaplan (1975).

1.3.5 Mineralisation

Mineralisation is the decomposition of organic matter to inorganic matter. During mineralisation organic nitrogen is degraded to simple nitrogen compounds with ammonium as the final product. The excretion of waste nitrogen as urea or uric acid (sometimes ammonium) by marine organisms also comes under mineralisation. However, the major process of mineralisation is the degradation of organic matter by heterotrophic bacteria that includes dissolution of soluble substances, autolysis, deamination, ammonification, coagulation of dissolved substances and bacterial growth (Wada 1980). Mineralisation usually causes a small fractionation (±2‰).

1.4 Global distribution of Nitrogen

The global distribution of various forms of nitrogen and its fluxes are listed in Table 1.2 as complied by Galloway et al. (2004) from different sources. This Table presents the present, past and predicted future estimates of nitrogen in different reservoirs of the earth.

1.5 Role of nitrogen and its isotopes in understanding the ocean biogeochemistry

Nitrogen availability in the marine euphotic zone is a significant modulator of the oceanic primary productivity and export production and, therefore, of C dynamics in diverse and expansive areas of the world's ocean. Intertwined sets of physical

processes and biological reactions of N contribute to N availability and the relative fertility of the upper ocean. However, the key processes of the N cycle and their

Table 1.2 Global distribution of nitrogen (Tg N yr^{-1}) compiled by Galloway et al. (2004).

	1860	Early 1990s	2050
Nr Creation			
Natural	246	233	224
Anthropogenic	15	156	267
Total	**262**	**389**	**492**
Atmospheric Emission			
NO_x			
Fossil Fuel Combustion	0.3	24.5	52.2
Lightning	5.4	5.4	5 4
Other emissions	7.4	16.1	23.9
NH_3			
Terrestrial	14.9	52.6	113
Marine	5.6	5.6	5.6
N_2O			
Terrestrial	8.1	10.9	13.1+?
Marine	3.9	4.3	5.1
Total (NO_x and NH_3)	**13.1**	**46**	**82**
Atmospheric deposition			
NO_y			
Terrestrial	6.6	24.8	42.2
Marine	6.2	21	36.3
Subtotal	12.8	45.8	78 5
NH_x			
Terrestrial	10.8	38.7	83
Marine	8	18	33.1
Subtotal	18.8	56.7	116 1
Total	**31.6**	**103**	**195**
Riverine Fluxes			
Nr input into rivers	69 8	118.1	149.8
Nr export to inland systems	7.9	11.3	11.7
Nr export to coastal areas	27	47.8	63.2
Denitrification			
Continental			
Terrestrial		67	95
Riverine		47 8	63.2
Subtotal	**98**	**115**	**158**
Estuary and Shelf			
Riverine nitrate	27	47.8	63 2
Open Ocean nitrate	145	145	145
Subtotal	**172**	**193**	**208**

Nr refers to all biologically active, photochemically reactive and radiatively active nitrogen compounds (NH_3, NH_4^+, NO_x, HNO_3, N_2O, NO_3^-, urea, amines and proteins).

relationships relating to upper ocean carbon dynamics vary among ocean environments. Our knowledge of the N cycle in the northeastern Arabian Sea and in particular, the Bay of Bengal remains rudimentary with respect to the quantitative relationships, controls and feedbacks. The present work aims to understand the biogeochemical aspect of nitrogen and its isotope in the northeastern Arabian Sea and the Bay of Bengal by estimating the natural isotopic variability in the surface suspended matter along with new and regenerated production using nitrogen isotope. The results obtained would help in understanding the nutrient utilization behavior and carbon fixation potential of the two basins. The following subsections discuss a few biogeochemical aspects relevant to the present work.

1.5.1 Primary production and biological pump: Role in carbon cycle

Carbon dioxide is a green house gas and has an important influence on the radiative budget of atmosphere (Hansen et al. 1981). The concentration of carbon dioxide in atmosphere is constantly increasing due to anthropogenic emissions by about 1ppm yr^{-1} (Keeling and Bacastow 1977) and is presently around more than 30% higher than before the industrial revolution (Keeling and Whorf 2000). Increasing concentration of CO_2 in atmosphere is known to increase the earth's temperature by trapping the long wavelength radiation emitted by earth. Houghton et al. (2001) have suggested the rise in earth's temperature by 0.6±0.2°C. The estimates of carbon sources and sinks for 1980s (Houghton et al. 2001) suggest that the rate of growth of CO_2 in atmosphere (3.3±0.1 Pg C Yr^{-1}) is less than the rate at which it is being injected (5.4±0.3 Pg C Yr^{-1}). This difference is being taken up by ocean and terrestrial biosphere. The ocean takes up CO_2 either chemically (solubility of CO_2 and chemical buffering capacity of seawater) or biologically; the latter by the process of photosynthesis mainly by unicellular microscopic organisms known as phytoplankton. During photosynthesis phytoplankton take dissolved CO_2 (or HCO_3^- depending on species) from the surface layer of ocean, and in presence of sunlight and water, make their bodies, essentially converting the inorganic carbon present in the surface ocean into organic carbon:

$$CO_2 + H_2O + \text{light} \xrightarrow{\text{Chl } a} (CH_2O)_n + O_2$$

The rate at which the inorganic carbon is converted into organic carbon is known as primary productivity (PP) or total productivity and is expressed in terms of mgC $m^{-2}d^{-1}$ or mgC $m^{-2}yr^{-1}$. The summary of US JGOFS primary productivity observations in

different parts of world ocean is shown in the Figure 1.4. Model estimates of global Net Primary Productivity (NPP) range from 45-57 Pg C yr^{-1}, which is almost one half of the total NPP on the earth (Field et al., 1998). Model estimates by Maier-Reimer et al. (1996) suggest that the stopping of photosynthesis by phytoplankton would cause a

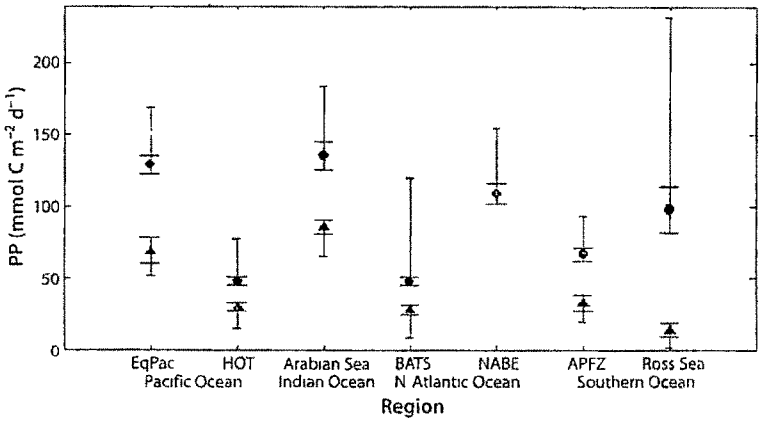

Figure 1.4 Summary of US JGOFS primary productivity observations as compiled by Falkowski et al. (2003). Data sources are: EqPac (Barber et al. 1996), HOT (Karl et al. 1996); Arabian Sea (Barber et al. 2001), BATS (Steinberg et al. 2000), NABE, APFZ, and Ross Sea (Smith et al. 2000).

doubling of the atmospheric CO_2. After completing their life cycle, organic matter produced in the surface layer of ocean sinks to the deeper layers and the sinking flux of organic matter (particle sinking, advection and diffusion of dissolved organic matter, and vertical migration of zooplankton) is said to be "exported". The fraction of PP exported to the ocean interior is called "Export Production" (Berger et al. 1987). Once the organic matter crosses the main ocean thermocline (ventilation depth) they cannot ascend to the euphotic zone and suffer intense biodegradation and recycling in ocean interior to release nutrients and dissolved CO_2. The upward transport of these released materials is very slow and they will not return to the surface water in centuries to millennium time scales, causing an enrichment of the ocean interior with inorganic carbon significantly higher than that predicted from equilibrium with the atmosphere. This process of organic matter sinking and regeneration of dissolved inorganic carbon effectively removes CO_2 from atmosphere by 400ppm (Watson and Orr 2003) and is known as the "Biological Pump".

Phytoplankton need nutrients like nitrogen (N) and phosphorus (P) along with light and CO_2 for photosynthesis. The growth of phytoplankton is hampered if any of

these factors are "limiting". The traditional stoichiometric formula for the composition of marine phytoplankton organic matter:

$106\ CO_2 + 16\ HNO_3 + H_3PO_4 + 122H_2O = (CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 138\ O_2$

suggests that the phytoplankton take up C: N: P in a fixed ratio of 106:16:1 known as the Redfield ratio (Redfield 1934), which is remarkably close to their ratio in the seawater. The productivity in the ocean is often limited by the supply of nutrients particularly N and P. There is considerable dispute as to which of these nutrients is limiting. Biologists favour N (Walsh 1981; Perry and Eppley 1981) whereas Geochemists (Broecker 1982) favour P as the limiting nutrient. However, nitrogen seems to be the limiting nutrient for life in the ocean today, whereas phosphorus may play a critical role on time scales of 10^5 years and longer (McElroy 1983).

1.5.2 Concept of New and Regenerated production

The concept of new and regenerated production was first proposed by Dugdale and Goering (1967) depending on the source of nitrogenous nutrients available in the euphotic zone for the phytoplankton to take up.

(I) **New Production:** Part of primary production resulting from exogenous nitrogen inputs in the euphotic zone like newly incorporated NO_3^- or N_2 from deeper waters and atmospheric or riverine input of nitrate and ammonium.

(II) **Regenerated production:** Part of primary production that sustains on recycled nitrogen in the form of NH_4^+, urea, amino acids and dissolved organic nitrogen (DON) derived from excretory activities of animals and metabolism of heterotrophic organisms. There can be a contribution to the regenerated production from nitrate, due to bacterial nitrification within the photic zone (Dore and Karl 1996).

A simplified cycle of nitrogen proposed by Dugdale and Goering (1967) is shown in Figure 1.5. Under a quasi-steady state condition or an ideal closed system, ammonium can circulate indefinitely if there is no loss from phytoplankton population. However, ocean primary production system is real and there are losses through sinking and mixing and by predation by zooplankton. The sum of losses in form of export production is balanced by nitrate uptake or by nitrogen fixation or by any other possible sources of non-regenerated nitrogen i.e., export production is equal to new production

under a steady state condition (Eppley and Peterson 1979). However, on longer time scales new production is known to be coupled to export production even under non steady state (Eppley et al. 1983) and is referred interchangeably as new production (Sarmiento and Siegenthaler 1992). The ratio of new to total production is called the f-ratio (Eppley and Peterson 1979):

New production / Total Production = f-ratio.

The f-ratio represents the probability that a nitrogen atom is assimilated by phytoplankton due to new production and (1-f) is the probability of assimilation by regenerated production. The number of times a nutrient is recycled in euphotic zone before sinking in particulate form is given by (1-f)/f.

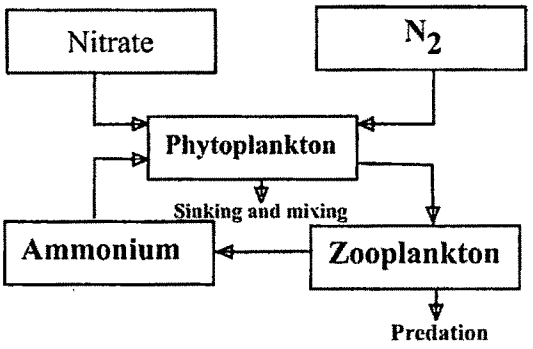

Figure 1.5 Simplified nitrogen cycle in euphotic zone modified after Dugdale and Goering (1967).

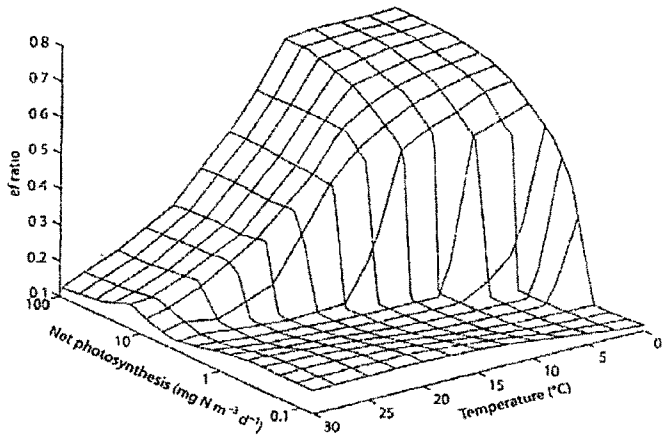

Figure 1.6 Export ratios calculated as a function of temperature and net photosynthesis rate (Laws et al. 2000).

In the open ocean approximately 90% of NPP is supported by regenerated nutrients produced by small grazers and heterotrophic bacteria (Harrison 1980) and bacterial

productivity may average 20% of the NPP (Cole et al. 1988; Ducklow 1999). In general, a hyperbolic relationship exists between primary production and f-ratio (Eppley and Peterson 1979). The ratio of export to primary production is referred as e-ratio (Murray et al. 1989) and is found to be a function of primary production per unit volume and temperature (Figure 1.6; Laws et al. 2000)

1.5.3 Estimation of New, Regenerated and Export production

The ^{15}N labelled nitrate and ammonium is used as a tracer for estimating new and regenerated production (JGOFS report 1996). New production has also been reported to be estimated from the rate of change of nitrate concentration (Allen et al. 1996). The methods and techniques used for new and regenerated production estimation during present study have been discussed in detail in the next chapter. Nitrogen fixation in some part of oceans (Karl et al. 1997; Zehr et al. 2001) and nitrification between 1 and 0.1% light level (Dore and Karl 1996) is known to contribute significantly to new production whereas release of $DO^{15}N$ from cells during incubation results in its underestimation (Bronk et al. 1994). Export flux is generally studied by sediment traps moored in the deep ocean (Honjo et al. 1992) but microbial activity at shallower depths and behaviour of traps in moving fluids pose limitations to the method. However, export production is estimated using ^{234}Th method where export flux of Th is converted to carbon knowing the ratio of carbon to ^{234}Th (Buesseler et al. 1992). Most estimates of export production provide only the flux of sinking organic matter and do not include advection of dissolved organic matter (DOM) and migration of zooplankton. Therefore, the estimates of new production using only $^{15}NO_3$ and export production for only

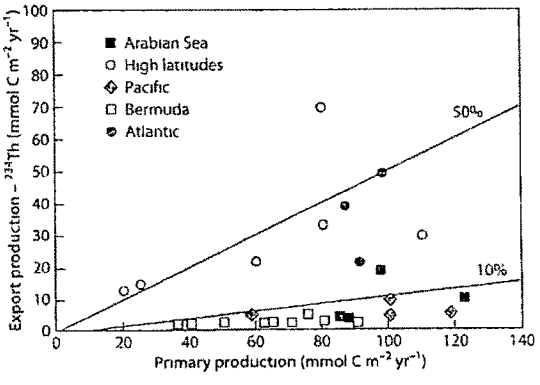

Figure 1.7 Export flux of particulate organic carbon (^{234}Th method) vs primary productivity (Buessler 1998) (source: Treguer et al. 2003).

particulate matter provide lower estimates of new and export productions. The relationship observed between primary production and export flux derived from ^{234}Th shows that the export flux is more than 50% of the annual primary productivity in high latitudes and usually less than 10% in oligotrophic gyres (Figure 1.7).

1.5.4 Basis for using nitrogen for new and regenerated production

New and regenerated production can be estimated from any major elements contained in phytoplankton but nitrogen is used for the following advantageous reasons (Dugdale and Goering 1967):

(i) It is a major structural component of cells and reasonably constant in its ratio to C and P.

(ii) It shows less scatter than C and P as these two are not only structural components but also continuously turned over in energetic processes of organisms.

(iii) Various forms of inorganic nitrogen allow to distinguish allochthonous and autochthonous inputs.

1.5.5 $\delta^{15}N$ in suspended particulate matter

Abundance of ^{15}N in marine organic and inorganic pools is known to vary significantly over range of spatial and temporal scales (Saino and Hattori 1980; Owens 1987; Altabet 1996; Rau et al. 1998). These variations are basically caused by mass dependent fractionations associated with various biogeochemical transformations. These ^{15}N signals have the potential to provide the information on the mechanisms and rates of these transformations and largely reflect the isotopically selective processing of nitrogen by biota (Rau et al. 1998). Isotopic fractionation associated with particulate nitrogen formation governs the isotopic signature in the particulate nitrogen and therefore $\delta^{15}N$ of suspended particulate matter ($\delta^{15}N_{sus}$) records the nitrogen availability in the euphotic zone (Wada and Hattori 1991). The isotopic fractionation imparted during the biological incorporation of nitrogen substrates into particulate matter varies with substrate concentration as well as with algal species, physiology and growth rate (Wada and Hattori 1978; Wada 1980; Montoya and McCarthy 1995; Waser et al. 1998). Observed significant correlation between $\delta^{15}N_{sus}$ and nitrate concentration and variation in $\delta^{15}N_{sus}$ have been explained by Rayleigh fractionation kinetics for

closed system (Altabet 1996) implying the usability of $\delta^{15}N_{sus}$ as index of nutrient availability and utilization. Consequently, $\delta^{15}N$ in sediments have been used to reconstruct paleonutrient conditions and biological productivity (Calvert et al. 1992; Francois et al. 1992; Altabet and Francois 1994; Farrell et al.1995).

1.6 Earlier productivity related work in the world ocean and the study Area

The quest for understanding the biogeochemical fluxes have evolved into various interdisciplinary programmes since mid-80's. The VERTEX (Vertical Exchange Processes) in the North Pacific was the first large-scale programme to focus on the coupling of new and export productions. Other programmes with focus on new production were 1888 WECOMA cruise in equatorial pacific (Barber 1992), JGOFS equatorial pacific (EQPAC, Barber et al. 1994), Research on Antarctic Coastal Ecosystem Rates (RACER; Huntley et al. 1991), Subarctic Pacific Ecosystem research (SUPER) in the north Pacific (Miller et al. 1991; Miller 1993), 1988 Black Sea Expedition (Murray 1991), the JGOFS North Atlantic Bloom Experiment (NABE, Ducklow and Harris 1993), and the JGOFS time series experiments at Bermuda and Hawaii (Lohrenz et al. 1992; Malone et al. 1993; Roman et al. 1993). The new or export production data obtained from different areas using different methods in world ocean are listed in Table 1.3.

Table 1.3 New or export production in different regions (compiled by Falkowski et al. 2003).

Areas	New or Export Production mg N m^{-2} d^{-1}	References
BATS	7.8	Michaels et al. (1994)
HOT	12.2	Emerson et al. (1997)
NABE	98	Bender et al. (1992)
		McGillicuddy et al. (1995)
EqPac-normal	32.1	McCarthy et al. (1996)
EqPac-El Nino	12.3	McCarthy et al. (1996)
Arabian Sea	29.2	McCarthy et al. (1999)
Ross Sea	165	Asper and Smith (1999)
Subarctic	40.3	Sambrotto and Lorenzen (1987)
Pacific		Emerson et al. (1993)
Station P		Wong et al. (1998)
Peru-normal	339	Wilkerson et al. (1987)
Peru-El Nino	256	Wilkerson et al. (1987)
Greenland Polynya	35.6	Smith (1995)

On the basis of new production global ocean can be divided into three regions (Ducklow 1995): (i) regions where nitrate is renewed each winter and depleted in spring (ii) regions where high level of nitrate persists throughout the year (iii) regions where nitrate is permanently depleted in the euphotic zone. The supply of nitrate due to mixing during winter is known to increase new production or causes phytoplankton blooms in the different oceanic regions of the world, such as coastal and shelf regions (Townsend et al. 1992; Hansell et al. 1993); Southern Ocean (Holm-Hansen and Mitchell 1991; Sullivan et al. 1993) and North Atlantic (Sambrotto et al. 1993). In such cases, production and consumption processes get uncoupled (Karl et al. 1991; Banse 1992) leading to episodic export of biomass (Honjo and Manganini 1993). There are regions like subarctic north Pacific and central equatorial Pacific where surface nitrate is high but biomass level is low and these are known as "high-nutrient, low-chlorophyll" or HNLC regions (Cullen 1991). In general new production has been reported to be low in HNLC (Dugdale et al. 1992). High grazing rate (Frost and Franzen 1992) or ammonium excretion from grazers are speculated to inhibit nitrate uptake (Wheeler and Kokkinakis 1990). In the oligotrophic gyres, the surface ocean is almost devoid of nitrate, but is known to maintain a significant new production even in the absence of new nitrate from deeper layers. The other sources suggested for such significant new production are nitrate enriched buoyant mats of diatoms (Villareal et al. 1993) or atmospheric inputs of nitrogen species. However, the latter causes only 1-2% of global new production. Sometimes the atmospheric inputs of nutrients can drive local blooms (Michaels et al. 1993) or can stimulate new production in nutrient poor waters (DiTullio and Laws 1991).

The western Arabian Sea has been studied thoroughly for its physical, chemical and biological characteristics during the JGOFS (Smith 2001). The northeastern Arabian Sea, a part of the present study area, was also studied for its physical, chemical and biological aspects. However, new production in this region was not measured. The present work is **the first attempt** to estimate the new production in the region. Another part of the study area, i.e., the Bay of Bengal, remains almost an unexplored basin regarding its biogeochemical aspect. The present work estimates the new production in the Bay of Bengal for **the first time** and correlates it with the organic carbon fluxes observed by the sediment trap data (Ittekkot et al. 1991; Unger et al. 2003).

New and regenerated production in the northwestern Arabian Sea was estimated thoroughly during JGOFS by three different groups: McCarthy et al. (1999);

Watts and Owens (1999) and Sambrotto (2001). McCarthy et al. (1999) focussed on nitrogen dynamics during the northeast (NE) monsoon to ascertain the relative importance of different nitrogenous nutrients and regeneration process. They found evidence for a widespread suppressing effect of NH_4^+ on the NO_3^- uptake and a high affinity for low concentrations of NH_4^+, leading to low f-ratios of 0.15 and 0.13 during the early and late NE monsoon. The regeneration rate of NH_4^+ was found comparable to its uptake rate maintaining a constant mixed layer concentration. Watts and Owens (1999) measured nitrate, ammonium and urea assimilation rates during intermonsoon and found the integrated total nitrogen assimilation rates varying between 1.1 and 23.6mmol N $m^{-2}d^{-1}$. Ammonium was found to be the preferred substrate at most of the stations, also reflected in the low f-ratios (≤0.52). Sambrotto (2001) measured planktonic nitrogen productivity and regeneration during the spring intermonsoon and the southwest monsoon in the northern Arabian Sea and found the new production and f-ratio varying from 0.1 to 13 mmol N $m^{-2}d^{-1}$ and 0.03 to 0.4 respectively. The inclusion of urea uptake rate in the total production lowered the f-ratio by 29%. Although the above mentioned three studies were carried out in different seasons, regenerated production was found to be consistently more important than new production in the Arabian Sea, leading to a lower f-ratio.

1.7 Scope of the present work

The present work investigates the biogeochemical aspects of nitrogen and its isotopes in the northeastern Arabian Sea and the Bay of Bengal by estimating the variations in natural nitrogen isotopic composition of suspended matter and new and regenerated production during different seasons. To achieve this goal the following studies were carried out:

1. Measurement of the natural isotopic composition and concentration of nitrogen in surface suspended particulate matter of the northeastern Arabian Sea during January and late February-early March 2003. The aim of this study was to assess the possible change in nutrient source and its effect on nitrogen isotopic composition of suspended matter during the middle and waning phases of winter cooling.

2. Measurement of the natural isotopic composition and concentration of nitrogen in surface suspended particulate matter in the Bay of Bengal during pre and

postmonsoon seasons. This would help in understanding the nitrogen isotope biogeochemistry of suspended matter and assessment of possible nutrient sources for the phytoplankton in the region, particularly the effect of freshwater discharge.

3. Obtaining the vertical profile of nitrogen isotopic composition and concentration of suspended matter in the Bay of Bengal. This would help in understanding the process of degradation or degeneration of suspended matter at depth.

4. New production estimation in the northeastern Arabian Sea during January and late February-early March 2003. This would help to understand the effects of winter cooling on new production and change in new production from one month to another.

5.The estimation of new and total production in the Bay of Bengal during pre and postmonsoon seasons. The result would help in understanding the possible role of moderately productive oceanic regimes in the global carbon cycle.

6. The estimation of primary productivity for the Bay of Bengal using indigenous satellite data (IRS P4 OCM - Ocean Colour Monitor) in order to have a wide spatial and temporal coverage of the region. The results obtained have been compared with *insitu* data.

7. Experiments were performed to assess the variation in the uptake rates of different nitrogenous nutrients due to variations in time and concentrations of substrates. This would help in fixing the right incubation period and substrate addition for future new production experiments for optimum results.

1.8 Outline of the thesis

This thesis has been divided into five chapters. Their contents are as follows:

Chapter 1 describes in general nitrogen isotopes and their fractionation behaviour during different biogeochemical transformations. It also deals with the natural variability of nitrogen isotopic composition along with the concepts of new and

regenerated productions and a brief review of relevant literature on the world ocean and the study area.

Chapter 2 deals with the sampling details during the cruises and experimental methods followed during present study.

Chapter 3 discusses the results obtained during present study for the Arabian Sea, including the natural variability of nitrogen isotopes and new and regenerated production estimates during January and late February-early March. It also discusses the effect of winter cooling on new production and the reason for bloom during early March.

Chapter 4 deals with the results of present study for the Bay of Bengal that include the results of the uptake experiments, new and conservative estimates of regenerated production during post and premonsoon seasons and also the surface and vertical variation in the nitrogen isotopic composition of suspended matter. It also investigates the reasons for comparable organic carbon fluxes in sediment traps in the Arabian Sea and the Bay of Bengal and possible nutrient sources for the sustenance of the observed new production.

Chapter 5 summarises the results obtained during present study, highlighting the important findings. It also presents the scope for future research that may lead to a better understanding of nitrogen and carbon cycles of this region.

1.9 Scientific questions addressed:

The present study has attempted to answer the following scientific questions:

Arabian Sea:

- What is the isotopic composition and concentration of particulate organic nitrogen (PON) during the middle and the waning phases of the northeast (NE) monsoon?
- What is the effect of winter cooling on the isotopic composition and the concentration of PON?

- Does the change in the isotopic composition and the concentration of PON a reflection of a changed nutrient regime?

- Has the change in nutrient regime to do with denitrification or is it a simple surficial phenomenon?

- What are the new and total production values during the NE monsoon?

- Does winter cooling influence the new production and the f-ratio?

- What is the change in new production from peak winter cooling to its waning phase?

- What are the possible sources of nutrients that sustain the bloom during the late NE monsoon?

- Why is there limited new production despite the availability of nitrate during winter cooling?

Bay of Bengal:

- What are the new and total production values during pre and post monsoon?

- What is the role of Bay of Bengal in the global carbon cycle?

- Do the moderately productive basins have really a limited role to play in carbon and nitrogen cycles?

- Is higher new production responsible for low surface pCO_2 as previously hypothesised?

- High new production: a possible reason for oxygen minimum zone (OMZ)?

- What are the possible nutrient sources?

- What are the isotopic composition and PON concentration during different seasons?

- Does terrestrial influence significantly modify the isotopic composition of suspended matter?

- How does the isotopic composition of suspended matter change with depth?

- Does the rapid sinking of organic matter influence the isotopic composition at depth?

- Does IRSP4 OCM data provide reliable estimates of total productivity?

General

- What is the reason for comparable organic carbon fluxes in sediment traps in the Arabian Sea and Bay of Bengal?

- What is the effect of incubation time and concentration on the uptake rate?