6. Natural Abundance of Stable Isotopes in some
Dissolved Nitrogen Species

6.1. Introduction:

Considerable amount of work on nitrogen cycling in suboxic waters of the Arabian Sea, carried out over the past two decades, has established it to be globally significant (Naqvi, 1994). However, these studies largely involved chemical and, to a lesser extent, biochemical measurements. Investigations on the natural abundance of stable isotopes in various dissolved nitrogen species is based on the fact that the biogeochemical processes involve characteristic mass-dependent discriminations between various isotopes. The isotopic data can provide useful insights into the pathways of nitrogen transformations (Wada and Hattori, 1991).

Abundance of $^{15}$N in various components of the biosphere varies typically within 1 or 2% of the atmospheric $N_2$ (Junk and Svec, 1958). Although this difference arising from isotopic discrimination is small it can be measured precisely using suitable instrumentation. These differences in the isotopic composition has been used to identify different sources by estimating relative contribution from two immediate sources of N to a common sink and also to delineate the mechanism of a metabolic process by studying the isotopic discrimination associated with it. The results of the measurements of isotopic composition of N in $N_2$ and $NO_3^-$, and N and O in $N_2O$ from the low oxygen environments of the Arabian Sea is presented below. The samples for these analyses were collected from the stations shown in Fig.6.1.
Results and Discussion

6.2. Nitrogen isotopic fractionation during denitrification:

The reduction of $\text{NO}_3^-$ to $\text{N}_2$ by denitrifying bacteria is believed to occur through the pathway (Payne, 1973):

$$\text{NO}_3^- \rightarrow \text{NO}_2^- \rightarrow \text{NO} \rightarrow \text{N}_2\text{O} \rightarrow \text{N}_2$$  \hspace{1cm} (6.1)

Nitrite ($\text{NO}_2^-$), the first intermediate of this reduction sequence, accumulates in the oceanic suboxic zones (Richards, 1965). In the Arabian Sea, as in the eastern tropical Pacific Ocean (Cline and Richards, 1972), the secondary nitrite maximum (SNM), located in the upper portion of the oxygen minimum zone (OMZ), is invariably associated with $\text{O}_2 < 0.1 \text{ ml l}^{-1}$, in contrast to the primary $\text{NO}_2^-$ maximum commonly found at the base of the euphotic zone. Precise $\text{O}_2$ measurements carried out during a U.S. JGOFS cruise in the Arabian Sea revealed that the threshold $\text{O}_2$ levels required for the $\text{NO}_2^-$ build-up lie between 0.01 and 0.02 ml l$^{-1}$ (S W A Naqvi and L A Codispoti, unpublished data). Dramatic changes in water chemistry are seen once this threshold is crossed. An
apparent spurt in denitrification activity causes a minimum in the vertical profile of NO$_3^-$ (Fig.6.2). Interestingly, while NO$_2^-$ accumulates under these conditions, N$_2$O, the other major intermediate, shows an opposite trend (e.g., Figs. 6.2 and 6.3), indicating that the reduction of NO$_2^-$ may be the rate limiting step. These microbially-mediated

![Graph 1](image1.png)

![Graph 2](image2.png)

Fig.6.2. Vertical profiles of (a) $\delta^{15}$N of N$_2$ ($^\circ$/oo relative to air) and (b) concentrations of NO$_3^-$ (µM), NO$_2^-$ (µM) and N$_2$O (nM) at Sta. 3448/SS141.

transformations leave a strong imprint on the isotopic composition of dissolved nitrogen species. This is because, of the two nitrogen isotopes with mass numbers of 14 and 15 ($^{14}$N and $^{15}$N), NO$_3^-$ ions containing the more abundant $^{14}$N are preferentially reduced during denitrification, leaving the residual NO$_3^-$ enriched with $^{15}$N. On the other hand N$_2$, the end product of denitrification, gets greatly enriched with $^{14}$N. This is strikingly demonstrated by the present results. The vertical profile of $\delta^{15}$N of N$_2$ at the strongly reducing Sta. 3448/SS141, located in the northeastern Arabian Sea, exhibits a pronounced minimum coinciding with the SNM with values dipping below 0.2 $^\circ$/oo (Fig.6.2) (the $\delta^{15}$N of
N₂ in surface waters in this region, not determined at this station, is generally greater than 0.5 %). Interestingly at 150 m depth, where the NO₃⁻ concentration was high (23 μM) and NO₂⁻ was not detectable, the δ¹⁵N was still quite low (0.25 %) i.e., only marginally higher than the minimal value but less than half of the values observed in waters outside the O₂-deficient zone. Even at 1000 m depth the δ¹⁵N was only 0.3 %.

6.3. Vertical profiles of (a) δ¹⁵N of NO₃⁻ and N₂O (‰ relative to air), (b) δ¹⁸O of N₂O (‰ relative to air) and (c) concentrations of NO₂⁻ (μM, triangles) and N₂O (nM, circles) at Sta. 3201/SS119 (modified from Naqvi et al., 1998).

This indicates that the denitrification signature extends well outside the SNM. Similar pattern is also seen at Sta. 3204/SS119 (Fig. 6.4). This station had a thin, weakly-developed SNM associated with a minimum in δ¹⁵N of N₂ (0.18 %) at 150-190 m. This was underlain by a layer with relatively high δ¹⁵N of N₂ (maximum 0.39 %) which, going by its high salinity, evidently originated in the Persian Gulf. The O₂ concentrations, as determined by the Winkler method, were not appreciably different from those at Sta. 3201/SS119 (Fig.6.5). The association of a maximum in δ¹⁵N of N₂ with the Persian Gulf salinity maximum layer shows that the former is a sensitive tracer of advection. Again the vertical extent of the δ¹⁵N-N₂ minimum is much larger than the SNM. This would mean
that substantial N₂ may be produced without the accumulation of NO₂⁻ or/and the rapid horizontal mixing results in the export of lighter N₂ out of the SNM.

6.4. Vertical profiles of (a) δ¹⁵N of N₂, NO₃⁻ and N₂O, (b) δ¹⁸O of N₂O and (c) concentrations of NO₂⁻ (µM, triangles) and N₂O (nM, circles) at Sta. 3204/SS119 (the δ¹⁵N-NO₃⁻ profile at this site was obtained during SS128) (modified from Brandes et al, 1998; Naqvi et al, 1998).

The distribution of δ¹⁵N of NO₃⁻ shows a good correspondence to that of secondary NO₂⁻ (Figs. 6.3, 6.4 and 6.6). Sharp increases in δ¹⁵N of NO₃⁻ (up to 15 ‰) were observed within the SNM at Stas. 3201/SS119 (Fig. 6.3) and 13/SK87 (Fig. 6.6) with both maxima being thicker at the latter site. In contrast, at Sta. 3204/SS119 where the SNM was weakly developed, the extent of ¹⁵N enrichment in NO₃⁻ was considerably smaller (Fig. 6.4). At all the three stations, significant ¹⁵N enrichment in NO₃⁻ [relative to the average value of 5.7 ‰ for the oceanic subsurface waters (Altabet et al, 1995)] persisted down to at least 1,500 m, consistent with the observed trends in δ¹⁵N of N₂.
6.5. A comparison of vertical profiles of O₂ (µM) at Stas. 3201/SS119 (circles joined by dotted lines) and 3204/SS119 (triangles, joined by continuous lines) (modified from Naqvi et al, 1998).

These data on δ¹⁵N of N₂ and NO₃⁻ can be used to compute the fractionation factor, εₕₚₚₚ [₋₁₀³(1-α)], where α is the ratio between the rates of utilisation of ¹⁵NO₃⁻ and ¹⁴NO₃⁻, during denitrification using simple advection-reaction and diffusion-reaction models (Brandes et al, 1998). In the first case, diffusion is ignored 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 (Bender, 1990):

\[ δ¹⁵N-NO₃ = 10³(α-1)lnf_{NO₃} + (δ¹⁵N-NO₃)_{init} \]  

(6.2)

where \( f_{NO₃} \) is the ratio between the observed and expected NO₃⁻ concentrations and \( (δ¹⁵N-NO₃)_{init} \) gives the isotopic composition of the initial (unaltered) material. Values of \( f_{NO₃} \) were computed using the relationships between a nitrate tracer (NO) and potential temperature and the observed NO₃⁻ and NO₂⁻ concentrations (Naqvi et al, 1990).
6.6. Vertical profiles of (a) $\delta^{15}$N of NO$_3^-$ and N$_2$O, (b) $\delta^{18}$O of N$_2$O and (c) concentrations of NO$_2^-$ (µM, triangles) and N$_2$O (nM, circles) at Sta. 13/SK87 (modified from Brandes et al, 1998; Yoshinari et al, 1997).

A plot of $\delta^{15}$N-NO$_3^-$ versus ln $f_{NO3}$ for the depth range 200-600 m (Fig.6.7) shows a good linear relationship between the two ($r^2=0.9$). The slope of the regression line yields a value of 22% for $\epsilon_{denit}$, not too different from a similarly computed value (25%) for the eastern tropical North Pacific (ETNP) (Brandes et al, 1998).

Fig.6.7. The $\delta^{15}$N-NO$_3^-$ (% relative to air) vs. The natural log of $f$, the ratio of measured to expected nitrate concentrations (pooled data from three stations). The line gives the least squares fit to the data (modified from Brandes et al 1998).
The opposite extreme to the advection-reaction model is the reaction-diffusion model having no advective component. Such a model is expected to yield a larger fractionation factor than the advective model because the system being “open” allows the addition of new, unaltered material into the reaction region and the removal of old, altered material.

The reaction-diffusion equation is:

$$\frac{\partial [^{14}NO_3]}{\partial t} = J_{14NO_3} + K_d \frac{\partial^2 [^{14}NO_3]}{\partial x^2}$$  \hspace{1cm} (6.3)

where J is the denitrification rate and $K_d$ the horizontal eddy diffusivity along the 300 m isopycnal which was chosen because it lies close to the core of the denitrifying layer (Naqvi, 1987); x increases from the edge to the centre of the denitrifying zone. For $^{15}NO_3$, the equation is:

$$\frac{\partial [^{15}NO_3]}{\partial t} = \alpha([^{15}NO_3]/[^{14}NO_3]) J_{14NO_3} + K_d \frac{\partial^2 [^{15}NO_3]}{\partial x^2}$$  \hspace{1cm} (6.4)

Because there is no exact analytical solution for these equations, the values of both $^{14}N$ and $^{15}N$ were calculated numerically using a tridiagonal matrix solution method (Press et al, 1992). The boundary conditions were that the NO$_3^-$ and $\delta^{15}N$-NO$_3$ compositions at x=0 were 28 $\mu$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. Alternative boundary conditions, such as an interior concentration boundary condition, would change $\varepsilon$ by no more than 2 (Brandes et al, 1998).

The value of J was set at $1x10^{-7}$ $\mu$moles N l$^{-1}$ sec$^{-1}$. Although this value is only 1/2 of the rate estimated by Naqvi and Shailaja (1993) from the ETS data, it gives realistic nitrate deficit given a $x_E$ of 500 km, which is the minimum distance between the southern boundary of the suboxic zone at 12°N and the southernmost station located at 17°N. The value of $K_d$ was taken as 1800 m$^2$ sec$^{-1}$ (Jenkins, 1990). Using these parameters, NO$_3^-$ concentrations dropped to
~70% of the initial values in the interior of the denitrification zone, in agreement with the observations (Naqvi, 1987). With these values of J and Kd, the best-fit to the data was obtained with a fractionation factor of 25% (Fig. 6.8), only slightly lower than a similarly calculated value of 30% for the ETNP (Brandes et al., 1998). These values of ε are higher than those (15-20%) derived from laboratory experiments of denitrification (Delwitche and Steyn, 1970; Mariotti et al., 1981), but lower than the estimate (30-60%) of Cline and Kaplan (1975) derived from one-dimensional model fits to their ETNP data. However, the same data when fitted to the advection-reaction model described above yielded a value of ε (25%) which compares very well with the present results.

![Figure 6.8](image)

**Fig. 6.8.** The $\delta^{15}$N of NO$_3$− (% relative to air) vs. $f$, the ratio of measured to expected nitrate concentrations. Also plotted are the diffusion-reaction model results with the numbers denoting fractionation factors (modified from Brandes et al., 1998).

Although, the above models ignore either diffusion or advection, and a more realistic approach should simultaneously consider both of these, the results of the two models are not too divergent. More significantly, as the estimates from the Arabian Sea and ETNP are not very different, it would appear that the fractionation factor is not strongly dependent on either the denitrification rate or the local hydrography of the region.
6.3. Nitrogen Fixation:

A very important aspect of the data is the strong decrease in $\delta^{15}$N-NO$_3^-$ in near-surface waters (Figs. 6.3 and 6.4). At 200 m, for example, the value is $>10\%$ but it declines to $\sim6\%$ (close to the oceanic background) at 80 m. This trend is exactly opposite to that seen outside the OMZ (Sigman et al., 1997). 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 (Naqvi, 1987; Olson et al., 1993) makes the first mechanism less likely, and so the most plausible mode of input 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 (Brandes et al., 1998). Assuming that the changes in isotopic composition below 80 m are due to dilution by remineralised nitrogen fixed at 0\%, about 40\% of the NO$_3^-$ present at 80 m should have been derived from nitrogen fixation. Using the data on primary productivity in this region this translates into a nitrogen fixation rate of up to 6 Tg N y$^{-1}$ (1 Tg = $10^{12}$ g) or about 25\% of the denitrification rate. 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 in this region (Codispoti, 1997).

6.4. Dual isotopic composition of nitrous oxide:

As stated earlier, the eastern boundary upwelling environments that contain O$_2$-depleted waters are important for global N$_2$O cycling. This is because
of the extreme sensitivity of the processes involved in \( \text{N}_2\text{O} \) production and consumption to minor changes in ambient \( \text{O}_2 \) levels in the low range (<\( -0.5 \) ml l\(^{-1}\)) (Codispoti and Christensen, 1985). An intense \( \text{N}_2\text{O} \) accumulation is found to occur as the \( \text{O}_2 \) concentrations approach, but do not reach, suboxia. However, under strongly reducing conditions, such as those found within the SNM, \( \text{N}_2\text{O} \) concentrations fall rapidly below saturation, evidently as a result of its reduction to \( \text{N}_2 \) (e.g., Figs. 6.2 and 6.3). Thus, the Arabian Sea contains sites, located in close proximity of each other, which act either as strong source or strong sink of \( \text{N}_2\text{O} \) (Naqvi and Noronha, 1991). Why a strong net accumulation of \( \text{N}_2\text{O} \) occurs in the low-\( \text{O}_2 \) zones is an issue that has not been fully resolved so far. This is because \( \text{N}_2\text{O} \) is an intermediate of both the oxidative and reductive sequences of the nitrogen cycle and can be produced both during nitrification and denitrification. The two pathways leave very different isotopic signatures: \( \text{N}_2\text{O} \) produced during denitrification is enriched with \( ^{15}\text{N} \) and \( ^{18}\text{O} \) while that formed during nitrification is depleted in these isotopes (e.g., Yoshida, 1988; Wada and Hattori, 1991; Yoshinari et al., 1997). Hence measurements of the \( ^{15}\text{N} / ^{14}\text{N} \) and \( ^{18}\text{O} / ^{16}\text{O} \) ratios in \( \text{N}_2\text{O} \) dissolved in seawater are expected to provide insights into the mechanisms of its transformations. However, while substantial data have now been generated on the dual isotopic composition of \( \text{N}_2\text{O} \) in seawater, their interpretation has not been straightforward, and indeed often contradictory (Yoshida et al., 1989; Kim and Craig, 1990). The Arabian Sea contains several diverse biogeochemical environments and offers the most extreme conditions for \( \text{N}_2\text{O} \) cycling (Burkill et al., 1993). The isotopic composition of \( \text{N}_2\text{O} \) in this region may therefore be helpful in improving the understanding of its transformations.

Data on the isotopic composition of \( \text{N}_2\text{O} \) at five stations (3201/SS119, 3204/SS119, 13/SK87, 11/SK87 and 14/SS106) are shown in Figs. 6.3, 6.4, 6.6, 6.9 and 6.10, respectively. The most prominent feature of the isotope profiles is the large enrichment of both \( ^{15}\text{N} \) and \( ^{18}\text{O} \) at all the stations although the degree of enrichment varies considerably. As stated earlier, Stas. 14/SS106 and
3204/SS119 experienced mildly reducing conditions (thin SNM) while the other three stations were strongly reducing. These differences in redox conditions are reflected in the isotope data. The greatest enrichment is seen at Sta. 13/SK87; peak $\delta^{15}$N and $\delta^{18}$O values at this site (37.54 and 83.6‰, respectively) are the highest reported yet from a natural environment.

Fig. 6.9. Vertical profiles of (a) $\delta^{15}$N and (b) $\delta^{18}$O of N$_2$O, and (c) concentrations of NO$_2^-$ (µM, triangles) and N$_2$O (nM, circles) at Sta. 11/SK87 (modified from Yoshinari et al., 1997).

Fig. 6.10. Vertical profiles of (a) $\delta^{15}$N and (b) $\delta^{18}$O of N$_2$O, and (c) concentration of NO$_2^-$ (µM) at Sta. 14/SS106.
(Yoshinari et al, 1997). In contrast, the most southern Sta. 14/SS106 exhibited the least enrichment. However, it may be mentioned here that the samples from Sta. 14/SS106 were analysed following an older method [combustion of N\textsubscript{2}O to N\textsubscript{2} and CO\textsubscript{2} (Yoshinari and Koike, 1994)]. It is possible that the oxygen isotope data at this station suffer from some contamination in CO\textsubscript{2} with traces of water leading to somewhat lower δ\textsuperscript{18}O values; this would, however, not affect the nitrogen isotope data.

Preferential loss of lighter N\textsubscript{2}O to N\textsubscript{2} within the SNM evidently leads to the observed enrichments of \textsuperscript{15}N and \textsuperscript{18}O in residual N\textsubscript{2}O. The N\textsubscript{2}O concentration minimum is embedded between two maxima, but the isotopic compositions of these N\textsubscript{2}O-rich layers are very different. Going upward from the OMZ, the δ\textsuperscript{15}N and δ\textsuperscript{18}O values fall sharply across the oxic-suboxic boundary with the former generally lower than the tropospheric value (7 %o - Kim and Craig, 1990) in the upper 150 metres. In contrast, although δ\textsuperscript{15}N and δ\textsuperscript{18}O also decrease below SNM, their levels remain much higher than the tropospheric values (20.7 %o for δ\textsuperscript{18}O - Kim and Craig, 1990) in the deep waters. Since the suboxic waters with huge enrichments of heavier isotopes are capped by a layer which has high concentrations of light N\textsubscript{2}O, the N\textsubscript{2}O escaping to the atmosphere in the region cannot be heavy. Thus the near-tropospheric isotopic values at the sea surface at the open ocean sites (mean±s.d = 7.65±0.47 %o for δ\textsuperscript{15}N and 23.45±1.35 %o for δ\textsuperscript{18}O; n=11) probably reflect an active air-sea exchange. The fate of heavy N\textsubscript{2}O is not known, but it is expected to be advected out of the region and contribute to the elevated δ\textsuperscript{15}N and δ\textsuperscript{18}O in N\textsubscript{2}O observed outside the suboxic zones (Kim and Craig, 1990).

An important aspect of the data is that the δ\textsuperscript{15}N of NO\textsubscript{3}\textsuperscript{−} is consistently lower than that of N\textsubscript{2}O at depths exceeding ~200 m, and higher at shallower
depths (Figs. 6.3 and 6.4). This indicates that the intense N₂O accumulation in
the upper and lower parts of the OMZ may be through different mechanisms.
Greater enrichment of δ¹⁵N in N₂O relative to NO₃⁻ appears to be characteristic of
denitrification as revealed by recent culture experiments (M.A. Altabet,
unpublished data). It may arise from a combination of much lower N₂O
concentration than the amount of denitrified nitrogen and large kinetic isotope
fractionation associated with the reduction of N₂O to N₂ (Yoshida et al., 1984).
This pattern is the most pronounced within N₂O-depleted SNM at 3201/SS119.
Its persistence even below SNM at 3201/SS119 and at depths exceeding ~200
m at 3204/SS119 suggests significant N₂O production through denitrification.
This observation is consistent with the view that denitrification may lead to a net
N₂O accumulation under certain conditions (Betlach and Tiedje, 1981; Capone,
1996). However, it has been noted that heavy isotope enrichment has also been
observed, albeit to a lesser degree, in the more oxygenated deep waters of the
Pacific Ocean by Kim and Craig (1990). It was attributed to partitioning of
isotopes during nitrification by which the precursor species of N₂O [such as
hydroxylamine(NH₂OH)] is enriched with ¹⁵N and ¹⁸O. But the problem with this
mechanism is that it cannot explain the observed large increases in N₂O at O₂
levels approaching suboxia (Law and Owens, 1990; Naqvi and Noronha, 1991)
over concentrations expected from linear relationships between N₂O production
and O₂ utilisation commonly observed in the oceans (Yoshinari, 1976; Elkins et
al., 1978). This obviously requires a reductive step in N₂O production. An
alternative mechanism of the observed heavy isotope enrichment could be the
consumption of N₂O within sediments (and in water in areas such as the Arabian
Sea and eastern tropical Pacific) and subsequent transport of heavy N₂O to the
ocean interior (Zafiriou, 1990). Lastly, coupling of nitrification and denitrification
through common intermediates/by-products may also influence the isotopic
composition of N₂O (Zafiriou, 1990; Naqvi and Noronha, 1991; Naqvi, 1991b).
Such a coupling should be especially important near the oxic-suboxic interface, and this could possibly account for the enigmatic isotopic trend seen in the upper layer of the Arabian Sea which defies conventional explanation. That is, while the lighter N₂O at depths less than ~200m is apparently not produced by denitrification, classical nitrification pathway (NH₄⁺ → NO₂⁻ → N₂O) (Yoshida, 1988) also cannot fully explain the observed data for two reasons. First, as stated earlier, the δ¹⁵N values are much higher than that reported (<-60 ‰) by Yoshida (1988) for or the production of N₂O from NH₄⁺ via NO₂⁻ by *Nitrosomonas europaea*. [One may question the applicability of these experimental results, conducted with a high ammonium concentration, to the substrate-limited natural environments, but it may be noted that N₂O emitted from the soils is quite depleted in both ¹⁵N and ¹⁸O (see Fig. 6.12)]. Secondly, what is more significant is that the observed δ¹⁸O is much higher than the value for nitrification expected from δ¹⁸O of H₂O and O₂ [assuming that one oxygen atom in NO₂⁻ is derived from H₂O and the other from dissolved O₂ (Yoshinari et al, 1997) and using the data from GEOSECS station 416 (Ostlund et al, 1987), the δ¹⁸O of nitrification-derived N₂O should have been <-3 ‰]. Given the very abrupt decrease in O₂ below the surface mixed layer and the expected abundance of large particles at this level, it seems very plausible (Naqvi and Noronha, 1991; Naqvi, 1991b) that an intermediate or by-product of nitrification such as NO enters the denitrification sequence and gets reduced to N₂O. As the oxygen atom of NH₂OH, the probable precursor of NO (Ward and Zafiriou, 1988), is derived from O₂ (Dua et al, 1979) which is characterised by high δ¹⁸O (Ostlund et al, 1987), N₂O produced through this pathway is expected to be enriched in ¹⁸O. Moreover, unlike N₂O, production of NO by nitrifying bacteria involves modest depletion of ¹⁵N (Yoshida, 1988). Thus, N₂O produced through this pathway is expected to be moderately depleted in ¹⁵N, but enriched in ¹⁸O, as observed.
Therefore, it may be concluded that, in conformity with previous suggestions (Zafiriou, 1990; Naqvi, 1991b), there are probably several mechanisms of N$_2$O production in the ocean involving different isotopic fractionations. The relative contribution from various pathways is probably determined by the O$_2$ distribution and organic carbon availability, both of which vary in space and time. This not only brings about large spatial changes in N$_2$O production and consumption but, in response to temporal changes in the geographical extent and intensity of the O$_2$ minimum zones (Altabet et al., 1995; Geneshram et al., 1995) the oceanic N$_2$O source strength may also vary greatly with time contributing to fluctuations in the atmospheric N$_2$O content as recorded in ice cores (Leuenberger and Siegenthaler, 1992).

As stated earlier, the Arabian Sea is a region of high N$_2$O efflux to the atmosphere; the emission rate is particularly high in the three upwelling centres located off Somalia, Arabia and Southwest India (Bange et al., 1996; de Wilde and Helder, 1997; Naqvi et al., 1998). Observations made off the southwest coast of India during the summer monsoon of 1995 yielded some of the highest N$_2$O levels reported from the sea. At 23 stations sampled during SK103 (Fig. 1.2) the surface concentrations and saturations were 11.2-62.5 nM (mean ± s.d. = 28.5 ± 14.7 nM) and 193-953% (458 ± 223%), respectively. These values were associated with intense upwelling as manifested by low sea surface temperatures (minimum 22.8°C) and high NO$_3^-$ (maximum 16 μM) which are comparable to those observed in the upwelling zones of the western Arabian Sea (Smith and Codispoti, 1980; Codispoti et al., 1996b). The $^{15}$N/$^{14}$N and $^{18}$O/$^{16}$O ratios in surface-water N$_2$O measured at eight of these stations together with those from eight open ocean stations are plotted versus percentage saturation in Fig. 6.11. The $\delta^{15}$N and percentage saturation appear to be negatively correlated, with N$_2$O in upwelling waters of the southeastern Arabian Sea being
the most depleted in $^{15}$N. A few measurements (not included in Fig. 6.11) were also made in subsurface waters. The lowest $\delta^{15}$N (0.8 $\%$o) was recorded at 26 m at 11°51'N, 75°09'E; the corresponding N$_2$O concentration and saturation were 115.6 nM and 1709%, respectively. Since this is the lowest $\delta^{15}$N ever recorded from the oceanic water column, and because at such high concentrations the signatures of background N$_2$O would be almost completely erased, it can be taken to represent the end-member composition of N$_2$O produced in seawater. It is substantially lower than the $\delta^{15}$N of tropospheric N$_2$O, but much higher than the expected $\delta^{15}$N of N$_2$O produced through nitrification (Yoshida, 1988). In contrast to $\delta^{15}$N, $\delta^{18}$O did not exhibit a discernible relationship with percentage saturation, and with the exception of one sample, all $\delta^{18}$O values were consistently higher than the $\delta^{18}$O of tropospheric N$_2$O.

6.11: The $\delta^{15}$N and $\delta^{18}$O of N$_2$O as a function of N$_2$O saturation at sea surface (depth < 5m). Horizontal dashed lines indicate isotopic composition of N$_2$O in marine air (Kim and Craig, 1990). Values with moderate saturation and $\delta^{15}$N close to the atmospheric value are from the northern Arabian Sea; all others are from the coastal upwelling zone off SW India (modified from Naqvi et al., 1998).
The above observations have an important implication for the atmospheric N\textsubscript{2}O budget. Isotopic analysis of stratospheric N\textsubscript{2}O at 68°N has shown large enrichments of $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ (~21 and 35 \%, respectively) relative to the troposphere (Kim and Craig, 1993). This trend has been confirmed by more recent observations at 33-48°N, albeit with somewhat smaller enrichments in the lower stratosphere, but the causative mechanism is still not fully understood (Rahn and Wahlen, 1997; Cliff and Thiemens, 1997; Yung and Miller, 1997). However, the magnitude of $^{15}\text{N}$ and $^{18}\text{O}$ fluxes (~400 and 500 TgN \%/y\textsuperscript{-1}, respectively, obtained from the older data and about half as much from recent results) are such that these cannot be balanced by air-sea exchange, as proposed (Kim and Craig, 1993; McElroy and Jones, 1996). Even if, as an extreme case, the lowest observed $\delta^{15}\text{N}$ value from the ocean (~1 \%) is combined with the largest estimate of oceanic N\textsubscript{2}O production (11 TgN y\textsuperscript{-1}) (Capone, 1996), the air-sea exchange can counter no more than 66 TgN \%/y\textsuperscript{-1} of the stratospheric $^{15}\text{N}$ flux.

The reported $^{18}\text{O}$ fluxes are even more problematic since the observed opposite trends of $^{15}\text{N}$ and $^{18}\text{O}$ imply that the air-sea exchange will lead to an increase in the tropospheric $^{18}\text{O}$ inventory. The gravity of this issue is evident from the fact that on a $\delta^{15}\text{N}$ vs. $\delta^{18}\text{O}$ diagram constructed with the published data representing various planetary reservoirs of N\textsubscript{2}O, the stratospheric composition conspicuously forms a "corner" (Fig. 6.12). Thus the tropospheric value, which does not fall on vectors joining the other end-members, cannot be explained by simple mixing between various reservoirs (Kim and Craig, 1993). In view of these observations, it is imperative that more measurements be made on N\textsubscript{2}O in the stratosphere and that emitted from different terrestrial reservoirs. If the published data are representative, however, then there ought to exist some hitherto poorly known sources and/or sink of N\textsubscript{2}O that may be vital for
tropospheric isotopic balance (Prasad, 1994; McElroy and Jones, 1996; Cliff and Thiemens, 1997).

Fig. 6.12. Comparison of isotope data from the Arabian Sea with representative data from other environments (Kim and Craig, 1990; Rahn and Wahlen, 1997) (stars - soil gas; triangles - upwelling zone off SW India; crosses - northern Arabian Sea; squares - stratosphere; circle - troposphere). Note that the tropospheric value does not fall on vectors joining the other end members (modified from Yoshinari et al, 1997; Naqvi et al, 1998).