CHAPTER 1

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Being an ingredient of proteins, nitrogen is an essential nutrient for all forms of life. Its speciation and chemical transformations in biogeochemical processes have played a key role in evolution of life on our planet. During the early part of the Earth's history, in the Archean atmosphere, its speciation was different from what we see today. Although dinitrogen (N₂) was, as it is today, the most stable and abundant form of nitrogen (Warneck, 1988; Kasting, 1990), the atmosphere was devoid of oxygen. Ammonification and ammonium assimilation were the two major pathways of nitrogen cycling. The anaerobic environment at that time favored the reduction of N₂ to NH₃ by N-fixing bacteria equipped with the enzyme nitrogenase. This process was of fundamental importance for supporting primitive life forms (Falkowski, 1997).

Subsequently, with the evolution of organisms capable of oxygenic photosynthesis, molecular oxygen was produced and the hydrosphere and atmosphere became aerobic. The evolution of molecular oxygen gave rise to the bacterially-mediated oxidation of ammonia to nitrate (NO₃⁻). This process, known as nitrification, is a crucial component of the continuing N-cycle. It consists of several reactions producing a number of intermediates of which nitrite (NO₂⁻) is the most important.
Since the evolution of oxic conditions in the Earth's surface environment most of the combined or fixed nitrogen has been existing in the form of NO$_3^-$ . However, the atmosphere continues to retain N$_2$ as its major component as well as the most abundant N species. This is because of two reasons. First, N$_2$ is chemically not very reactive; and secondly, nature has also provided a mechanism for the conversion of the NO$_3^-$ to N$_2$ , but for which all N$_2$ would have been fully converted to NO$_3^-$ over geological time scales. This process, called denitrification is again mediated by bacteria that operate under anaerobic or near-anaerobic conditions. Of all the major processes involved in the nitrogen cycle, denitrification was the last to evolve (Falkowski, 1997). Denitrification and N-fixation therefore have opposing functions: one serves as a source and the other a sink of fixed nitrogen. Nevertheless, the two processes are coupled, and their balance determines the size of fixed nitrogen pool (predominantly comprising NO$_3^-$ ) in the oceanic as well as terrestrial systems, which in turn modulates photosynthetic production limited largely by the availability of fixed nitrogen.

An important chemical property of nitrogen is that it is a polyvalent element that occurs in oxidation states ranging from -3 to +5 (Table 1.1). In the organic matter nitrogen is found in the most reduced form (-3) as amino acids and their polymers, proteins. However, as pointed above, in the Earth's surface environment (soil and seawater) it is mostly present in the most oxidized form (as NO$_3^-$ ). Photosynthetic organisms must therefore reduce NO$_3^-$ during its uptake. As the organic matter is degraded, nitrogen is first released as NH$_4^+$ , but it is soon converted to NO$_3^-$ by nitrifying bacteria. Of the intermediate forms N$_2$ (oxidation state 0) is, of course, the most stable (Fig.
Table 1.1 Nitrogen speciation and oxidation states.

<table>
<thead>
<tr>
<th>Molecular formula</th>
<th>Oxidation number</th>
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<tbody>
<tr>
<td>NO₃⁻</td>
<td>+5</td>
</tr>
<tr>
<td>N₂O₄</td>
<td>+4</td>
</tr>
<tr>
<td>NO₂⁻</td>
<td>+3</td>
</tr>
<tr>
<td>NO</td>
<td>+2</td>
</tr>
<tr>
<td>N₂O</td>
<td>+1</td>
</tr>
<tr>
<td>N₂</td>
<td>0</td>
</tr>
<tr>
<td>NH₂OH</td>
<td>-1</td>
</tr>
<tr>
<td>N₃H₄</td>
<td>-2</td>
</tr>
<tr>
<td>NH₃</td>
<td>-3</td>
</tr>
<tr>
<td>NH₄⁺</td>
<td>-3</td>
</tr>
<tr>
<td>RNH₂</td>
<td>-3</td>
</tr>
</tbody>
</table>
1.1) because of the high energy required to break the N=N bond. Nitrous oxide (N₂O, N oxidation state +1) comes next while others [nitrite (NO₂⁻, N oxidation state +3), nitric oxide (NO, N oxidation state +2) and hydroxylamine (NH₂OH, N oxidation state −1)] are largely transient species (Table 1.1).

The inability of most autotrophs to utilize the abundant N₂ owes to the fact that the responsible enzyme nitrogenase cannot function in aerobic environments. This is one handicap the N-fixing organisms have not been able to overcome in the last few billion years. Only a few organisms, mostly bacteria, have the capability to fix N₂. Some well known examples are non-symbiotic Azotobacter and symbiotic Rhizobium found in soil plants and the filamentous oceanic bacterium Trichodesmium.

Next to N₂, N₂O is the second most abundant species of nitrogen in the atmosphere. It is an important trace gas that plays significant roles in global warming and stratospheric ozone depletion. Aside from its reaction with ozone in the stratosphere, N₂O is quite inert in the atmosphere and also in the surface layer of the ocean. However, as it is an intermediate of the redox chemistry of the nitrogen system it is involved in chemical transformations where rapid changes in nitrogen oxidation state take place (e.g. in soils and subsurface waters).

The global nitrogen budget has been impacted over the last one-and-a-half centuries to a very large extent as a result of anthropogenic activities. The two major drivers of this change are food and energy demands. As most plants depend on fixed nitrogen for their growth, soils need to be enriched with nitrogenous nutrients. Hence, in order to boost agriculture production man has resorted to use of synthetic fertilizers. For instance, in India the
Fig. 1.1. Stability of nitrogen species in seawater (Obtained from Wong, 1980).
consumption of nitrogenous fertilizers has increased from just about 0.05 million metric tonnes in 1951-52 to 12 million metric tonnes in 2000-2001 (Fig. 1.2). Although the enhanced production of food grains so achieved has made the country self-reliant, the excessive application of fertilizers seems to be affecting the environment and ecosystem not only on land but also in the sea. Globally, anthropogenic N-fixation is estimated to be equal to, if not more than, the natural fixation (140Tg N y\(^{-1}\)). Accordingly, the riverine fluxes of dissolved inorganic nitrogen to the ocean have gone up by a factor of 2-3 in recent times (Rabalais and Nixon, 2002). The other major perturbation is through the combustion of fossil fuel, which leads to emissions of NO\(_x\) to the atmosphere. The acidic nature of these emissions not only affects the atmospheric chemistry, but their long range transport and deposition, both wet and dry, can affect biogeochemical processes even at locations farther from their releases.

### 1.2 Oceanic Nitrogen Cycle

A simplified presentation of the oceanic nitrogen cycle is made in Fig. 1.3 (adopted from Codispoti et al., 2001). Nitrogen is taken up by phytoplankton in the euphotic zone mostly as NO\(_3^-\). It is reduced to NH\(_4^+\) through NO\(_2^-\), a process known as the assimilatory nitrate reduction, before incorporation into the cell body. Upon death the organic material undergoes degradation during which nitrogen is first regenerated as NH\(_4^+\). The step is referred to as ammonification. However, in the presence of O\(_2\), NH\(_4^+\) gets oxidized to NO\(_3^-\), with NO\(_2^-\) as an intermediate and N\(_2\)O as a byproduct. Nitrification is mediated by microbes like *Nitrosomonas* and *Nitrobacter*. On
Fig. 1.2. Nitrogenous fertiliser consumption in India
Fig. 1.3. A view of oceanic nitrogen cycle (adopted from Codispoti et al., 2001)

(X) and (Y) represent intra-cellular intermediates that do not appear to accumulate in seawater. The diagram has been modified to suggest $N_2O$ production as well as consumption during denitrification in the sea.
the other hand, the absence of adequate oxygen supply and/or its excessive consumption arising from high organic loading may lead to the development of reducing conditions under which the facultative bacteria utilize NO$_3^-$ as the terminal electron acceptor for the oxidation of organic matter. This process (denitrification) terminates with the production of gaseous nitrogen compounds (mostly N$_2$ and, to a lesser extent, N$_2$O), again with NO$_2^-$ as an intermediate. Like nitrification, the denitrification is also central to global and marine nitrogen cycles. Nitrate required for this process is supplied either from the overlying water or oxic sediment surface where NH$_4^+$ is oxidized to NO$_3^-$ by the process of nitrification. As an alternative process of denitrification, certain bacteria — mostly fermentative ones belonging to genera *Aeromonas*, *Vibrio*, *Clostridium* and *Desulfovibrio* — reduce NO$_3^-$ to NH$_4^+$, a process known as nitrate ammonification. The significance of this process owes to the fact that unlike denitrification (which results in a loss of fixed nitrogen from the sea with important implications for oceanic productivity and atmospheric CO$_2$ - McElroy, 1983; Altabet et al., 1995; Ganeshram et al., 1995), nitrate ammonification enables the retention of nitrogen in the bioassimilable form. The importance of nitrate ammonification vis-à-vis denitrification in coastal marine systems has not been fully evaluated.

Nitrogen utilized by plants in the ocean belongs to one of two categories: (1) "regenerated" nitrogen that is biologically recycled within the surface layer and is available as NH$_4^+$ or in the dissolved organic form such as urea and also in the form of NO$_3^-$, and (2) "new" nitrogen added from outside the surface layer, mostly as NO$_3^-$, through upwelling and vertical mixing, river runoff, atmospheric deposition and nitrogen fixation (Dugdale and Goering,
1967). As stated above deposition of nitrogen from the atmosphere is also a significant source of new nitrogen to the ocean especially in offshore areas (Bange et al., 2000). For example in highly stratified oligotrophic waters the nitrogen input through rainwater (~ 10 μM) may be a significant source for primary production (Wada and Hattori, 1991). In the open ocean, the regenerated fraction accounts for the bulk of total production in the surface waters, whereas the "new" production becomes increasingly more important towards the coast. In coastal waters, nutrient exchanges with sediments must also be taken into consideration, particularly where the mixed layer touches the sea floor.

Table 1.2 reproduces the budget of fixed nitrogen in the ocean prepared by Codispoti et al., 2001. While the magnitudes of various source and sink terms of the budget are still being debated, it is almost certain that the budget is severely out of balance with the net losses from the ocean exceeding net inputs. To what extent human activities discussed above have contributed to this imbalance is not clear, but there is a good reason to believe that even prior to human interference the ocean was losing more nitrogen than received. This situation can only arise from a high denitrification rate in the oceans during the Holocene, and there is sedimentary evidence suggesting that such was also the case during most warm (interglacial) stages in the last few hundred thousand years for which sedimentary records are documented (Altabet et al., 1995, 2002). Conversely, the cold (glacial) stages have been postulated to experience an opposite imbalance (fixed nitrogen inputs to the ocean exceeding losses from it). These oscillations in the nitrogen balance of the ocean are expected to have altered the oceanic fixed
Table 1.2. Marine combined nitrogen budget (from Codispoti et al., 2001)

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<thead>
<tr>
<th></th>
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<tbody>
<tr>
<td></td>
<td>$10^{12}$ g N yr$^{-1}$</td>
<td>$10^{12}$ g N yr$^{-1}$</td>
</tr>
<tr>
<td><strong>Sources</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pelagic N$_2$ fixation</td>
<td>110 ± 40</td>
<td>110</td>
</tr>
<tr>
<td>Benthic N$_2$ fixation</td>
<td>15 ± 10</td>
<td>15</td>
</tr>
<tr>
<td>River Input (DN)</td>
<td>34 ± 10</td>
<td>34</td>
</tr>
<tr>
<td>River input (PON)</td>
<td>42 ± 10</td>
<td>42</td>
</tr>
<tr>
<td>Atmospheric deposition (Net)</td>
<td>30 ± 10</td>
<td>30</td>
</tr>
<tr>
<td>Atmospheric deposition (DON)</td>
<td></td>
<td>56</td>
</tr>
<tr>
<td><strong>Total Sources</strong></td>
<td>231 ± 44</td>
<td>287</td>
</tr>
<tr>
<td><strong>Sinks</strong></td>
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<td></td>
</tr>
<tr>
<td>Organic N export</td>
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<td>1</td>
</tr>
<tr>
<td>Benthic denitrification</td>
<td>95 ± 20</td>
<td>300</td>
</tr>
<tr>
<td>Water column denitrification</td>
<td>80 ± 20</td>
<td>150</td>
</tr>
<tr>
<td>Sedimentation</td>
<td>25 ± 10</td>
<td>25</td>
</tr>
<tr>
<td>N$_2$O loss</td>
<td>4 ± 2</td>
<td>6</td>
</tr>
<tr>
<td><strong>Total Sinks</strong></td>
<td>204 ± 30</td>
<td>482</td>
</tr>
</tbody>
</table>
nitrogen inventory, oceanic productivity and consequently the atmospheric CO$_2$ content (Codispoti et al., 2001). Sequestration of CO$_2$ from the atmosphere should be lower when losses of combined nitrogen through denitrification exceed inputs from land and atmosphere (as happens today). Conversely, during periods of weak pelagic denitrification, combined nitrogen should accumulate in the ocean, stimulating new production and consequently draw-down of atmospheric CO$_2$; such a condition probably prevailed during glacial times. Thus nitrogen cycling in the ocean, particularly in the Arabian Sea, could well modulate global climatic changes (Altabet et al., 2002).

1.3 Significance of Nitrogen Biogeochemical Cycling in the Arabian Sea

The Arabian Sea is a small ocean basin but houses several diverse biogeochemical provinces such as eutrophic, oligotrophic and low oxygen areas. The presence of such diverse regimes within a small basin makes it an ideal natural laboratory for biogeochemical investigations.

One of the distinguishing features of the Arabian Sea oceanography is the strong seasonality in physical, chemical and biological variables due to the unique physical forcing it experiences in the form of the Southwest (SWM) and Northeast (NEM) monsoons. The mixing processes associated with these monsoons fertilizes the surface waters with essential nutrients. For example, summer upwelling can raise surface NO$_3^-$ concentrations to 16-22 µM off Somalia, India and Oman, while winter convection can result in an enrichment of 4-6 µM NO$_3^-$ in surface waters of the northern Arabian Sea (Naqvi et al., 2003). This greatly stimulates the growth of phytoplankton, leading to the formation of blooms. It is estimated that the annual averaged primary
production (PP) in the Arabian Sea is as high as in the North Atlantic during
the spring blooms (Barber et al., 2001). The ensuing downward export of
particulate organic carbon (POC) and its decomposition contribute to the
maintenance of high nutrient concentrations in subsurface waters. However,
as the decomposition process requires O₂, its consumption rate is high in
subsurface waters of the region, and this in conjunction with limited O₂ supply
(arising from the blocking of the northern Indian Ocean by the Asian land
mass at low latitudes, ~25°N) leads to the formation of the thickest and the
most intense oxygen minimum zone (OMZ) found in any oceanic basin. The
OMZ, located in the depth range ~150-1000 m, has O₂ < 0.1 ml l⁻¹ (~4 μM).
The most O₂-deficient waters are found north of ~12°N the approximate
position of the zero wind stress curl (Warren, 1994).

The subsurface O₂ deficiency makes a tremendous impact on nitrogen
cycle. Due to the near total absence of O₂, denitrification sets in a layer of
150-600 m. Denitrification occurs round the year within this layer over a well
defined geographical area in the central and northeastern Arabian Sea
(Naqvi, 1991). Such environments that experience denitrification but not
sulphate reduction are generally termed as ‘suboxic’. There are two other
major sites in the ocean that also experience the mid-depth suboxia of the
magnitude and intensity observed in the Arabian Sea: the eastern tropical
North Pacific (ETNP – off Mexico-Panama) (Cline and Richards, 1972;
Codispoti and Richards, 1976) and the eastern tropical South Pacific (ETSP -
off Chile-Peru) (Codispoti and Packard, 1980; Codispoti and Christensen,
1985). What makes the Arabian Sea different from these two regions,
however, is that the zone of most intense denitrification is geographically
separated from the zones of intense upwelling and high primary productivity in the western Arabian Sea (Naqvi 1991). This is because for denitrification to occur, as identified from the accumulation of secondary NO$_2^-$, O$_2$ concentration must fall below an abruptly-defined threshold value of $\sim 1 \mu$M ($\sim 0.02$ ml l$^{-1}$; Morrison et al., 1999; Naqvi et al., 2003). Outflows from the Red Sea and the Persian Gulf and advection of waters from the south in the western Arabian Sea generally keep minimum O$_2$ levels marginally above this threshold (Naqvi et al., 2003). A seasonal undercurrent bringing relatively oxygenated waters from the south during the SWM similarly suppresses denitrification just off the Indian continental margin (Naqvi et al., 1990).

Unlike the more intense upwelling zones of the western Arabian Sea suboxic conditions develop seasonally (during late summer and autumn) associated with modest upwelling in the eastern Arabian Sea. But these conditions are confined to the inner and mid-shelf region and cannot be considered analogous to the suboxic zone off Peru that extends offshore from the coastal waters (Codispoti and Packard, 1980). In fact, in the Arabian Sea the coastal and offshore suboxic systems are always separated. Although short lived, denitrification over the Indian shelf is far more intense and often leads to complete NO$_3^-$ utilization and the onset of sulphate reduction. The present study focuses largely on this shallow system.

1.4 Previous Work

The Arabian Sea was first observed to experience intense oxygen depletion in subsurface waters during the John Murray Expedition (1933-34); that is also found to affect nitrogen cycling (Gilson, 1937). This was the first
observation of its kind anywhere in the oceans. It is surprising that the follow-up studies to investigate these effects in detail were not undertaken until the 1970s. Wyrtki (1971) provided detailed maps of the distributions of nutrients (including nitrate but not nitrite) along various horizontal and vertical sections based on extensive data collected during the International Indian Ocean Expedition (IIOE). These led to the realization of the extent and intensity of the oxygen minimum and also showed that NO$_3^-$ concentrations in intermediate layers are much lower in the Arabian Sea than in the Bay of Bengal (see, for example, NO$_3^-$ distribution at 300 m). Even prior to that, in his classical treatment of anoxic basin and fjords, Richards (1965) had made a mention of the Arabian Sea as an open ocean denitrification site. However, it was left to Sen Gupta and coworkers (Sen Gupta et al., 1976 a, b) to initiate the first major investigation and show evidence on pelagic denitrification in the region.

Following the approach of Cline and Richards (1972) in the ETNP that is based on the Redfield-Ketchum-Richards (RKR) model (Redfield et al., 1963), Sen Gupta et al. (1976 a, b) provided the first estimates of NO$_3^-$ losses resulting from denitrification. They calculated deficits amounting to $-25 \ \mu$M and the process to extend to $-4^\circ$N. These results have been questioned by Deuser et al. (1978) who computed NO$_3^-$ losses from NO$_3^-$-salinity relationship. The deficits computed by these authors were lower by a factor of 3 and limited the southern boundary to $-14^\circ$N. Deuser et al. (1978) are the first to quantify the denitrification rate. This estimate (range between 0.1 and 1 Tg N y$^{-1}$; 1 Tg = $10^{12}$ g) has been arrived at first by calculating the inventory of NO$_3^-$ deficits and then dividing it by the renewal time. Results of Deuser et al.
(1978) are, in turn, countered by Naqvi et al. (1982) who argued that the NO$_3^-$-salinity relationship led to an underestimation of NO$_3^-$ deficits. The deficits computed by Naqvi et al. (1982) are intermediate to the earlier two estimates. The process has been found to extend to 12°N in the south with the overall rate of 3.2 Tg N y$^{-1}$.

Naqvi and Sen Gupta (1985) introduced the use of the nitrate tracer NO (defined as O$_2$+8.65*NO$_3^-$ following Broecker, 1974) to compute NO$_3^-$ losses from potential temperature, nitrate and O$_2$ values and obtained both NO$_3^-$ deficits and rate (5 Tg N y$^{-1}$) which agreed with those of Naqvi et al. (1982). This procedure has also been followed by Naqvi (1987), but he combined the estimated deficits with dynamic computations and diffusion coefficients (cf. Codispoti and Richards, 1976) and estimated a much higher denitrification rate (~30 Tg N y$^{-1}$). Except for the estimate by Mantoura et al. (1993), who estimated the denitrification rate to be 12 Tg N y$^{-1}$, most of the subsequent estimates are consistent with that of Naqvi (1987): Naqvi and Shailaja (1993) estimated denitrification rate to be 24-33 Tg N y$^{-1}$ from the activity of respiratory electron transport system (ETS; cf. Codispoti and Packard, 1980); Howell et al. (1997) combined his estimates of NO$_3^-$ deficit with the chlorofluorocarbon (CFC)-derived ages to arrive at 21 Tg N y$^{-1}$; and a one-dimensional model employed by Yukashev and Neretin (1997) led to a rate of 34 Tg N y$^{-1}$. Most recently, Bange et al. (2000) have reviewed all data and based on a new set of measurements proposed a rate of 33 Tg N y$^{-1}$.

Naqvi et al. (1990) investigated the temporal variability of denitrification and found substantial seasonal oscillations in denitrification along the Indian continental margin. This was attributed to the presence of an undercurrent
that supplies oxygen to intermediate layers in this region; the supply of which is associated with the SWM circulation. Understandably lower deficits were found during this season. Otherwise, geographical boundaries of the denitrifying zone, demarcated by Naqvi (1991) based on the occurrence of \( \text{NO}_2^- \), appear to be fairly stable. It was pointed out by Naqvi (1987) that the most intense denitrification occurs in the open Arabian Sea outside the continental shelf. This represents a departure from the pattern seen in the other two major denitrifying sites of the Pacific Ocean where denitrification begins from the continental shelf. Naqvi (1991) estimated the area of the denitrification zone to be \( 1.37 \times 10^6 \text{ km}^2 \).

Naqvi et al. (1993) found an intermediate nepheloid layer (INL) associated with denitrification in the Arabian Sea. As in case of the Pacific denitrifying sites (Garfield et al., 1983; Spinrad et al., 1989) the INL in the Arabian Sea also contained a particle protein maximum and a bacterial biomass maximum. Like the secondary nitrite maximum (SNM), the INL was also found to intensify offshore. It was concluded that the INL was not formed through the lateral advection of the bottom nepheloid layer from the continental margin. Instead, it was proposed that the INL was formed due to proliferation of denitrifying bacteria that presumably used the dissolved organic carbon as a carbon source.

That \( \text{N}_2 \) is the end product of denitrification has also been demonstrated by results of measurements of the \( \text{N}_2/\text{Ar} \) ratio in seawater. This ratio shows a prominent maximum coinciding with the SNM indicating the presence of excess \( \text{N}_2 \) arising from nitrate reduction (Codispoti et al., 2001). In fact the quantity of excess \( \text{N}_2 \) estimated from the ratio appears to be
substantially higher than the maximal NO$_3^-$ deficit. This led Codispoti et al. (2001) to suggest that the deficits-based approaches might underestimate the extent of denitrification, which could be as much as 60 Tg y$^{-1}$.

Measurements of stable isotope abundance ($\delta^{15}$N, a measure of $^{15}$N/$^{14}$N ratio) in NO$_3^-$ and N$_2$ provide additional evidence for the reduction of NO$_3^-$ to N$_2$ (Brandes et al., 1998). This approach is based on the observation that various biologically mediated processes involve mass-dependent fractionation of isotopes as a result of which the lighter isotopes are generally consumed preferentially and the residual reactants are enriched with heavier isotopes. For the two natural isotopes of nitrogen ($^{14}$N and $^{15}$N), NO$_3^-$ containing $^{14}$N is lost more easily than that containing $^{15}$N during denitrification. Consequently N$_2$, the end product of denitrification, gets depleted with $^{15}$N while an enrichment of this isotope takes place in the residual NO$_3^-$. Such has been found to be the case: within the core of the SNM the $\delta^{15}$N of NO$_3^-$ has been found to reach up to 15%o while the $\delta^{15}$N of N$_2$ concomitantly decreased to 0.2 %o (Brandes et al., 1998). Using these data Brandes et al. (1998) computed the fractionation coefficient to be 25-28%o.

As stated earlier, suboxic conditions also develop seasonally in shallow subsurface waters over the western continental shelf of India. The O$_2$-deficiency is most severe in late summer when the entire shelf is covered by waters with $O_2 < 0.5$ ml l$^{-1}$ (22 $\mu$M). The factors responsible for the occurrence of O$_2$-deficient conditions are primarily of natural origin and have been recognized for quite some time (Banse, 1959; Carruthers et al., 1959). However, these conditions have intensified in recent years as shown by Naqvi
et al. (2000). The complete nitrate consumption and accumulation of hydrogen sulphide provides strong evidence for the intensification of reducing conditions, which had not been reported previously from the Arabian Sea. It is likely that fertilizer inputs from land have further enhanced the naturally high PP rates in coastal waters bringing about an ecosystem shift in recent years, but subtle changes in hydrography cannot be excluded as an additional or alternative cause.

1.5 Nitrous Oxide cycling

$N_2O$ is an important intermediate of denitrification and a byproduct of nitrification. In the stratosphere $N_2O$ reacts with $O_3$ and forms 'NO' radical thereby depleting stratospheric ozone (Andrea and Crutzen, 1997; Nevison and Holland, 1997). It also affects the atmospheric radiation balance because it has a global warming potential about ~ 200 times greater than $CO_2$ on a molecular basis. The atmospheric concentration of $N_2O$ is currently rising at a rate of 0.2-0.3% per year. These observations have led to several studies to better quantify sources and sinks of atmospheric $N_2O$. The oceans play an important role in this regard accounting for one-third of the natural inputs to the atmosphere (Nevison et al., 1995). However, $N_2O$ flux to the atmosphere is not uniformly distributed over the oceanic surface and the tropical upwelling zones containing $O_2$-deficient waters make a disproportionately large contribution (Codispoti and Christensen, 1985; Suntharalingam and Sarmiento, 2000). This is because the low $O_2$ conditions favour greater production of $N_2O$, through both nitrification and denitrification (Codispoti and Christensen, 1985; Suntharalingam and Sarmiento, 2000). The intense
reducing conditions within the SNM of the open ocean suboxic zone force N$_2$O to serve as an electron acceptor for respiration of organic matter resulting in low N$_2$O concentrations (<10 nM). However, the peripheries of the SNM are always characterized by N$_2$O accumulation, which supports a high rate of N$_2$O supply to the surface layer. This pattern, characteristic of all oceanic suboxic zones (Cohen and Gordon, 1978), was first reported from the Arabian Sea by Law and Owens (1990) and Naqvi and Noronha (1991). It has been confirmed by several subsequent studies undertaken in the region (Bange et al., 1996, 2001; de Wilde and Helder, 1997; Lal and Patra, 1998; Patra et al., 1999; Upstill-Goddard et al., 1999). These studies have established that the Arabian Sea is an important area for emissions of N$_2$O to the atmosphere. However, estimates of total N$_2$O-flux from the region stretch over a wide range (0.16-1.5 Tg N$_2$O y$^{-1}$; Law and Owens, 1990; Naqvi and Noronha, 1991; Bange et al., 1996, 2000; Lal and Patra, 1998; Upstill-Goddard et al., 1999). Recently, the range has been narrowed down to 0.33-0.70 Tg N$_2$O y$^{-1}$ by Bange et al. (2001) who have synthesized all data available from the region. This work revealed that the fluxes are dominantly contributed by coastal regions during the SWM. However, this study did not take into consideration recent measurements from the west coast of India that have revealed the highest concentrations recorded anywhere in the ocean.

1.6 Geographical Setting

The Arabian Sea forms the northwestern arm of the Indian Ocean. It is bounded by the African and Asian landmass in the west and by Asia in the north and east. Unlike these natural boundaries, the southern boundary
separating the Arabian Sea from the greater Indian Ocean is arbitrarily defined. For the oceanographic purpose it is generally taken to run from Goa (India) along the western side of the Laccadive and Maldives Islands to the equator and then slightly to the south to Mombassa (Kenya) (Schott, 1935). The region so demarcated occupies an area of $6.225 \times 10^6 \text{ km}^2$. It does not include the Gulfs of Aden and Oman, through which the Arabian Sea is connected to two Mediterranean-type marginal seas – Red Sea and Persian Gulf, respectively. Also excluded by the above demarcation is the Laccadive Sea, a smaller water body (area $0.23 \times 10^6 \text{ km}^2$) that lies to the east of the Laccadive islands. However, oceanographers often do not make a distinction between the Arabian Sea and the Laccadive Sea, especially while dealing with the processes along and off the continuous west coast of India. Such a distinction will not be made in this study either.

The most prominent bathymetric feature of the Arabian Sea is the northwest-southeast trending Carlsberg Ridge that divides the Arabian Sea into two major and deep (>4000 m) basins - the Arabian Basin in the northeast and the Somali Basin in the southwest. A deep passage in the Owen Fracture Zone connects the two basins. While almost the entire Arabian Basin is located within the Arabian Sea, a large portion of the Somali Basin falls outside. The latter is, in turn, serially connected to the Mascarene, Madagascar and Crozet Basins. A less pronounced feature is the Murray Ridge that extends southwest from the Makran margin to join the Carlsberg Ridge thereby separating the Arabian Basin from the relatively narrow and shallow (<2000 m) Oman Basin. The continental shelf is generally wide (often exceeding 100 km west of Karachi) along the Pakistani coast and all along the
Indian west coast with the maximal width (350 km) occurring off the Gulf of Cambay. Elsewhere the shelf width rarely exceeds 40 km (Fig. 1.4).

1.7 Climate

The climate of the North Indian Ocean region is strongly influenced by its proximity to landmasses. The Indian Ocean is the only ocean that is terminated at low latitudes (≈25°N) due to presence of land in the north. This gives rise to the unique phenomenon of periodic reversal of winds, which is usually referred to as monsoon system. The excessive heating of land as compared to the sea during summer causes the development of low pressure zone over land, driving strong southwesterly winds. Opposite conditions prevail during winter when northeasterly winds blow from the continent to the sea. Of the two monsoons, the SWM is far more energetic. It starts in the month of June and lasts till September. During this period wind speeds frequently exceed 30 knots, especially along a strongly sheared low-level atmospheric jet (the Somali Jet that is often referred to as Findlater jet – Findlater, 1971), the axis of which extends toward the northeast from the Somali coast. The NEM begins in November and continues through March. The winds are lighter during this season. The periods intervening the two monsoons – March to May and October to November – are referred to as Spring Inter-monsoon (SI) and Fall Inter-monsoon (FI), respectively. These transition months are characterized by weak, slowly-reversing winds.

Almost all of the rainfall over the Arabian Sea occurs during the SWM that may exceed ~300 cm y\(^{-1}\) along its eastern shores. The amount of precipitation decreases towards the northwest, and so the balance between
Fig. 1.4 Bathymetry of eastern Arabian Sea
evaporation and precipitation (E-P) is at its maximum off the Arabian coast and its minimum along the Indian west coast. The Arabian Sea does not receive much river runoff, the combined discharges by the main rivers (the Indus, the Narmada and the Tapti), all draining in the northeastern Arabian Sea; probably do not exceed 200 km$^3$ y$^{-1}$. However, there are scores of other small rivers originating in the Western Ghats (a mountain range separating the narrow western coastal plain from the Deccan Plateau and interior areas), which together may transport about 150 km$^3$ of freshwater annually (most of it during the SWM period; Dr. S.R. Shetye, personal communication). The large rainfall and land runoff combine to result in a positive water balance (excess of precipitation and runoff over evaporation) over a few hundred kilometer wide belt along the Indian coast. The net water balance is negative elsewhere making it a climatic feature of the Arabian Sea as a whole. Consequently, the surface waters are the least saline in the southeast and the most saline in the northwest (Wyrtki, 1971).

1.8 Importance, Objectives and Scope of the Study

While nitrogen cycling in the offshore suboxic zone has been studied in great detail over the past 25 years, as described above, very little information is available from the suboxic system over the shelf. Aside from its seasonal occurrence, the coastal system is expected to function differently from the deeper $O_2$-deficient zone for a variety of reasons. For instance, due to the high biological productivity and shallow depths the POC settled on the seafloor remains available for decomposition and denitrification is not limited by the supply of organic carbon. This along with the higher ambient
temperatures should result in higher denitrification rates as compared to the open ocean. Secondly, due to the proximity of land, the impact of anthropogenic activities mentioned above will be much greater in the coastal environment. The enhanced nutrient inputs through both eolian and fluvial pathways are expected to lead to coastal eutrophication. Whereas such eutrophication is occurring globally, its impact on the coastal environment of the eastern Arabian Sea is expected to be a lot more severe due to the already existing naturally-caused O₂ depletion. Finally, as the suboxic waters are directly in contact with the sediments the exchanges of material across the sediment water interface are extremely important. The settling and burial of copious amounts of organic matter are expected to result in high rates of respiration including denitrification and sulphate reduction in the continental margin sediments. This issue is important because benthic denitrification can counter to some extent the effect of coastal eutrophication. However, practically nothing is known about the role of coastal sediments in biogeochemical cycling in the Arabian Sea. In fact, there are no published measurements on the rate of sedimentary denitrification not only from the Arabian Sea but also from the Indian Ocean as a whole. The present study was therefore aimed to collect the much-needed data and gain insights into nitrogen biogeochemical cycling in this unique environment.

The main objectives of the study are:

i) To understand the physical and biological processes leading to the development of O₂-deficient conditions in near-bottom waters over
the western continental shelf of India and to investigate their variability in space and time,

   ii) To assess the impact of O$_2$-deficiency on benthic nitrogen cycling especially N$_2$O production and consumption,

   iii) To quantify the rates of denitrification in water column and shelf sediments and evaluate the impact of coastal eutrophication, and

   iv) To improve understanding of pathways of nitrogen transformations in the shallow O$_2$-depleted environments.

In order to fulfill these objectives extensive measurements were carried out and the results are presented here. The organization of the thesis is as follows:

Chapter 2 provides details about the field work, techniques used for the collection and handling of samples and their analyses on board research vessels and in the shore laboratory.

Chapter 3 gives the salient feature of the hydrography and circulation in the Arabian Sea highlighting the seasonal changes that affect the biogeochemical cycling over the western continental margin of India.

Chapter 4 presents the results of observations made during various seasons along a number of cross-shelf sections off the west coast of India, as well as along a more-frequently-visited shallow (depth < 30 m) section off Candolim (Goa). The latter are used to construct the first-ever complete picture of seasonality of oceanographic variables, including the evolution of the O$_2$-deficiency in shallow waters, in response to the monsoonal forcing. An
assessment of inter-annual changes in the suboxic conditions is also made. Also presented for the first time are data on primary productivity based on in-situ measurements of $^{14}$C uptake. An estimate of the denitrification rate in the water column is made and the flux of N$_2$O to the atmosphere is quantified.

Chapter 5 examines the relationships between biogeochemical variables in order to gain insights into pathways of nitrogen transformations. The first ever data on the isotopic composition of NO$_3^-$ from the shallow suboxic zone are also used and compared with those from the open ocean.

Chapter 6 deals with sedimentary nitrogen cycling. Experimental details of incubation of sediment cores for measurements of denitrification rates and of benthic flux measurements are also given. Results of sedimentary denitrification rate determined with the acetylene block technique are presented. Porewater profiles of NO$_3^-$, NO$_2^-$ and NH$_4^+$ are also included as are the N$_2$O profiles to assess whether the sediments serve as a net source or sink of N$_2$O for the overlying water column. Porewater profiles of NO$_3^-$ are used in a one-dimensional model, and the first ever data on benthic fluxes obtained with an indigenous benthic chamber are presented and discussed.

Chapter 7 summarizes the major findings of the study and makes recommendations for future research.