

NITROGEN CYCLING IN THE SUBOXIC ARABIAN SEA: IMPLICATIONS FOR ATMOSPHERIC CHEMISTRY AND CLIMATE

S W A Naqvi

National Institute of Oceanography

Dona Paula 403 004, Goa

An acute oxygen deficiency at mid-depths in the Arabian Sea leads to large-scale microbial conversion (denitrification) of the oxidised combined nitrogen species to molecular nitrogen (N_2) at an estimated rate of $25\text{-}30 \times 10^{12}$ g $N\ y^{-1}$. Denitrification in the region appears to be decoupled from the overhead primary production as evident from the chemical, biochemical and microbiological data. This anomaly requires inputs of organic matter to the subsurface layers through some hitherto poorly understood processes (e.g., vertical migration of mesopelagic fish and transport of dissolved or suspended matter including the transparent exopolymer particles).

The reducing conditions greatly affect the abundance of stable isotopes in dissolved nitrogen species. Large enrichment of ^{15}N relative to ^{14}N in nitrate (NO_3^-) and a corresponding depletion in N_2 occur within the denitrifying layer. The isotopic fractionation factor during denitrification estimated using simple advection-reaction and diffusion-reaction models ranges between 22 and 25 per mil. The near-surface isotopic composition of NO_3^- is, however, remarkably close to the oceanic average value, presumably due to the input of isotopically light nitrogen through nitrogen fixation.

(The oxygen-deficient conditions cause rapid turnover of nitrous oxide (N_2O) in the water column, and large emissions of N_2O to the atmosphere. Huge enrichments of ^{15}N and ^{18}O occur within the N_2O -poor denitrifying layer. However, just above this layer, isotopically light N_2O accumulates in high concentrations, implying that N_2O emitted to the atmosphere from this region cannot be very heavy. Analysis of the N_2O -rich upwelled water off the southwest coast of India reveals contrasting trends (moderate depletion of ^{15}N , but slight enrichment of ^{18}O relative to air), indicating that the ocean-atmosphere exchange cannot counter inputs of heavier isotopes (particularly ^{18}O) associated with the stratospheric back flux, as proposed by previous workers. Also, these results rule out nitrification as the major mechanism of N_2O production in the oceanic oxygen-depleted zones.)

Nitrogen isotope records in sediment cores reveal large cyclic changes in $^{15}N/^{14}N$, evidently caused by the variability in denitrification in the past associated with the climatic cycles. This reinforces the view that the ocean oscillates between a net source and a net sink of combined nitrogen on geological time scales and that the resultant changes in the combined nitrogen inventory could modulate climatic changes through the carbon dioxide link.

INTRODUCTION

Nitrogen is an essential nutrient element the non-availability of which often limits biological production in the oceanic environment.¹ It is a polyvalent element occurring in nature in oxidation states ranging from -3 to +5 (Fig. 1). The most abundant form of nitrogen on the earth is molecular nitrogen (N_2) which accounts for roughly four-fifth by volume of its atmosphere. But N_2 is chemically inactive and only a few organisms have the capability to utilise or "fix" it as such. The forms that can be readily assimilated by plants are the "combined" nitrogen species such as nitrate (NO_3^-) and ammonium (NH_4^+). NO_3^- is the predominant form of combined nitrogen in the sea because of the generally oxidising nature of seawater. However, in the organic matter nitrogen occurs in the most reduced form (as amino nitrogen). Most photosynthetic organisms are equipped with the enzyme systems needed to reduce nitrogen from +5 to -3. The reduced nitrogen regenerated from the decaying organic matter is readily oxidised to NO_3^- with nitrite (NO_2^-) as an intermediate and Nitric Oxide (NO) and nitrous oxide (N_2O) as either intermediates or by-products (Fig. 1). This process is known as nitrification. The reverse of nitrification is denitrification which takes place when the ambient oxygen (O_2) concentrations are close to zero and the bacteria begin to utilise NO_3^- for the decomposition of organic matter reducing it to N_2 with NO_2^- , NO and N_2O as intermediates (Fig. 1). Denitrification is of vital biogeochemical importance since it is the major pathway by which combined nitrogen is converted to the gaseous forms.^{2&3}

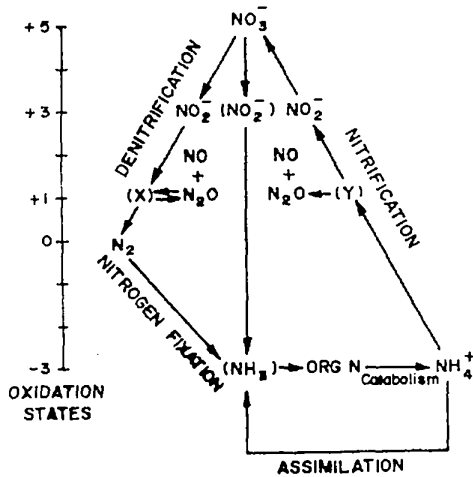


Figure 1. The marine nitrogen cycle. 'X' and 'Y' are intra-cellular intermediates that do not accumulate in water column (after Codispoti and Christensen, 1985).²

Conditions favourable for the occurrence of denitrification commonly develop in soils and in oceanic sediments. In the water column, on the other hand, the dissolved O_2 concentrations are normally high enough to prevent the onset of denitrification. However, there are three areas of the open ocean where O_2 concentrations within its minimum at intermediate depths fall to nearly zero levels (Fig. 2). Two of these sites lie in the eastern tropical Pacific Ocean – one on each side of the equator – whereas the third is found in the northern Indian Ocean especially in the Arabian Sea.^{1&4} Together these regions account for <5 % of the total area of the oceans, but they make disproportionately large contributions to the global nitrogen cycle. This is because of the high rate of water column denitrification in these areas which is roughly 1/3 of the total oceanic denitrification rate.³

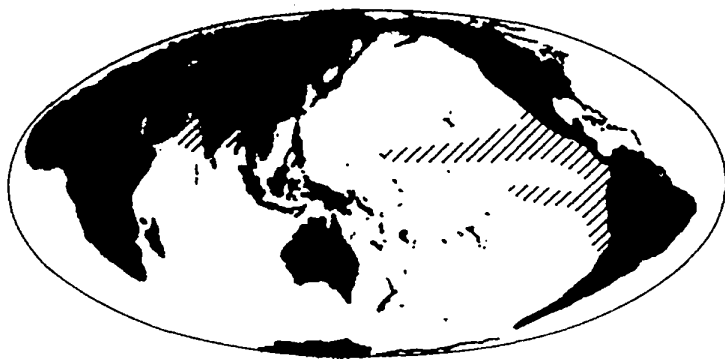


Figure 2. The oxygen-deficient zones ($O_2 < 0.1 \text{ ml l}^{-1}$) of the world oceans (after Olson et al.).³⁵

Recent estimates of various source and sink terms of the oceanic combined nitrogen budget (Table I) suggest a non-steady state where the total losses from the sea, occurring mainly through denitrification, seem to exceed net inputs by a wide margin. The magnitude of this imbalance is such that it would lead to complete removal of combined nitrogen from the oceans in a few tens of thousand years. Obviously such a state cannot persist over long periods of time, and the only way the atmospheric nitrogen content and the oceanic combined nitrogen inventory can remain constant over geological time scales is that there should be times when the balance is the other way around.³ In other words, the oceans probably alternate between a net source and a net sink of fixed nitrogen determined essentially by the relative rates of nitrogen fixation and denitrification. These changes in the oceanic combined nitrogen budget have the potential to substantially alter the combined nitrogen inventory on time scales of hundreds to thousands of years. And as nitrogen is the principal biolimiting element, it can bring

about large variations in oceanic productivity and hence in the rate at which carbon dioxide is sequestered from the atmosphere. This in turn can lead to climatic changes since carbon dioxide is the most important greenhouse gas.^{3&5} How and over what time scales is the nitrogen budget balanced is an important problem that is currently attracting attention of the biogeochemists, and it is in this context that the Arabian Sea has assumed a lot of importance. This is because it is not only a very important denitrification site, but it also makes contributions to nitrogen fixation and N_2O cycling that are far in excess to what is expected from its limited size.⁶ This paper provides a review of recent developments in the study of nitrogen cycling in this region.

**Table I: Oceanic Combined Nitrogen Budget ($Tg\ N\ y^{-1}$)
(Modified after Codispoti et al. 1996)³**

<i>Inputs</i>	
Riverine	45
Ground water	10
Atmospheric (DON+DIN)	100
Nitrogen Fixation	150
Totals	
	305
<i>Sinks</i>	
Water column denitrification	110
Sedimentary denitrification	255
Burial	35
Exports of organic N	16
Inorganic loss to atmosphere	13
N_2O loss to atmosphere	7
Totals	
	436
Deficit	
	131

1. SUBOXIA AND DENITRIFICATION

As stated earlier, the Arabian Sea experiences an acute mid-water O_2 deficiency. In fact it contains the thickest and the most intense O_2 minimum found in any oceanic basin. This is clearly seen in Fig. 3 which gives O_2 distribution with depth and geographical location along a transect that extended from 8 °N in the central Arabian Sea to about 24 °N off the Omani coast. Oxygen levels in excess of 25 μ M are not shown, but the surface concentrations are generally around 200 μ M (Fig. 4). Thus, concentrations within a wide depth range (bounded by the 1 μ M O_2 contour) in the northern and central Arabian Sea are <0.5 % of the surface values. These conditions are most conducive for the occurrence of denitrification as evident from Fig. 4 which shows vertical profiles of O_2 , NO_2^- and NO_3^- at a typical station located within the suboxic zone. The broad minimum in NO_3^- and a maximum in NO_2^- [referred to as the Secondary Nitrite Maximum (SNM)] at ~150-550 m are characteristic signatures of nitrate

reduction. The concentrations of NO_3^- expected in these waters in the absence of denitrification, based on relationships with other physico-chemical parameters observed outside the suboxic zones, far exceed the sum of the observed NO_2^- and NO_3^- concentrations.⁶⁻⁸ As will be shown later, N_2O concentrations are also minimal at these depths, and so N_2 should be the dominant end product of denitrification. This is corroborated by recent measurements of the ratio between dissolved nitrogen and argon (N/Ar) that reveal up to 3 % excess of N_2 over the background values observed at comparable depths in the more oxygenated southern Arabian Sea.^{9&10}

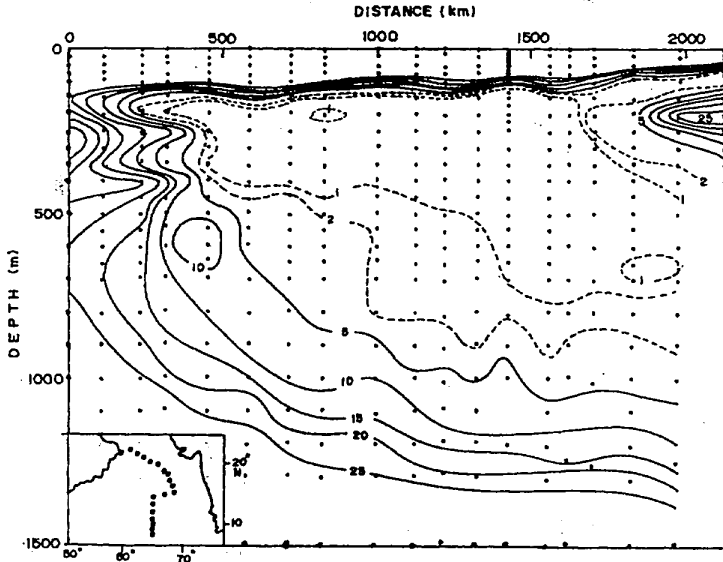


Figure 3. Colorimetrically-determined O_2 levels (μM) in the O_2 minimum of the Arabian Sea based on observations made by the author in collaboration with L.A. Codispoti during the US JGOFS Arabian Sea Process Study (RV Thompson, Cruise 39) along the transect shown in the inset.

As NO_2^- is regarded as a mandatory intermediate of denitrification, its distribution can be used to demarcate the geographical boundaries of denitrification zone (Fig. 5). As a first approximation, NO_2^- concentrations reflect the intensity of this process.¹¹ Counter intuitively the highest nitrite concentrations are found in the central parts of the Arabian Sea, while the highest photosynthetic production occurs close to the coast particularly within the three upwelling centres located off Somalia, Arabian and SW India.¹² This indicates that the zones of the most intense denitrification and the highest biological production are geographically separated, an observation which differentiates the Arabian Sea from the two other open ocean denitrifying sites.¹¹

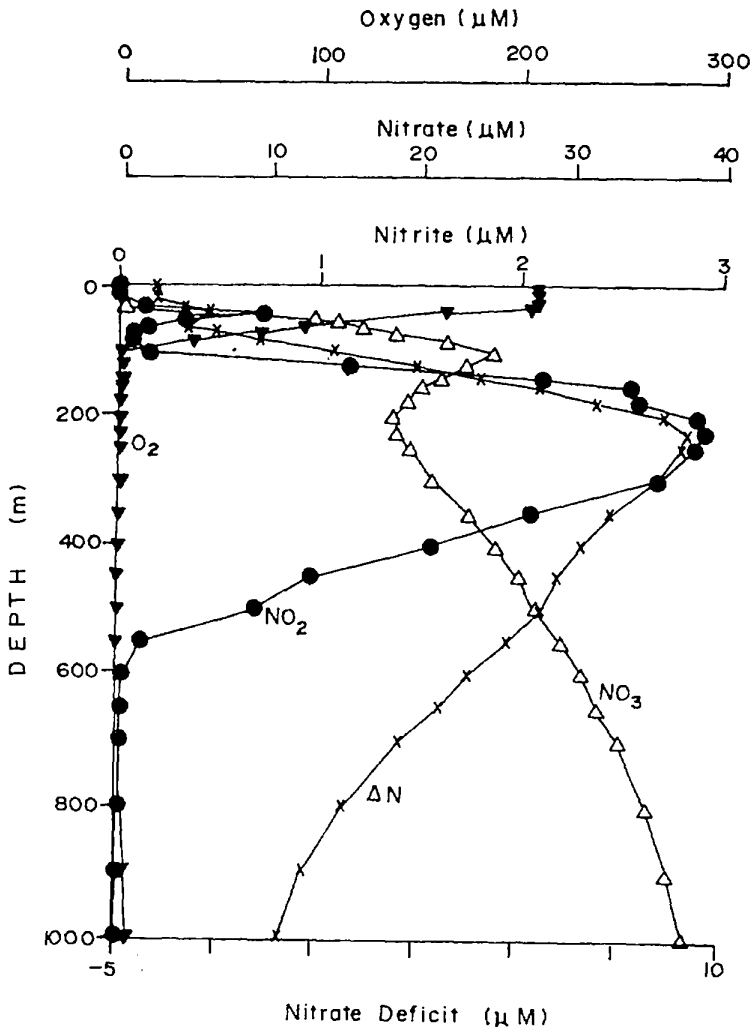


Figure 4. Vertical profiles of O_2 , NO_3^- , NO_2^- and NO^- deficit at the US JGOFS, Sta. N7 (19° N, 67° E, Thompson Cruise).³⁹

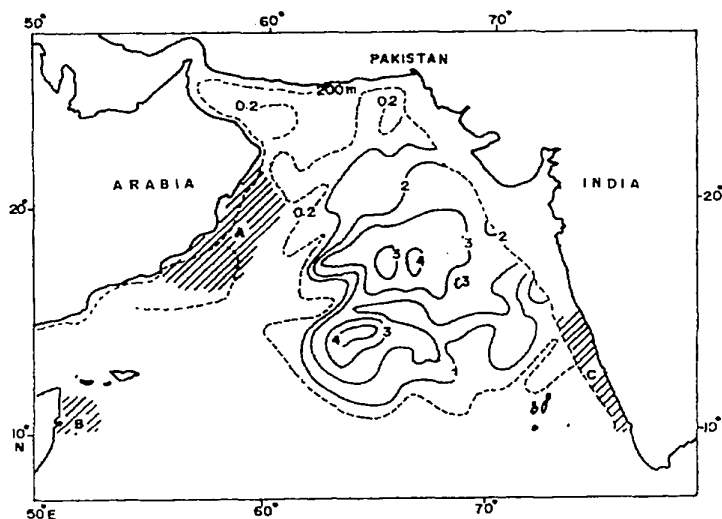


Figure 5. Distribution of NO_2^- (μM) within suboxic waters. The highest NO_2^- concentrations in historical data were averaged for each 1-degree square to construct this map. The hatched areas represent the upwelling zones off Arabia (a), Somalia (b) and southwest India (c).¹¹

2. DENITRIFICATION RATE

For the global budgeting of nitrogen, quantification of denitrification rate in the Arabian Sea is of vital importance. This has been done following three different approaches: physico-chemical, biochemical and isotopic. The physico-chemical approach involves an estimation of the amount of NO_3^- reduced beyond NO_2^- (NO_3^- deficit) by exploiting the remarkable constancy of the ratio between concomitant changes in O_2 and NO_3^- in seawater during photosynthesis/respiration¹³. Thus the property 'NO', defined as $\text{O}_2 + 9.1 \text{NO}_3^-$ ¹⁴ appears to behave conservatively outside the denitrification zone and bears a definite relationship with temperature. Assuming that any departure from this behaviour in suboxic waters results from denitrification, it is possible to compute NO_3^- deficits.^{15&16} A typical profile of NO_3^- deficit is included in Fig. 4. These deficits can then be combined either with dynamic computations and suitable diffusion constants¹⁷ or with Chlorofluorocarbon (CFC)-derived ages¹⁸ to calculate the denitrification rate. It ranges between 20 and 30 Tg N y^{-1} (1 $\text{Tg} = 10^{12}$ g). It will, however, be better to determine the amount of nitrogen produced rather than that of nitrate consumed. This can be done using the N/Ar ratio. As stated above, large increases in this

ratio occur within the suboxic zone. However, the amount of excess nitrogen estimated from N/Ar is substantially higher (by as much as a factor of 2) than the NO_3^- deficit.^{9&10} Regeneration of nitrogen from organic matter can only account for a part of this imbalance^{2&16} and so additional sources of N_2 such as sedimentary denitrification must exist in the region.¹⁰ Unfortunately, there is no information available on denitrification rate in the continental margin sediments. In any case, it appears that the estimates of denitrification rate in the Arabian Sea derived from NO_3^- deficits should be conservative.

The biochemical approach involves the activity of the respiratory Electron Transport System (ETS). In this method, the activity of the enzyme system that controls respiration is measured by extracting the enzyme from microplankton and incubating it with an electron acceptor and with the natural substrates of the enzyme system.¹⁹ However, the ETS method yields potential rate that is converted into denitrification rate using a suitable conversion factor obtained through culture experiments. These conversion factors suffer from considerable uncertainties; nevertheless, the rate obtained by this method ($24\text{--}33 \text{ Tg N y}^{-1}$) agrees quite well with that estimated from the physico-chemical technique.²⁰

Both of the methods described above are indirect. A more direct approach is based on the application of isotopic tracers. In this technique water samples spiked with N-15 labeled NO_3^- can be incubated for a few hours either on the deck or *in situ*. The change in isotopic composition of N_2 can then be determined from which the denitrification rate can be obtained. Alternately, the incubation can be carried out in the presence of acetylene which blocks the reduction sequence at the N_2O stage.²¹ The shift in isotopic composition of N_2O can provide rapid and precise estimation of the denitrification rate. However, these methods are still being developed and are yet to be applied on an adequate scale.

3. SOURCES OF CARBON TO SUBOXIC WATERS

As indicated earlier water column denitrification does not show a direct correspondence with the overhead primary production in the Arabian Sea. Such a decoupling is supported by enzymatic data as well. The ETS activity within the Oxygen Minimum Zone (OMZ) is generally higher in the oligotrophic central Arabian Sea than in the more productive waters near the continental margin.²⁰ Moreover, the ETS-based respiration rates are also too high to be supported by particulate organic matter sinking from the surface layer. For example, at an open ocean site, the data from where are shown in Fig. 6, the vertically integrated denitrification rate corresponds to a carbon demand of $95 \text{ g m}^{-2} \text{ y}^{-1}$. Against this the amount of carbon that can be made available through sedimentation of particles from the surface layer is only $8\text{--}26 \text{ g m}^{-2} \text{ y}^{-1}$.²⁰ Measurements of bacterial production also reveal a

similar discrepancy.²² Therefore, in addition to the vertical flux of sinking particles, there must be some other hitherto poorly-understood modes of input of organic matter to the OMZ.

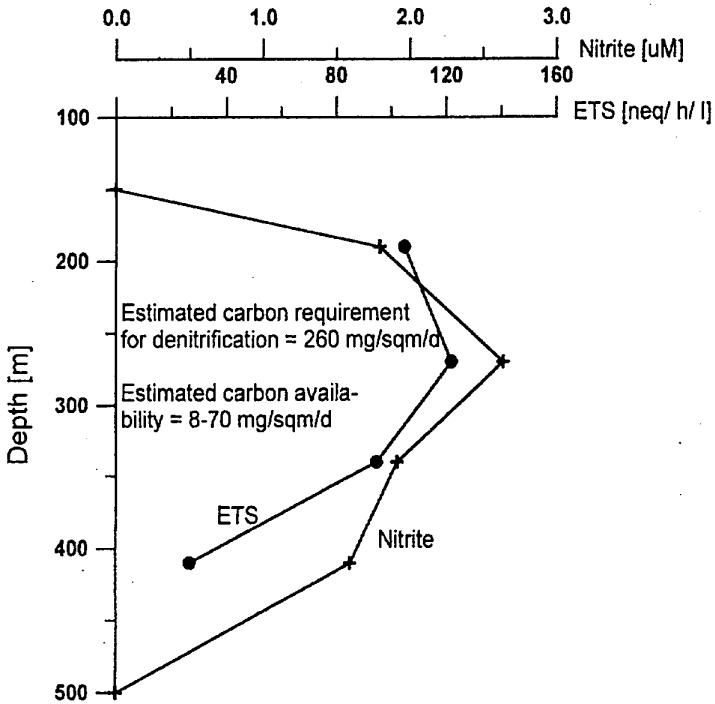


Figure 6. Vertical profiles of respiratory Electron Transport System (ETS) activity and NO_2^- at $19^\circ 30' \text{ N}$, 67° E (modified after [20]).

Both the bacterial biomass and ETS activity exhibit peak values within the denitrifying layer associated with maxima in particulate protein and beam attenuation (Figs. 7 and 8). The beam attenuation maximum (also referred to as the subsurface particle maximum and the intermediate nepheloid layer) is a characteristic feature of all denitrifying zones²³⁻²⁶; it is commonly accompanied by a bacterial biomass maximum.^{22,26 & 27} The excellent

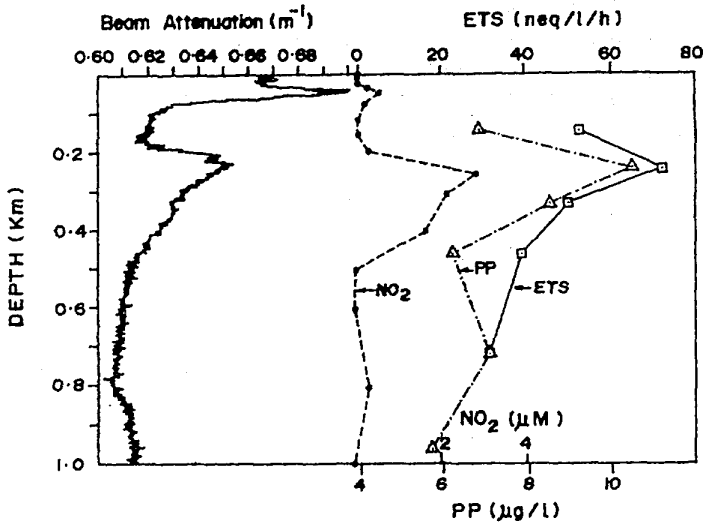


Figure 7. Vertical profiles of NO_2^- , ETS activity and Particulate Protein (PP) in relation to beam attenuation at $17^\circ 30' \text{ N}$, $67^\circ 30' \text{ E}$ (modified after [24]).

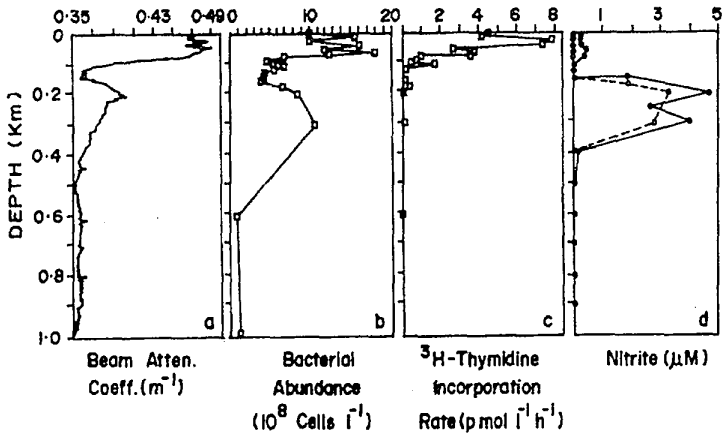


Figure 8. Vertical profiles of (a) beam attenuation coefficient, (b) bacterial abundance, (c) thymidine incorporation and (d) NO_2^- . The bacterial abundance data at the Charles Darwin Sta. 5 ($14^\circ 23' \text{ N}$, $66^\circ 53' \text{ E}$)²² NO_2^- data at the same station (open circles) are from²²; beam attenuation and NO_2^- (solid circles) data at the Sagar Sampada Sta. 2514 (15° N , 67° E).²⁴

correlation of the turbidity maximum with maxima in NO_2^- , ETS activity, particulate protein and bacterial biomass suggest a biological origin.^{24&26} What makes the bacteria proliferate under energetically less favourable conditions to such an extent that it results in a pronounced increase in water turbidity, and what is the source of carbon that sustains the observed high respiration rates are unresolved issues. There are two possible explanations: (a) Denitrifiers may efficiently utilise the dissolved organic matter supplied to the OMZ either quasi horizontally from the continental margins²⁸ or vertically through diurnal migrations of organisms particularly the mesopelagic fish such as myctophids.²⁹ The Arabian Sea is known to contain huge stocks (~100 million tonnes) of mesopelagic fish that are specially adapted to low (< 0.1 ml l⁻¹) ambient oxygen levels.³⁰ However, how such a large myctophid biomass is sustained is another major question concerning the Arabian Sea biogeochemistry that is yet to be satisfactorily answered. (b) There may be an additional carbon pool in the form of Transparent Exopolymer Particles (TEP) that could be formed from extracellular metabolites.³¹ The TEP levels within the OMZ (averaging around 10 mg equivalents of alginic acid l⁻¹) are apparently more than enough to support the bacterial activities. The relative importance of the above processes in maintaining high metabolic rates and the consequent reducing environment remains to be assessed.

4. NATURAL ISOTOPE ABUNDANCE

Some insights into the biogeochemical processes can be gained through studies of natural abundance of stable isotopes in various dissolved nitrogen species. The approach is based on the principle that all biological processes involve varying degrees of mass dependent isotopic fractionations.³² In the case of nitrogen, for example, the two major isotopes are ¹⁴N and ¹⁵N with ¹⁴N being much more abundant. During denitrification ¹⁴NO₃⁻ is more readily used up. Consequently, the remaining NO₃⁻ gets enriched with ¹⁵N while N₂, which is the end product of denitrification, is depleted in this isotope. An excellent example of this fractionation is provided by the ¹⁵N/¹⁴N data from the Arabian Sea³³; marked enrichment of ¹⁵N in NO₃⁻ and a corresponding depletion in N₂ are seen within the SNM (Fig. 9). These data can be used to compute the fractionation factor, $\epsilon_{\text{denit}} [=10^3(1-\alpha)]$, where $\alpha = ^{15}\text{N}/^{14}\text{N}$, during denitrification using simple advection-reaction and diffusion-reaction models.³³ In the first case, we ignore diffusion and the water mass is assumed to advect into the OMZ without undergoing any mixing in the vertical and horizontal directions. The isotopic distribution can then be modelled with a simple Rayleigh equation:

$$\delta \text{ } ^{15}\text{N-NO}_3 = 10^3(\alpha - 1) \ln f_{\text{NO}_3} \dots(1)$$

where $\delta^{15}\text{N-NO}_3^-$ is a measure of the $^{15}\text{N}/^{14}\text{N}$ ratio in NO_3^- relative to a standard (atmospheric N_2) and $f_{\text{NO}_3^-}$ is the ratio between the observed and expected NO_3^- concentrations. ϵ_{denit} can be obtained from the slope of the regression between $\delta^{15}\text{N-NO}_3^-$ and $\ln f_{\text{NO}_3^-}$. Using the data between 200 and 600 m at the stations shown in Fig. 9, a fractionation factor of 22 ‰ was obtained (Fig. 10).

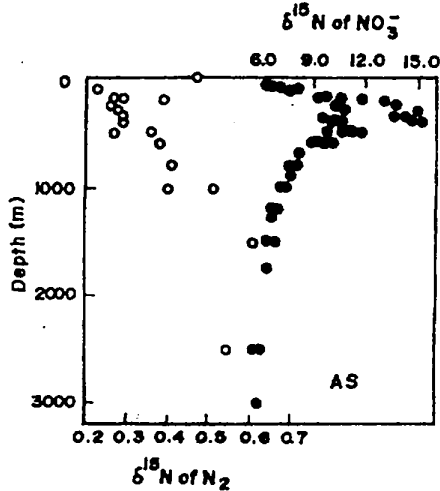


Figure 9. Nitrogen isotopic composition (expressed as ‰ $\delta^{15}\text{N}$ relative to atmospheric N_2) of NO_3^- (solid circles) and N_2 (open circles) plotted versus depth at three stations ($19^\circ\text{N}, 67^\circ\text{E}$; $19^\circ 45' \text{N}, 64^\circ 37' \text{E}$; and $17^\circ\text{N}, 68^\circ\text{E}$).³³

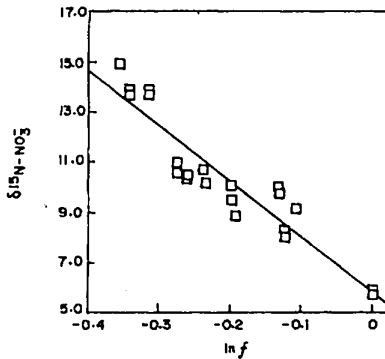


Figure 10. The $\delta^{15}\text{N}$ of NO_3^- (‰ relative to atmospheric N_2) vs. the natural log of f , the ratio of measured to expected nitrate concentrations. The line gives the least squares fit to the data).³³

The opposite extreme to the advection-reaction model is the reaction-diffusion model having no advective component. The reaction-diffusion equation is:

$$\partial [^{14}\text{NO}_3]/\partial t = J^{14}_{\text{NO}_3} + K_d \partial^2 [^{14}\text{NO}_3]/\partial x^2, \quad \dots(2)$$

where J is the denitrification rate and K_d the horizontal eddy diffusivity¹³ along the isopycnal; x increases from the edge to the centre of the denitrifying zone. For $^{15}\text{NO}_3$ the equation is:

$$\partial [^{15}\text{NO}_3]/\partial t = \alpha ([^{15}\text{NO}_3]/[^{14}\text{NO}_3])J^{14}_{\text{NO}_3} + K_d \partial^2 [^{15}\text{NO}_3]/\partial x^2 \quad \dots(3)$$

Because of the nonlinear nature of this equation, there is no exact analytical solution. The values of both ^{14}N and ^{15}N were calculated numerically using a tridiagonal matrix solution method. The boundary conditions were that the NO_3^- and $\delta^{15}\text{N}-\text{NO}_3$ compositions at $x=0$ were $28\mu\text{M}$ (NO_3^- deficit=0) and 6‰, respectively, and that there was no NO_3^- or isotopic flux out of the centre of the OMZ. Using suitable values of J and K_d , the best-fit to the data was obtained with a fractionation factor of 25‰ (Fig. 11).

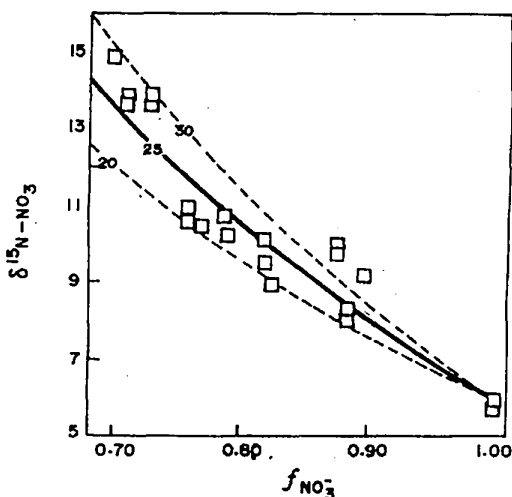


Figure 11. The $\delta^{15}\text{N}$ of NO_3 (‰ relative to atmospheric N_2) vs. f , the ratio of measured to expected nitrate concentrations. Also plotted are the diffusion-reaction model results with the numbers denoting fractionation factors.³³

These two models are either purely advective or purely diffusive. A more realistic model should include both mixing and advection. The difference between the two estimates is surprisingly small, however, and

the data from the eastern tropical North Pacific also yield very similar values.³³ This indicates that the fractionation factor is not strongly dependent on either the denitrification rate or the local hydrography of the region thereby justifying the application of ^{15}N for determining oceanic denitrification rates in the past.

A very important aspect of the data is a strong decrease in $\delta^{15}\text{N-NO}_3^-$ in near-surface waters (Fig. 9). At 200 m, for example, the value is $>10\text{‰}$ but declines to $\sim 6\text{‰}$ (close to the oceanic background) at 80 m. This trend is exactly opposite to that seen outside the OMZ.³⁴ The observed decrease can only result from an input of light nitrogen to the surface waters. The two possible sources are unaltered NO_3^- horizontally advected from outside the central Arabian Sea, and nitrogen fixation. The known pattern of water circulation in the Arabian Sea^{17&35} makes the first mechanism less likely, and so the most plausible source of isotopically light NO_3^- to the surface layer appears to be nitrogen fixation.

If NO_3^- from 200 m at 11 % is being upwelled to the surface, and all nitrogen is removed by primary producers at 70-80 m, one can estimate the amount of nitrogen reaching the surface ocean that originally came from nitrogen fixation. Assuming that the changes in isotopic composition below 80m are due to dilution by remineralised nitrogen fixed at 0‰, about 40 % of the NO_3^- present at 80 m originally came from nitrogen fixation. Using the data on primary productivity in this region this translates into a nitrogen fixation rate of up to 6 TgN y^{-1} or about 25 % of the denitrification rate.³³ Thus, in spite of a high rate of nitrogen fixation, the Arabian Sea still serves as a net sink of combined nitrogen. This is consistent with the data on N:P ratios.³⁶

5. NITROUS OXIDE CYCLING

Apart from nitrogen fixation and denitrification, the other important term in the nitrogen budget to which contribution from the Arabian Sea is very significant is the N_2O efflux to the atmosphere. N_2O is not only an important greenhouse gas, but it also contributes to the stratospheric ozone depletion. The rate of N_2O loss in the stratosphere through photolysis and reaction with the excited atomic oxygen [$\text{O}(^1\text{D})$], which should be equal to the natural flux of N_2O to the atmosphere from all sources, is about 12 $\text{Tg N}_2\text{O-N y}^{-1}$.³⁷ Of this at least half seems to come from the oceans.³⁸ But the N_2O efflux is not uniformly distributed over the oceanic surface with the eastern boundary environments underlain by low- O_2 waters making disproportionately large contributions.^{2&40} Large supersaturations of N_2O have been observed in the surface waters of the Arabian Sea especially in the three seasonal upwelling centres off Somalia, Oman and southwest India.^{39,41-44} Consequently, the atmospheric flux from this region alone could be as much as 0.5-1 $\text{Tg N}_2\text{O-N y}^{-1}$.³⁹ This is because N_2O cycling is greatly affected by the ambient O_2 levels in the low range ($< 0.5\text{ml l}^{-1}$). It

accumulates in high concentrations when the O_2 levels approach but do not reach suboxia; however, in strongly reducing environments such as those found within the core of the denitrifying zone, N_2O is itself reduced to N_2 by bacteria

(Fig. 12). Thus the Arabian Sea contains sites located very close to each other, vertically as well as horizontally, that serve both as strong sources and strong sinks of N_2O leading to a turnover which may be most rapid on our planet.^{42&45}

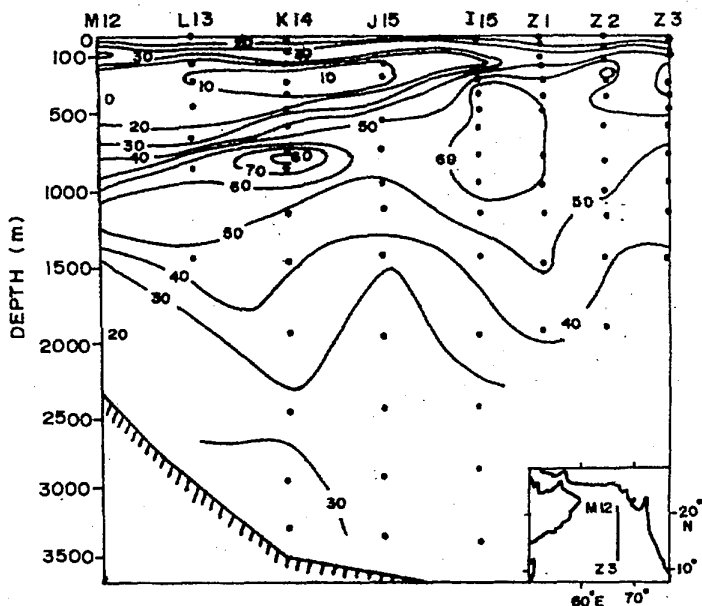


Figure 12: A meridional section (along $67^\circ E$ - inset) showing the distribution of N_2O (nM).⁴²

Why does such an intense accumulation of N_2O occur in the low- O_2 zones is an issue that has not been fully resolved so far. This is because N_2O is an intermediate of both the oxidative and reductive sequences of the nitrogen cycle and can be produced both during nitrification and denitrification (Fig. 1). The two pathways leave very different isotopic signatures: N_2O produced during denitrification is enriched with ^{15}N and ^{18}O while that formed during nitrification is depleted in these isotopes.^{32,46&47} Hence, measurements of the $^{15}N/^{14}N$ and $^{18}O/^{16}O$ ratios in N_2O dissolved in seawater can provide insights into the mechanisms of its transformations. However, while substantial data have now been generated on the nitrogen and oxygen isotopic composition of N_2O in seawater, there still remains considerable

disagreement in the literature as to the dominant pathway of N_2O production.^{48&49} The Arabian Sea contains several diverse biogeochemical environments and offers the most extreme conditions for N_2O cycling.⁵⁰ The isotopic composition of N_2O in this region may therefore be helpful in improving the understanding of its transformations.

Measurements of $^{15}N/^{14}N$ and $^{18}O/^{16}O$ in N_2O have been made recently in the surface waters of the Arabian Sea which showed a wide range of N_2O supersaturations some of which (in the upwelling zone off southwest India) are among the highest observed in the oceans.⁴⁴ These are reproduced in Fig. 13. The $\delta^{15}N$ and per cent saturation appear to be negatively correlated, with N_2O in the upwelled waters off southwest India being the most depleted in ^{15}N . Although these $\delta^{15}N$ values are the lowest ever reported for seawater also substantially lower than the $\delta^{15}N$ of tropospheric N_2O (7 ‰)⁴⁹, these are much higher than the expected $\delta^{15}N$ of N_2O produced through nitrification.⁴⁶ By contrast, $\delta^{18}O$ does not exhibit a discernible relationship with per cent saturation, and with the exception of one sample, all $\delta^{18}O$ values are consistently higher than the $\delta^{18}O$ of tropospheric N_2O (20.7 ‰).⁴⁹

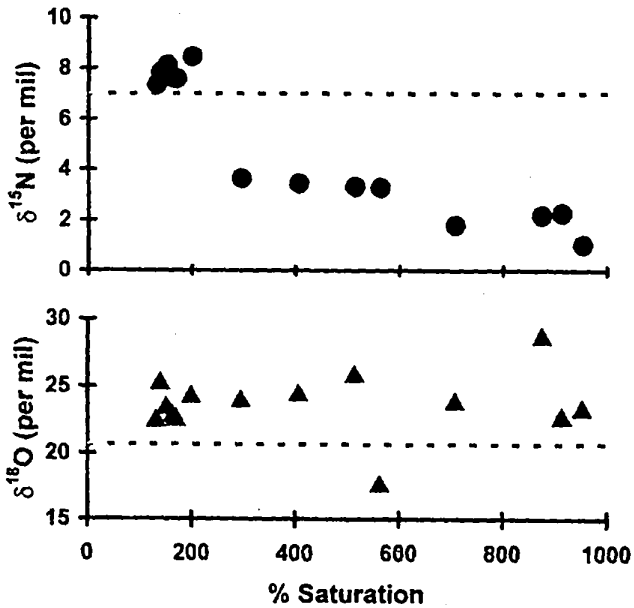


Figure 13. Nitrogen and oxygen isotopic composition of N_2O vs. % saturation at the sea surface (depth < 5 m). Horizontal dashed lines indicate the composition of N_2O in marine air.⁵¹ Values with moderate saturation and $\delta^{15}N$ close to the tropospheric value are from the northern Arabian Sea; all other data are from the coastal upwelling zone off SW India (from Naqvi et al., 1998).

Vertical profiles of the isotopic ratios at two stations in the central Arabian Sea are shown in Fig. 14. One of these (SS 3201) was located within the zone of intense denitrification while the other (SS 3204) was situated at its periphery. The N_2O minimum observed at 200-500 m at SS 3201 coincided with an intense SNM and a pronounced peak of $\delta^{15}N-NO_3^-$. Preferential loss of lighter N_2O to N_2 within this layer evidently led to enrichments of ^{15}N and ^{18}O in residual N_2O which are by far the greatest reported from any natural environment.⁴⁴ The N_2O concentration minimum was embedded

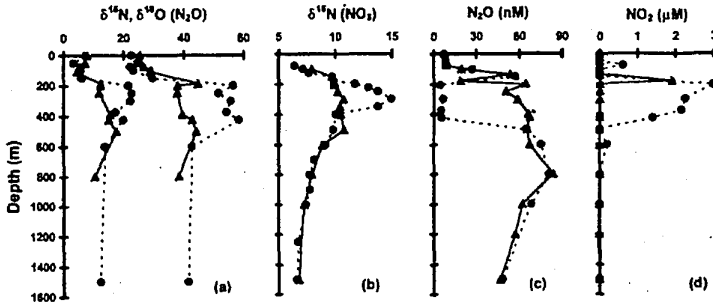


Figure 14. Vertical profiles of $\delta^{15}N$ and $\delta^{18}O$ (‰ relative to air) in N_2O (a), $\delta^{15}N$ in NO_3^- (b) and concentrations of N_2O (c) and NO_2^- (d) at Sagar Sampada Stas. SS 3201 (17°N, 68°E; circles joined by dotted lines) and SS 3204 (19.75°N, 64.62°E; triangles, joined by continuous lines). Both stations experienced suboxic conditions ($O_2 < 5 \mu M$) at ca. 150-800 m.⁴⁴

between two maxima, but the isotopic compositions of these N_2O -rich layers were very different. Going upward from the OMZ, the $\delta^{15}N$ and $\delta^{18}O$ values fell sharply across the oxic-suboxic boundary with the former generally lower than the tropospheric value in the upper 150 m. In contrast, although $\delta^{15}N$ and $\delta^{18}O$ also decreased below SNM, their levels remained much higher than the tropospheric values down to 1500 m. Similar pattern was also seen at the mildly reducing SS 3204 although the $\delta^{15}N$ and $\delta^{18}O$ increases within OMZ were smaller. An important aspect of the data is that the $\delta^{15}N$ of NO_3^- is consistently lower than that of N_2O at depths exceeding ~200 m, and higher at shallower depths at both stations (Fig. 14). This indicates that the intense N_2O accumulation in the upper and lower parts of the OMZ may be through different mechanisms. Greater enrichment of $\delta^{15}N$ in N_2O relative to NO_3^- appears to be characteristic of denitrification as revealed by recent culture experiments (M.A. Altabet, unpublished data). This pattern is the most pronounced within N_2O -depleted SNM at SS 3201. Its persistence even below SNM at SS 3201 and at depths exceeding ~200 m at SS 3204 suggests significant N_2O production through denitrification.

This observation is consistent with the view that denitrification may lead to a net N_2O accumulation under certain conditions.⁵¹

While the isotopically lighter N_2O in waters above the suboxic zone is apparently not produced by denitrification, classical nitrification pathway ($NH_4^+ \rightarrow NO_2^- \rightarrow N_2O$) also cannot fully explain the observed data for two reasons. First, the $\delta^{15}N$ values are much higher than that reported for denitrification.⁴⁶ Secondly, the observed $\delta^{18}O$ is much higher than the value for nitrification (< -3 ‰) expected from $\delta^{18}O$ of H_2O and O_2 .⁴⁷ A more likely pathway of N_2O production in the upper layer which can account for both the isotope and concentration data is a nitrification-denitrification coupling ($NH_4^+ \rightarrow NH_2OH \rightarrow NO \rightarrow N_2O$).⁵²

The isotopic data from the Arabian Sea also have an important implication for the atmospheric N_2O budget. Analysis of stratospheric N_2O has shown⁵⁴ large enrichments of heavier isotopes ($\delta^{15}N$ and $\delta^{18}O$ values of ~ 21 and 35 ‰, respectively). It is believed that the resultant fluxes of ^{15}N and ^{18}O (400 and 500 TgN ‰ y^{-1} , respectively) to the troposphere are balanced largely through exchange with the ocean where isotopically light N_2O may be produced by nitrifying bacteria.^{37&53} However, the opposing trends in ^{15}N and ^{18}O and modest departures from tropospheric isotopic composition observed in the surface waters of the Arabian Sea clearly indicate that the ocean-atmosphere exchange cannot counter inputs of heavier isotopes (particularly ^{18}O) associated with the stratospheric back flux, calling for additional sources and/or sinks of N_2O in the atmosphere.⁴⁴

6. TEMPORAL CHANGES IN THE ARABIAN SEA DENITRIFICATION REGIME

The traditional view about the Arabian Sea O_2 deficiency has been that it results from a combination of stagnation of intermediate waters, brought about by the semi-enclosed nature of the basin, and high biological productivity facilitated by nutrient enrichment through upwelling, vertical mixing and winter cooling.⁵⁴⁻⁵⁶ However, it was pointed out by Swallow⁵⁷ that a long renewal time of intermediate waters cannot explain the salinity distribution, and that the renewal should instead be fairly rapid. Subsequent studies utilizing chemical tracers have provided observational support to this view, yielding estimates of renewal time ranging from ~ 1 to 10 yr.^{17,20,35& 58} An important consequence of the quick renewal is that it leads to substantial changes in the suboxic environment on both seasonal and interannual time scales^{16&45} in response to the monsoon-related changes in water circulation and biological production. This short-term variability makes the Arabian Sea vulnerable to human interference.

Variability in the mid-depth redox conditions is also expected to occur on longer (geological) time scales driven by both global and regional changes in climate and circulation. These changes can be inferred from sedimentary records of $^{15}\text{N}/^{14}\text{N}$. It has been shown earlier that denitrification produces a pool of ^{15}N enriched NO_3^- . As the water upwells to the surface this NO_3^- is used up by phytoplankton. And while nitrogen fixation does lead to some dilution with the lighter nitrogen in near surface waters, the analysis of sediment trap material shows that sinking organic matter is still much more enriched with ^{15}N than in other parts of the ocean Table II.⁵⁹

Table II: $^{15}\text{N}/^{14}\text{N}$ Ratio in Sinking Organic Matter⁵⁹

Site	Depth (m)	$\delta^{15}\text{N}$ (‰)		$\delta^{15}\text{N}$ (‰) Sediment
		Setting Particles Range	Mean	
Bay of Bengal				
Northern	1700-2100	3.0-4.6	3.5	7.4
Central	2300	2.0-6.2	4.2	7.7
Southern	3000	3.8-5.9		
Arabian Sea				
Western	3000	5.3-8.8	7.1	9.2
Central	2300-3100	6.3-8.7	7.4	11.0
Eastern	2800-2900	4.7-8.0	5.9	9.7
Lofoten Basin	3000	2.7-8.8	4.2	
Sargasso Sea	3200	0.1-2.8	1.2	

The isotopic composition of nitrogen in the sediments is thus expected to reflect the intensity of denitrification at the time the sediments were deposited. A record of $\delta^{15}\text{N}$ covering the past 450,000 years has been generated by Altabet *et al.*⁶⁰ from a deep sea core collected from the western Arabian Sea (Fig. 15). The modern or core-top $\delta^{15}\text{N}$ values are among the highest observed in the core indicating that denitrification in the Arabian Sea has been the most intense during the Holocene. By contrast, lighter isotopic values occur in sediments that accumulated during the last glacial maximum (approximately 20,000 years ago) and indeed during all glacial stages. These values are typical of non reducing environments in today's ocean. This implies that the water column denitrification was either absent or it was much weaker during glacial times. A spectral analysis of the record showed a high degree of cyclicity associated with the three Milankowitch bands of 100,000, 41,000 and 23,000 years frequency. The association with the 23,000 year precessional band which dominantly regulates the monsoon strength is particularly strong.

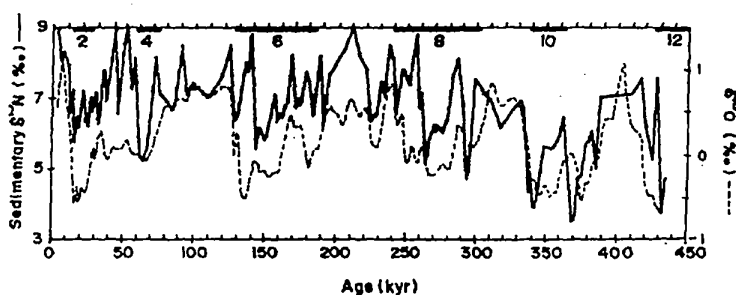


Figure 15. Downcore profiles of isotopic composition of nitrogen in organic matter and oxygen in the shells of planktonic foraminifera in RC27-61 raised from the Owen Ridge (16°39.5 'N, 59°31.4 'E). The solid bars at the top of the figure marked by even numbers represent cold oxygen isotope stages (modified from ref. [51]).

Thus the sedimentary record supports the view that large changes in denitrification intensity were associated with climatic cycles resulting in cyclic fluctuations in the oceanic combined nitrogen balance. The latter are not only necessary for keeping the oceanic combined nitrogen inventory constant over extended time periods but probably also played an important role in modulating the climatic cycles through controls on atmospheric carbon dioxide.^{5&60}

7. CONCLUDING REMARKS AND RECOMMENDATIONS FOR FUTURE WORK

It is obvious that while substantial progress has been made towards understanding complex transformations within the Arabian Sea suboxic zone, which make the biogeochemical cycling in this region globally significant, a great deal of work still remains to be done. There are several important unresolved problems, alluded to above, which need to be addressed by future research. One of these is the poorly-constrained carbon budget in the OMZ. The greatest uncertainty in this budget is perhaps due to the unknown fluxes associated with the diurnal migrations of organisms particularly the mesopelagic fish. Detailed studies on the distribution and behaviour of these animals and their role in carbon and nitrogen cycling must be initiated. Another aspect of biological research, that is extremely relevant in the context of the Arabian Sea but has attracted little attention so far, is the microbiology of the suboxic ecosystem. For example, we have presently no idea about the composition of the large bacterial biomass. Also, while these organisms apparently bring about extremely large changes in chemical fluxes in response to minor changes in ambient environmental conditions (particularly O₂ levels), the mechanisms of this response is not known. These aspects should be

investigated using modern immunological and molecular techniques.⁶¹ Enzymatic work must also be expanded both in terms of scope and spatial and temporal coverage.

Limited isotopic studies carried out so far have yielded some very intriguing results, but the full potential of this approach is yet to be realized. Additional data on natural isotope abundance, including those species which have not been investigated so far (such as NH_4^+ and NO_2^-), should be obtained. These should be supplemented with experimental work (e.g., incubations studies using suitable tracers and inhibitors) in order to gain insights into the mechanisms of biogeochemical transformations and for constraining their rates. In particular, the extent of nitrogen fixation in this area needs to be more precisely quantified.

Another poorly-understood aspect of biogeochemical research in this region is the role of continental margins in influencing carbon-nitrogen cycling in the open ocean. A quantitative assessment of this role requires several concomitant interdisciplinary measurements in the water column and sediments. Hydrographic work must be supplemented by the deployment of sediment traps and benthic chambers for quantifying particulate fluxes to the seafloor, benthic mineralisation and exchanges across the sediment-water interface. Also, a good time series of the physical, biological and chemical changes in both the coastal zone and open ocean must be initiated.

The ultimate goal of future research should be the development of realistic models for the region. At present we only have limited budget models. The next step should be to develop process models and finally system models. It is only after we have good biogeochemical models by integrating physical, chemical and biological data that we will be able to predict the response of the suboxic ecosystem to potential anthropogenic perturbations. This must be given a high priority because the suboxic Arabian Sea is a zone with extremely delicate biogeochemical balance and hence it is expected to be among the first to react to global change that could affect the living resources of the region.

REFERENCES

1. L.A. Codispoti, (1989). Phosphorus vs. nitrogen limitation of new (export) production. In: *Productivity of the ocean: present and past* (Eds. W. Berger, et al.), John Wiley and Sons, New York, pp. 377.
2. L.A. Codispoti, and J.P. Christensen (1985). Nitrification, denitrification and nitrous oxide cycling in the eastern tropical South Pacific Ocean, *Mar. Chem.*, **16**, pp 277.
3. L.A. Codispoti, A. Devol, A. Minas, H. Paerl, S.W.A. Naqvi, J. Christensen, P. Becker, and T. Yoshinari (1996). A revised oceanic combined nitrogen budget and its implications for exchange of carbon dioxide between the atmosphere and ocean. *Carib. J. Sci.*, **32**, pp. 284.

4. A. Hattori, (1983). Denitrification and dissimilatory nitrate reduction. In: *Nitrogen in the Marine Environment* (Eds. Carpenter, E.G. and D.G. Capone), Academic Press, New York, pp. 191.
5. M.B. McElroy, (1983). Marine biological controls of atmospheric CO₂ and climate. *Nature*, **302**, pp. 328.
6. S.W.A. Naqvi, (1994). Denitrification processes in the Arabian Sea. *Proc. Indian Acad. Sci. (Earth & Planet. Sci.)*, **103**, pp. 279.
7. R. Sen Gupta, M.D. Rajagopal and S.Z. Qasim (1976). Relationships between dissolved oxygen and nutrients in the north-western Indian Ocean. *Indian J. Mar. Sci.*, **5**, pp. 201.
8. W.G. Deuser, E.H. Ross and Z.J. Mlodzinska (1978). Evidence for and rate of denitrification in the Arabian Sea. *Deep-Sea Res.*, **25**, pp. 431.
9. A.H. Devol, J.A. Brandes, T. Yoshinari and S.W.A. Naqvi (1996). Denitrification in the Arabian Sea as evidenced by water column N:Ar ratio. *EOS - Trans. Amer. Geophys. Union.*, **76**, OS2.
10. S.W.A. Naqvi, and A.H. Devol (1996). Sedimentary denitrification in the northwestern Indian Ocean. Abstract TO-18, *The Role of Ocean in Global Change Research*, The Oceanography Society, Amsterdam.
11. S.W.A. Naqvi, (1991). Geographical extent of denitrification in the Arabian Sea in relation to some physical processes. *Oceanolog. Acta.*, **14**, pp. 281.
12. S.Z. Qasim, (1977). Biological productivity of the Indian Ocean. *Indian J. Mar. Sci.*, **6**, pp. 122.
13. A.C. Redfield, B.H. Ketchum and F.A. Richards (1963). The influence of organisms on the composition of seawater. In: *The Sea*, (Ed. M.N.Hill), Interscience, New York, **2** pp. 26.
14. W.S. Broecker, (1974). 'NO', a conservative water mass tracer. *Earth Planet. Sci. Lett.*, **23**, pp. 100.
15. S.W.A. Naqvi and R. Sen Gupta (1985). 'NO', a useful tool for the estimation of nitrate deficits in the Arabian Sea. *Deep-Sea Res.*, **32**, pp. 665.
16. S.W.A. Naqvi, R.J. Noronha, K. Somasundar and R. Sen Gupta (1990). Seasonal changes in the denitrification regime of the Arabian Sea. *Deep-Sea Res.*, **37**, pp. 693.
17. S.W.A. Naqvi, (1987). Some aspects of the oxygen-deficient conditions and denitrification in the Arabian Sea. *J. Mar. Res.*, **49**, pp. 1049.
18. E.A. Howell, S.C. Doney, R.A. Fine and D.B. Olson (1997). Geochemical estimates of denitrification in the Arabian Sea and the Bay of Bengal during WOCE. *Geophys. Res. Lett.*, **24**, pp. 2549.
19. L.A. Codispoti, and T.T. Packard (1980). Denitrification rates in the eastern tropical South Pacific. *J. Mar. Res.*, **38**, pp. 453.
20. S.W.A. Naqvi, and M.S. Shailaja (1993). Activity of the respiratory electron transport system and respiration rates within the oxygen minimum layer of the Arabian Sea. *Deep-Sea Res. II*, **40**, pp. 687.
21. T. Yoshinari and R. Knowles (1976). Acetylene inhibition of nitrous oxide reduction by denitrifying bacteria. *Biochem. Biophys. Res. Comm.*, **69**, pp. 705.
22. H.W. Ducklow, (1993). Bacterioplankton distributions and production in the north-western Indian Ocean and Gulf of Oman, September 1986. *Deep-Sea Res. II*, **40**, pp. 753.

23. P.C. Garfield, T.T. Packard, G.E. Friederich and L.A. Codispoti (1983). A subsurface particle maximum layer and enhanced microbial activity in the secondary nitrite maximum of the northeastern tropical Pacific Ocean. *J. Mar. Res.*, **41**, pp. 747.
24. S.W.A. Naqvi, M. Dileep Kumar, P.V. Narvekar, S.N. de Sousa, M.D. George and C. D' Silva (1993). An intermediate nepheloid layer associated with high microbial metabolic rates and denitrification in the northwest Indian Ocean. *J. Geophys. Res.*, **98**, pp. 16469.
25. H. Pak, L.A. Codispoti and J.R.V. Zaneveld (1980). On the intermediate particle maxima associated with oxygen-poor water off western South America. *Deep-Sea Res.*, **27**, pp. 783.
26. R.W. Spinrad, H. Glover, B.B. Ward, L.A. Codispoti and G. Kullenberg (1989). Suspended particle and bacterial maxima in Peruvian coastal waters during a cold water anomaly. *Deep-Sea Res.*, **36**, pp. 715.
27. B.B. Ward, M.E. Hogan, S.W.A. Naqvi and A. Jayakumar (1998). Distribution of bacteria, particles and denitrification parameters in water of the oxygen minimum zone in the Arabian Sea. *EOS - Trans. Amer. Geophys. Union.*, **79**, OS83.
28. B.L.K. Somayajulu, M.M. Sarin and R. Ramesh (1996). Denitrification in the eastern Arabian Sea: evaluation of the role of continental margins using Ra isotopes. *Deep-Sea Res. II*, **43**, pp. 111.
29. K. Banse, (1994). On the coupling of hydrography, phytoplankton, zooplankton, and settling organic particles offshore in the Arabian Sea. *Proc. Indian Acad. Sci. (Earth Planet. Sci.)*, **103**, pp. 125.
30. US GLOBEC, (1993). Implementation Plan and Workshop Report for U.S. GLOBEC Studies in the Arabian Sea, Report No. 9, US GLOBEC Office, University of California, Davis, 105.
31. M.D. Kumar, V.V.S.S. Sarma, N. Ramaiah, M. Gauns and S.N. de Sousa (1998) Biogeochemical significance of transparent exopolymer particles in the Indian Ocean. *Geophys. Res. Lett.*, **25**, pp. 81.
32. E. Wada and A. Hattori (1991). *Nitrogen in the Sea: Forms, Abundances and Rate Processes*, CRC Press, Boca Raton, 208.
33. J.A. Brandes, A.H. Devol, D.A. Jayakumar, T. Yoshinari and S.W.A. Naqvi. Isotopic composition of nitrate in the central Arabian sea and eastern tropical north Pacific: A tracer for mixing and nitrogen cycles *Limnol. Oceanogr.* (in press).
34. D.M. Sigman, M.A. Altabet, R. Michener, D.C. McCorkle, B. Fry and R.M. Holmes (1997). Natural abundance-level measurement of the nitrogen isotopic composition of oceanic nitrate: an adaptation of the ammonia diffusion method. *Mar. Chem.*, **57**, pp. 227.
35. D.B. Olson, G.L. Hitchcock, R.A. Fine and B.A. Warren (1993). Maintenance of the low- oxygen layer in the Arabian Sea. *Deep-Sea Res. II.*, **40**, pp. 673.
36. L.A. Codispoti, (1997). The limits to growth. *Nature*, **387**, pp. 237.
37. M.B. McElroy, and D.B. Jones (1996). Evidence for an additional source of atmospheric N₂O. *Global. Biogeochem. Cycles.*, **10**, pp. 651.
38. H.W. Bange, S. Rapsomanikis and M.O. Andreae (1996). Nitrous oxide in coastal waters. *Global Biogeochem. Cycles*, **10**, pp. 197.
39. H.W. Bange, S. Rapsomanikis and M.O. Andreae (1996). Nitrous oxide emissions from the Arabian Sea. *Geophys. Res. Lett.*, **23**, pp. 3175.

40. L.A. Codispoti, J.W. Elkins, T. Yoshinari, G.E. Friederich, C.M. Sakamoto and T.T. Packard (1992). On the nitrous oxide flux from productive regions that contain low oxygen waters. In: *Oceanography of the Indian Ocean* (Ed. B.N. Desai), Oxford-IBH, New Delhi, pp. 271.
41. C.S. Law, and N.J.P. Owens (1990). Significant flux of atmospheric nitrous oxide from the northwestern Indian Ocean. *Nature*, **346**, pp. 826.
42. S.W.A. Naqvi, and R.J. Noronha (1991). Nitrous oxide in the Arabian Sea. *Deep-Sea Res.*, **38**, pp. 871.
43. H.P.J. de Wilde and W. Helder (1997). Nitrous oxide in the Somali Basin: the role of upwelling. *Deep-Sea Res.* **II 44**, pp. 1319.
44. S.W.A. Naqvi, T. Yoshinari, D.A. Jayakumar, M.A. Altabet, P.V. Narvekar, A.H. Devol, J.A. Brandes and L.A. Codispoti (1998). Budgetary and biogeochemical implications of N_2O isotope signatures in the Arabian Sea. *Nature*, **394**, pp. 492.
45. S.W.A. Naqvi, T. Yoshinari, M.A. Altabet, D.A. Jayakumar, P.V. Narvekar and L.A. Codispoti (1996). Variability of redox conditions in intermediate waters of the Arabian Sea: Effect on nitrous oxide cycling. *EOS - Trans. Amer. Geophys. Union*, **76**, OS2
46. N. Yoshida, (1988). ^{15}N -depleted N_2O as a product of nitrification. *Nature*, **335**, pp. 528.
47. T. Yoshinari, M.A. Altabet, S.W.A. Naqvi, L. Codispoti, A. Jayakumar, M. Kuhland and A. Devol (1997) Nitrogen and oxygen isotopic composition of N_2O from suboxic waters of the eastern tropical North Pacific and the Arabian Sea - measurement by continuous-flow isotope ratio monitoring. *Mar. Chem.*, **56**, pp. 253.
48. N. Yoshida, H. Morimoto, M. Hirano, I. Koike, S. Matsuo, E. Wada, T. Saino and A. Hattori (1989). Nitrification rates and ^{15}N abundances of N_2O and NO_3^- in the western North Pacific. *Nature*, **342**, pp. 895.
49. K.R. Kim and H. Craig (1990). Two isotope characterisation of N_2O in the Pacific Ocean and constraints on its origin in deep water. *Nature*, **347**, pp. 58.
50. P.H. Burkill, R.F.C. Mantoura and N.J.P. Owens (1993). Biogeochemical cycling in the northwestern Indian Ocean: a brief overview. *Deep-Sea Res. II*, **40**, pp. 643.
51. M.R. Betlach and J.M. Tiedje (1981). Kinetic explanation for accumulation of nitrite, nitric oxide and nitrous oxide during bacterial denitrification. *Appl. Environ. Microbiol.*, **42**, pp. 1074.
52. S.W.A. Naqvi, (1991). N_2O production in the ocean. *Nature*, **349**, pp. 373.
53. K.R. Kim and H. Craig (1993). Nitrogen-15 and oxygen-18 characteristics of nitrous oxide: a global perspective. *Science*, **262**, pp. 1855.
54. K. Wyrski, (1973). *Physical Oceanography of the Indian Ocean*. In: *The Biology of the Indian Ocean* (Ed. B. Zeitzschel), Springer-Verlag, Berlin, pp. 18.
55. S.Z. Qasim, (1982). Oceanography of the northern Arabian Sea. *Deep-Sea Res.*, **29**, pp. 1041.
56. R. Sen Gupta and S.W.A. Naqvi (1984). Chemical oceanography of the Indian Ocean, north of the equator. *Deep-Sea Res.*, **31**, pp. 671.
57. J.C. Swallow, (1984). Some aspects of the physical oceanography of the Indian Ocean. *Deep-Sea Res.*, **31**, pp. 639.
58. K. Somasundar and S.W.A. Naqvi (1988). On the renewal of the denitrifying layer in the Arabian Sea. *Oceanolog. Acta*, **11**, pp. 167.

59. P. Schafer and V. Ittekkot (1995). Isotope biogeochemistry of nitrogen in the northern Indian Ocean. *Mitt. Geol.-Palaont. Inst. Univ. Hamburg*, **78**, pp.67.
60. M.A. Altabet, R. Francois, D.W. Murray and W.L. Prell (1995). Climate-related variations in denitrification in the Arabian Sea from sediment $^{15}\text{N}/^{14}\text{N}$ ratios. *Nature*, **373**, pp. 506.
61. B.B. Ward, (1996). Nitrification and denitrification: probing the nitrogen cycle in aquatic environments. *Microb. Ecol.*, **32**, pp. 247.
62. P.M. Saager, H.J.W. De Baar and R.J. Howland (1992). Cd, Zn, Ni and Cu in the Indian Ocean. *Deep-Sea Res.*, **39**, pp. 9.