

# Ocean biogeochemistry and atmospheric composition: Significance of the Arabian Sea

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**The Arabian Sea is an important site of biogeochemical ocean-atmosphere transfers, which play a crucial role in regulating the atmospheric chemical composition and the earth's climate. Widespread denitrification resulting from an intense oxygen-deficiency at mid-depths in this region modulates oceanic combined nitrogen inventory and consequently biological productivity. Due to a delicate biogeochemical balance the Arabian Sea is expected to be among the first to react to potential anthropogenic perturbations.**

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## Oceanic carbon cycle

THE chemical composition of the earth's atmosphere greatly differs from those of its two immediate neighbouring planets in that while carbon dioxide forms the bulk (>95%) of the atmospheres of Venus and Mars, nitrogen and oxygen are the two most abundant gases in the earth's atmosphere with CO<sub>2</sub> ranking a poor fifth (0.036%). This is primarily due to the presence of large amounts of *liquid* water on earth, which is the only body in the solar system endowed with this wealth, on account of being of the right size, having the right chemical composition, and located at the right distance from the sun. Because of these favourable conditions life originated and thrived on earth. This, in turn, drastically modified the earth's surface environment, particularly its atmospheric composition which, with the exception of argon, is controlled mainly by biological processes.

It is believed that during the early years of the earth's history, its atmosphere was also predominantly comprised of CO<sub>2</sub>, which was produced as a result of oxidation of methane (CH<sub>4</sub>) by O<sub>2</sub> generated through photolysis of water vapour. The resultant greenhouse warming probably maintained a very high (90°C) temperature at the earth's surface at that time<sup>1</sup>. However, as the liquid water filled the depressions to form primitive oceans, it rapidly sequestered atmospheric CO<sub>2</sub>. The property which differentiates CO<sub>2</sub> from most other atmospheric constituents is that it reacts with water to form carbonic acid (H<sub>2</sub>CO<sub>3</sub>), which undergoes dissociation to yield bicarbonate (HCO<sub>3</sub><sup>-</sup>) and carbonate (CO<sub>3</sub><sup>2-</sup>) ions. This chemical reactivity makes CO<sub>2</sub> highly soluble in water. The dissolved CO<sub>2</sub> facilitates

weathering of rocks. The CO<sub>3</sub><sup>2-</sup> ions interact with cations, mainly Ca<sup>2+</sup>, to form sparingly-soluble carbonates. The carbonate production can occur both chemically and biochemically. In today's ocean, chemical precipitation is confined to just a few areas such as the Persian Gulf, but early in the earth's history it was an important mechanism that led to a decrease in atmospheric CO<sub>2</sub>. The carbonates precipitated chemically on the young earth have since been recycled many times over, and the present carbonate deposits are mainly of biogenic origin<sup>1</sup>. Many organisms secrete CaCO<sub>3</sub> to build their hard skeletal parts either in the form of aragonite (e.g. corals) or calcite (e.g. foraminifera). The oceanic surface waters are supersaturated with respect to both these polymorphs, especially in the tropical regions, facilitating biological CaCO<sub>3</sub> production.

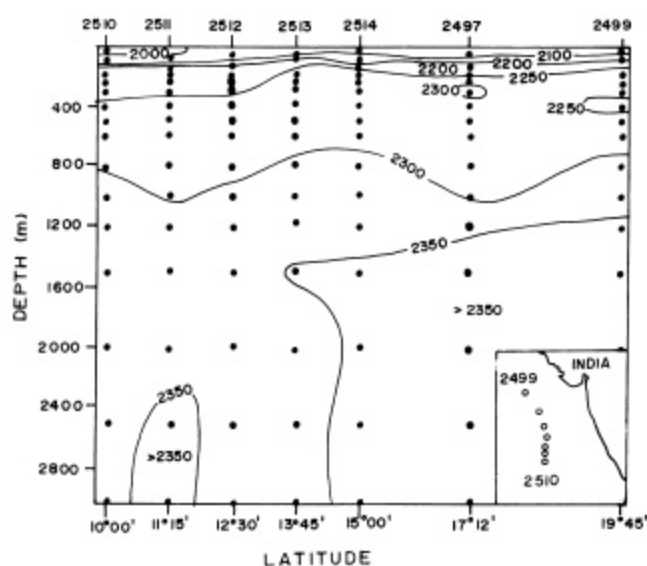
The most important pathway through which the biota affects the carbon cycle is the fixation of inorganic carbon by organisms to build soft tissues. This is done by autotrophs, some of which can derive the energy needed for biosynthesis of organic matter through chemical reactions such as sulphide oxidation (chemosynthesis), but most use solar energy trapped with the help of pigments such as chlorophyll (photosynthesis). The annual rate of photosynthetic (primary) production on earth is estimated to be about 230 Tg C y<sup>-1</sup> (1 Tg = 10<sup>12</sup> g); of this the oceanic contribution is about 60 Tg C y<sup>-1</sup> (ref. 2). Most of the photosynthetic production in the sea is carried out by tiny organisms known as phytoplankton within the upper 100 m or so of the water column which is illuminated by sunlight. The phytoplanktons require some trace elements (nutrients) such as nitrogen and phosphorus for their growth, and the biological uptake leads to decreases in nutrient concentrations in surface waters. While most of the organic matter thus produced gets recycled in the surface layer, a significant fraction escapes to the deep sea through sedimentation where it is decomposed by bacteria. This process results in the consumption of O<sub>2</sub> and regeneration of carbon (as CO<sub>2</sub>) and nutrients [as nitrate (NO<sub>3</sub><sup>-</sup>) and phosphate (PO<sub>4</sub><sup>3-</sup>)]. Thus, photosynthesis and respiration cause depthwise fractionation of nutrients, i.e. their near-surface depletion and deep-water enrichment. These gradients are maintained because the oceans are not well-mixed vertically, but are generally stratified. The stratification is most pronounced in the tropics where strong solar heating results in the generation of a well-mixed surface layer which is a few tens of metres thick. Below the mixed layer, temperature decreases rapidly with the

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zone of sharp temperature and consequently density gradients, known as the thermocline, inhibiting mixing between the surface and deep waters. It is only in the areas where the subsurface waters are brought up close to the surface through divergence of currents (upwelling), or where the thermocline is weakened by vertical mixing, the euphotic zone gets adequate supply of nutrients; such areas are biologically most productive.

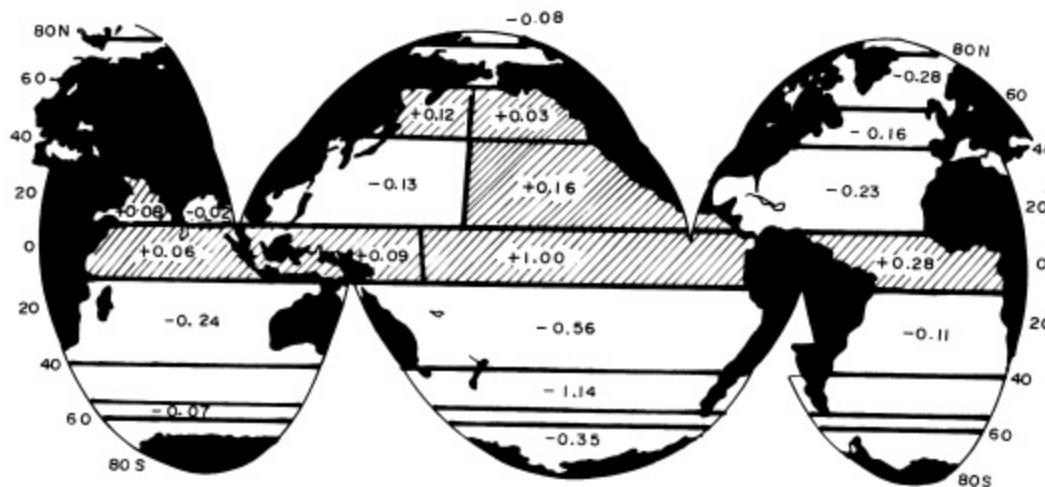
Since the 'biological pump' involves continuous export of carbon from the surface to subsurface waters, it makes the deep sea the repository of the bulk (> 90%) of the carbon in the biosphere-atmosphere-hydrosphere system. However, as  $\text{CO}_2$  is dissolved in sea water in very high concentrations (> 2 mM), the decrease in total dissolved inorganic carbon (DIC or  $\Sigma\text{CO}_2$ ) in the surface layer relative to the deep sea is no more than 20% (Figure 1). On the other hand, biological activity plays a more important



**Figure 1.** Vertical (north-south) section of  $\Sigma\text{CO}_2$  ( $\mu\text{M}$ ) in the Arabian Sea. Station locations are shown in the inset (from George *et al.*<sup>8</sup>)

role in regulating the speciation of DIC, which is strongly dependent on pH. In the pH range normally encountered in oceanic surface waters,  $\text{HCO}_3^-$  is the predominant species (90%); only about 1% of  $\Sigma\text{CO}_2$  is present in the aqueous or hydrated form [ $\text{CO}_2(\text{aq})$  and  $\text{H}_2\text{CO}_3$ ] with the rest occurring as  $\text{CO}_3^{2-}$ . It is only the 'free' (unionized) form which can be exchanged with the atmosphere; its concentration is represented as  $\text{pCO}_2$ , the equilibrium partial pressure of  $\text{CO}_2$ . It is this parameter which determines the direction, and in part the magnitude, of the air-sea  $\text{CO}_2$  flux. The oceanic surface waters normally have  $\text{pCO}_2$  values very close to that in the atmosphere (currently  $\sim 360 \mu\text{atm}$ ). If  $\text{pCO}_2$  in water is higher than this value, there is a net emission of  $\text{CO}_2$  from water and vice versa. Both the physical and biological processes affect  $\text{pCO}_2$ . The cooling and deep-water formation at high latitudes result in lowering of surface water  $\text{pCO}_2$  through an increase in  $\text{CO}_2$  solubility and changes in  $\text{H}_2\text{CO}_3$  dissociation constants; such areas serve as important sites of  $\text{CO}_2$  removal from the atmosphere. Conversely, oceanic areas of divergence, such as the eastern boundary upwelling zones and the equatorial Pacific are principal sites of  $\text{CO}_2$  efflux from the ocean (Figure 2)<sup>3</sup>. The net global air-sea flux of  $\text{CO}_2$  is directed into the oceans, and it is estimated that the oceans are currently removing about 2000 Tg of  $\text{CO}_2\text{-C}$  annually, which is about 25% of the rate at which  $\text{CO}_2$  is being added to the atmosphere due to human activities (mainly fossil fuel combustion and deforestation)<sup>4</sup>.

The uptake of  $\text{CO}_2$  for building soft tissues as well as hard skeletons affects the pH and alkalinity of sea water. Due to the acidic character of  $\text{CO}_2$ , respiration and photosynthesis cause a decrease and an increase of sea water pH, respectively. The relatively high pH of oceanic surface waters keeps  $\text{pCO}_2$  at moderately low levels (Figure 3). This is largely responsible for



**Figure 2.** The mean annual net  $\text{CO}_2$  exchange across the air-sea interface. Positive (negative) numbers within shaded (unshaded) areas indicate sea to air (air to sea) fluxes in  $\text{Gg C y}^{-1}$  (modified from Takahashi<sup>3</sup>).

maintaining low levels of  $\text{CO}_2$  in the atmosphere; in the absence of this mechanism the atmospheric  $\text{CO}_2$  content would have been several-fold higher and consequently the earth would have been much warmer. Conversely, the high  $\text{pCO}_2$  values in subsurface waters (particularly at intermediate depths) are the consequence of respiration. The production and dissolution of  $\text{CaCO}_3$ , on the other hand, have opposite effects on  $\text{pCO}_2$  – biological secretion of  $\text{CaCO}_3$  in surface waters leads to an increase in  $\text{pCO}_2$ . Fortunately, on an average, for each atom of carbon fixed into skeletal carbonate, about 4 atoms of carbon are utilized to build the soft tissue<sup>5</sup>, and so the biological activity results in a net decrease in  $\text{pCO}_2$  at the sea surface.

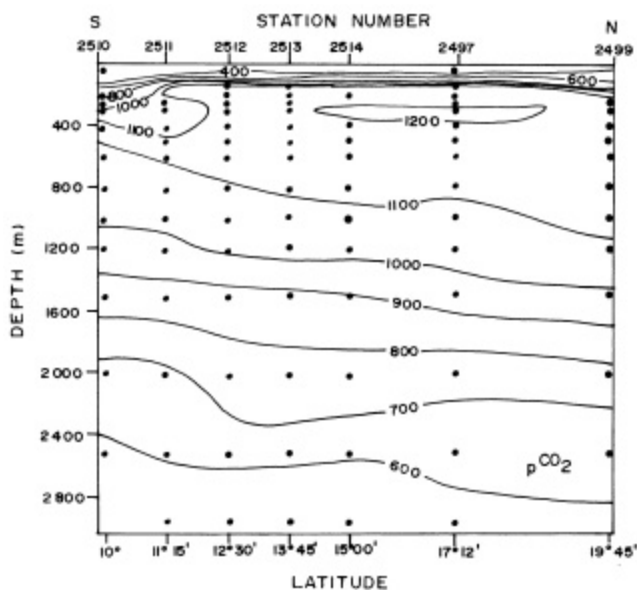
As stated above, most of the removal of atmospheric  $\text{CO}_2$  through the solubility pump occurs in the temperate or polar seas where dense surface waters sink and flow into the deep basins of all the oceans. Although the biological pump operates in all areas, the rate at which it removes  $\text{CO}_2$  from surface waters varies a great deal due to the large geographical changes in biological productivity. Obviously the rate of biological removal should be the highest in regions of high biological production. However, the high biological production is itself sustained by upwelling and vertical mixing which tend to increase  $\text{pCO}_2$  in surface waters, and so whether or not a given region serves as a net source or a net sink of atmospheric  $\text{CO}_2$  depends upon the balance between the two opposing processes. In most cases the biochemical decrease of  $\text{pCO}_2$  is overwhelmed by the physicochemical increase. The north-western Indian Ocean is one such area. It houses three centres located off Somalia, Arabia and south-west India where vigorous upwelling occurs during the south-west monsoon, making this region highly productive. However, because of the high  $\text{pCO}_2$  in the upwelled water the surface water  $\text{pCO}_2$  levels are invariably higher than those in the atmosphere. In fact, the  $\text{pCO}_2$  in the upwelling zones of this region is among the highest observed in the

oceans. For example, values as high as  $\sim 700 \mu\text{atm}$  have been recorded in the upwelling zone off south-west India. However, as upwelling is a spatially-confined, seasonal phenomenon, the distribution of  $\text{pCO}_2$  shows large variability in both space and time<sup>6,7</sup>. The seasonally-changing atmospheric circulation also brings about significant changes in the atmospheric  $\text{pCO}_2$  over the Arabian Sea<sup>7</sup>. The highest  $\text{pCO}_2$  values in water observed during the south-west monsoon are associated with low  $\text{pCO}_2$  in the atmosphere, and since the winds are also the strongest during this season (which enhances the air-sea gas exchange), maximal emission of  $\text{CO}_2$  from the Arabian Sea occurs during this season<sup>7</sup>. On an annual basis the emission rate of  $\text{CO}_2$  from the Arabian Sea has been estimated as 79 Tg (ref. 8). Although this value is an order of magnitude lower than the flux from the equatorial Pacific<sup>3</sup>, the single largest source of atmospheric  $\text{CO}_2$ , and consequently globally not so significant, the important point is that this is maintained in spite of a high rate of photosynthetic carbon fixation in the region.

### Role of nitrogen

The Arabian Sea plays a more important role in regulating the atmospheric composition through controls on global nitrogen budget. Among the nutrient elements essential for the growth of plants, nitrogen is perhaps the most important. Although it is the most abundant constituent of the atmosphere, occurring predominantly as  $\text{N}_2$ , this form of nitrogen is chemically inert, and only a few organisms have the capability to utilize or 'fix' it as such. Most organisms can only use nitrogen in 'combined' forms such as  $\text{NO}_3^-$  and ammonium ( $\text{NH}_4^+$ ) which are less abundant in nature but are more easily assimilated. The availability of such forms often limits photosynthesis in the marine environment<sup>9</sup>.

The inventory of combined nitrogen in oceans is regulated by several processes. Inputs of nitrogen occur mainly through river runoff, atmospheric deposition and nitrogen fixation, while its loss is principally through conversion of the combined nitrogen to  $\text{N}_2$ . This process, known as denitrification, takes place when the ambient  $\text{O}_2$  concentrations are close to zero and bacteria begin to utilize  $\text{NO}_3^-$  instead of  $\text{O}_2$  as an oxidant for decomposing organic debris<sup>10</sup>. Conditions favourable for denitrification commonly develop within sediments of shallow seas. In the water column, however, oceanic currents supply enough  $\text{O}_2$  at all depths to prevent the development of anoxic conditions in most oceanic areas. However, there are three regions where unusual oceanographic processes cause the  $\text{O}_2$  demand to exceed its supply leading to an almost complete  $\text{O}_2$  depletion at mid-depths. Two of these sites are located in the eastern Pacific – one on each side of the equator – while the third is found in the northern Indian Ocean, particularly in the Arabian Sea. Although these regions account for  $< 2\%$  of the total oceanic area, they make disproportionately large contribution to global biogeochemical cycles. This is because  $\text{N}_2$  produced during denitrification makes up for the inputs of combined nitrogen from various sources. In the absence of this process, the atmospheric  $\text{N}_2$  would be depleted in a few tens of million years. In fact, the most recent estimate of



**Figure 3.** Vertical (north-south) section of  $\text{pCO}_2$  ( $\mu\text{atm}$ ) in the Arabian Sea. Station locations are shown in the inset of Figure 1 (from George *et al.*<sup>8</sup>).

various source and sink terms of the combined nitrogen budget (Table 1)<sup>11</sup> indicates that the loss of N<sub>2</sub> through denitrification may actually exceed the net inputs by a substantial margin. The magnitude of imbalance is such that it would lead to a complete removal of combined nitrogen from oceans in a few tens of thousand years. Obviously such a state cannot persist over a long period of time, and the only way the atmospheric N<sub>2</sub> content and oceanic combined nitrogen inventory could have remained constant over geological time scales is that there should be times when the balance is the other way around. In other words, the oceans may alternately serve as a net source and a net sink of combined nitrogen depending on the relative rates of nitrogen fixation and denitrification<sup>9</sup>. Such fluctuations in oceanic combined nitrogen budget have the potential to substantially alter the combined nitrogen inventory on time scales of hundreds to thousands of years. Since nitrogen is the principal limiting nutrient, and the C : N ratio during phytoplankton uptake is high (6.6 by atoms), such changes in the oceanic combined nitrogen inventory can bring about large variations in biological productivity and hence in the rate at which CO<sub>2</sub> is removed from the atmosphere; this in turn can force climate changes<sup>12</sup>. How the balance is achieved on geological time scales is an important problem that is currently attracting the attention of biogeochemists the world over, and it is in this context that areas such as the Arabian Sea assume a lot of importance.

### Oxygen-deficiency and denitrification

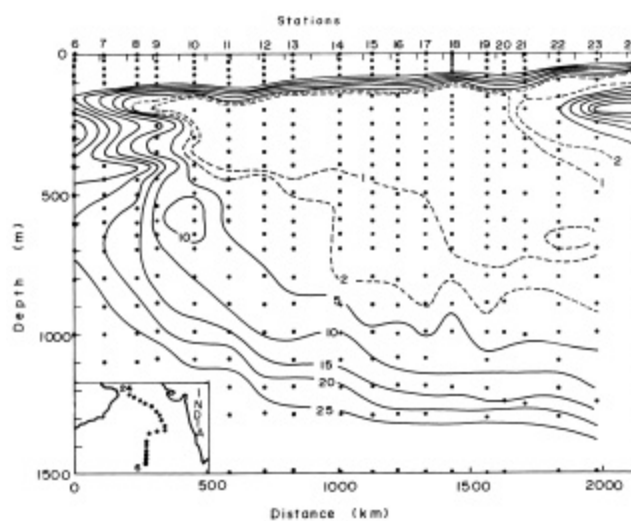
The mid-depth O<sub>2</sub> deficiency in the Arabian Sea is perhaps the most severe observed anywhere in oceans, as the concentrations within ~ 150–1000 m are less than 0.1 ml/l (4 μM) within a large part of the central and north-eastern Arabian Sea (Figure 4). This deficiency is caused by a high subsurface O<sub>2</sub> demand arising from high surface productivity coupled with low O<sub>2</sub> content of water flowing into the Arabian Sea from the south<sup>13</sup>. Vigorous denitrification, however, does not occur within the entire oxygen minimum zone (OMZ) as evident from the distribution of nitrite (NO<sub>2</sub>), the first intermediate of the reduction sequence, that

accumulates in the water column to produce what is often referred to as the secondary nitrite maximum (SNM). This feature, which is associated with pronounced deficiencies in NO<sub>3</sub>, develops only when the O<sub>2</sub> levels fall below 0.015–0.02 ml/l (Figure 5). Such a strong dependence of redox processes on minor changes in ambient O<sub>2</sub> levels implies an extremely sensitive ecosystem with a delicately poised biogeochemical balance which is expected to react rapidly to anthropogenic perturbations.

An anomalous feature of the Arabian Sea OMZ is that the zones of the highest primary production and the most vigorous denitrification are geographically separated here<sup>14</sup>. This is demonstrated by both chemical and biochemical data. For example, the highest NO<sub>2</sub> and lowest NO<sub>3</sub> concentrations as well as the highest electron transport system (ETS) activities are observed not beneath the biologically productive surface waters close to the continental margin but in the oligotrophic central Arabian Sea<sup>14,15</sup>. Another unexpected result is that the ETS-based respiration rates are about an order of magnitude higher than the sinking flux of particulate organic carbon from the surface layer as measured by drifting sediment traps or estimated from global relationships between primary production and sinking carbon fluxes<sup>15,16</sup>. Moreover, the rates in the suboxic waters are higher than those in the overlying and underlying oxic parts of the water column; in fact, the former are so high and the bacteria that carry out degradation proliferate to such an extent that there is a marked increase in water turbidity within the denitrifying zone (Figure 6)<sup>16</sup>. It is still not clear as to what produces this bacterial biomass maximum under energetically less favourable conditions and, given the apparent inadequacy of the sinking flux to meet the observed respiration rates, what is the additional mode of organic carbon input to the denitrifying layer. Two possible explanations have been offered: (a) Denitrifiers may efficiently utilize the dissolved organic matter supplied to the OMZ<sup>15,16</sup> either quasi-horizontally from the continental margins or vertically through diurnal migrations of organisms particularly the mesopelagic fish such as

**Table 1.** Oceanic combined nitrogen budget (Tg N y<sup>-1</sup>) (from Codispoti *et al.*<sup>11</sup>)

<i>Inputs</i>	
Riverine	45
Groundwater	10
Atmospheric (DON + DIN)	100
Nitrogen fixation	150
Total	305
<i>Sinks</i>	
Water column denitrification	110
Sedimentary denitrification	255
Burial	35
Export of organic N	16
Inorganic loss to atmosphere	13
N <sub>2</sub> O loss to atmosphere	7
Total	436
Deficit	131



**Figure 4.** Vertical (north-south) section of dissolved O<sub>2</sub> (μM) in the Arabian Sea. Locations of stations worked during the US JGOFS (R.V. *Thompson* Cruise 39) are shown in the inset. O<sub>2</sub> concentrations above 25 μM are not shown.

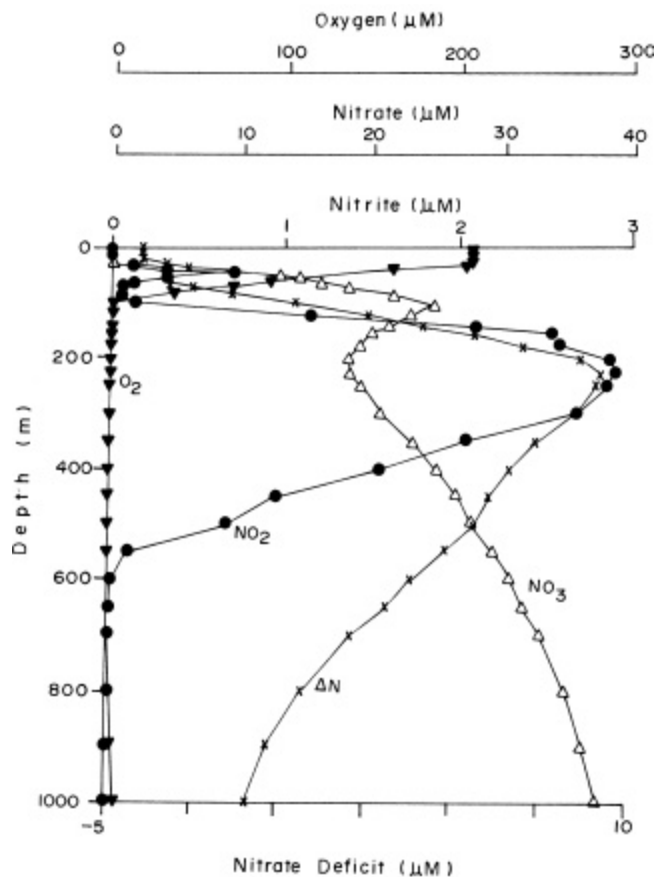
myctophids<sup>17</sup>. Significantly, the Arabian Sea contains huge stocks (~ 100 million tonnes) of myctophids which are specially adapted to low (< 0.1 ml l<sup>-1</sup>) ambient O<sub>2</sub> levels<sup>18</sup>. The presence of these organisms is evident from the acoustic data (Figure 7)<sup>19</sup> although how such a large 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<sup>20</sup>. The TEP levels within the OMZ 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.

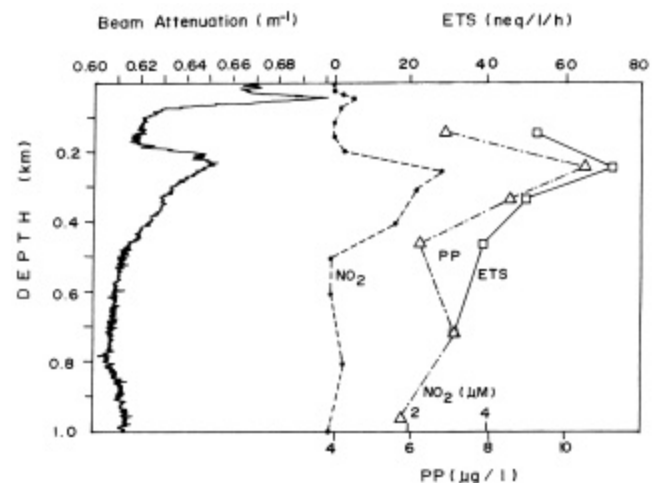
The rate of denitrification in the Arabian Sea has been quantified following physico-chemical and biochemical techniques. In the first approach, deficiencies in NO<sub>3</sub><sup>-</sup> relative to the concentration expected from correlations with some other chemical tracers (such as O<sub>2</sub>) are estimated, and these 'nitrate deficits' (cf. Figure 5) are combined with dynamic computations and suitable diffusion coefficients to work out the rate at which the deficits are exported out of the reducing zone through advection and mixing<sup>13</sup>. Assuming a steady state, this should be the same as the rate at which the deficits are produced. In the biochemical method, the denitrification rate is obtained from the ETS activity using suitable

conversion factors<sup>15</sup>. In spite of the differences between the two methods and the uncertainties inherent in them, they have yielded remarkably similar estimates of denitrification rate – around 30 Tg N y<sup>-1</sup>. This is about one-third the estimated global water column denitrification rate<sup>13</sup>, and its significance could be gauged from the fact that this rate can alter the total inventory of marine combined nitrogen by 0.5% in just a hundred years.

As mentioned above, in view of the extreme sensitivity of denitrification to small changes in ambient O<sub>2</sub> concentrations, large variability in its rate may be expected on a variety of time scales. Long-term trends in denitrification could be reconstructed utilizing the sedimentary record of nitrogen isotopes. This approach is based on the principle 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 example, of the two natural isotopes of nitrogen with mass numbers of 14 and 15 (<sup>14</sup>N and <sup>15</sup>N), NO<sub>3</sub><sup>-</sup> containing <sup>14</sup>N is lost more easily than that containing <sup>15</sup>N during denitrification. Consequently N<sub>2</sub>, the end product of denitrification, gets depleted with <sup>15</sup>N while an enrichment of this isotope takes place in the residual NO<sub>3</sub><sup>-</sup> (Figure 8). These data have been used to calculate the isotopic fractionation factor (ε) during denitrification from simple advection–reaction and diffusion–reaction models, yielding ε values of 22 and 25‰, respectively<sup>21</sup>. These estimates are similar to those computed for the eastern tropical Pacific Ocean indicating that the fraction factor may be independent of denitrification rate and local hydrography of the region.



**Figure 5.** Vertical profiles of O<sub>2</sub>, NO<sub>2</sub>, NO<sub>3</sub> and NO<sub>3</sub><sup>-</sup> deficit at the US JGOFS Station N7 (19°N, 67°E, R.V. *Thompson* Cruise 39).

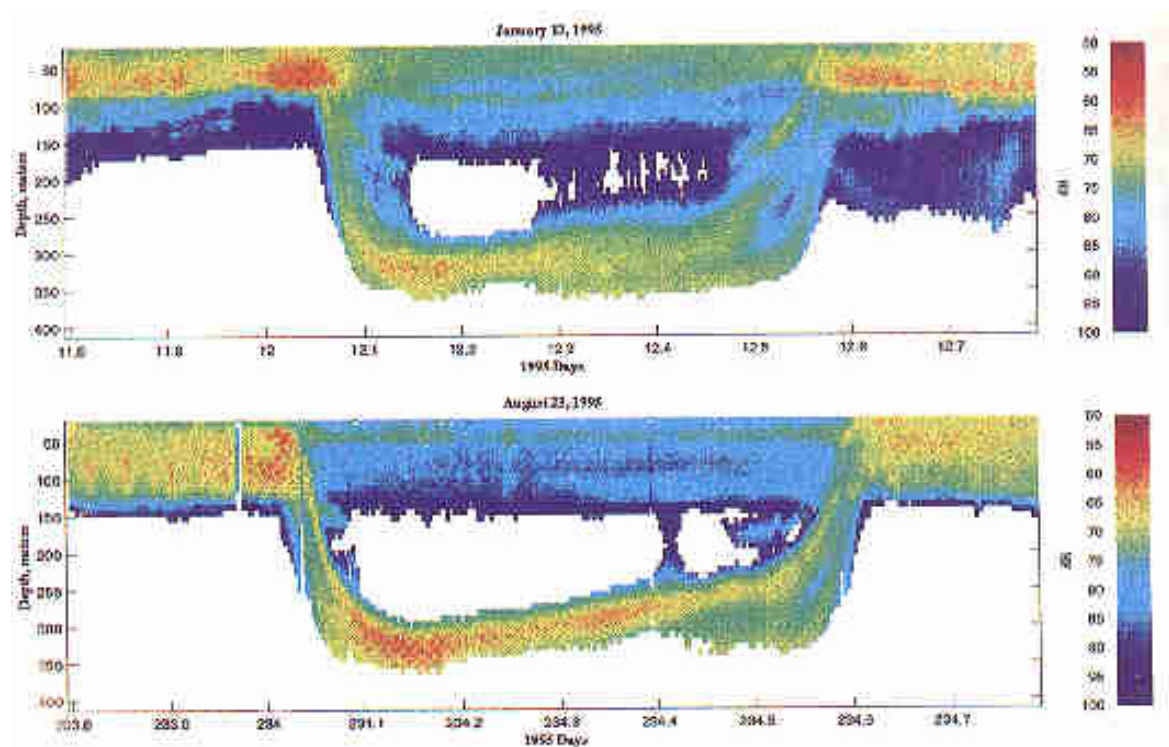


**Figure 6.** Vertical profiles of NO<sub>2</sub>, ETS activity and particulate protein (PP) in relation to beam attenuation at Station SS 2496 (17°30'N, 67°30'E) (from Naqvi *et al.*<sup>16</sup>).

In view of the large enrichment of  $^{15}\text{N}$  in  $\text{NO}_3^-$  within the denitrifying layer, it is expected that the nitrogen incorporated in organic matter produced in the surface water overlying the reducing zones would be enriched with this isotope. Measurement of nitrogen isotope abundance in sinking matter collected by sediment traps and in the surficial sediments of the Arabian Sea provides observational support for this hypothesis (Table 2)<sup>22</sup> – in both cases the  $\delta^{15}\text{N}$  (a measure of the  $^{15}\text{N}/^{14}\text{N}$  ratio) of organic nitrogen is much higher in the denitrifying Arabian Sea than the non-denitrifying Bay of Bengal. This property could thus be utilized to reconstruct past changes in the extent of denitrification.

A record of  $\delta^{15}\text{N}$  covering the past 450,000 years has been generated by Altabet *et al.*<sup>23</sup> from a deep sea core raised from the western Arabian Sea (Figure 9). 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. Incidentally, the glacial stages were also characterized by lower  $\text{CO}_2$  partial pressures in the atmosphere as revealed by the analysis of gases trapped in polar ice<sup>24</sup>. A spectral analysis of the record showed a high degree of cyclicity associated with frequencies of the three Milankowitch bands of 100,000, 41,000 and 23,000 years. The association with the 23,000 year precessional band which dominantly regulates the monsoon strength is particularly strong. Thus the sedimentary record supports the view that large climatic 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 climatic cycles through controls on atmospheric  $\text{CO}_2$  (refs 12, 23, 25).



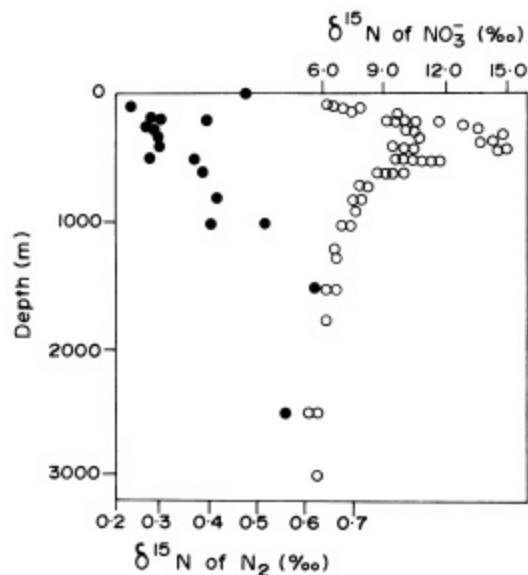
**Figure 7.** Acoustic backscatter for 24 h around US JGOFS Station N7 indicating diurnal migration of organisms (mostly myctophids) (from Morrison *et al.*<sup>19</sup>).

### 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 N<sub>2</sub>O efflux to the atmosphere. N<sub>2</sub>O is not only an important greenhouse gas, but it also contributes to the stratospheric ozone depletion. The rate of N<sub>2</sub>O loss in the stratosphere through photolysis and reaction with the excited atomic oxygen [O(<sup>1</sup>D)], which should be equal to the natural flux of N<sub>2</sub>O to the atmosphere from all sources, is about 12 Tg N<sub>2</sub>O-N y<sup>-1</sup> (ref. 26). Of this at least half seems to come

from the oceans<sup>27</sup>. But the N<sub>2</sub>O efflux is not uniformly distributed over the oceanic surface with the eastern boundary environments underlain by low-O<sub>2</sub> waters making disproportionately large contributions<sup>28</sup>. Measurements of N<sub>2</sub>O in the upwelling zones off Oman<sup>29</sup> and Somalia<sup>30</sup> have revealed large surface saturations (up to 230 and 330%, respectively), indicating that the annual flux of N<sub>2</sub>O from the Arabian Sea alone may be as much as 0.5–1 Tg N y<sup>-1</sup>. More recent observations in the lesser-known third upwelling centre (off SW India) yielded more extreme data: at 23 stations (Lat. 8.58–11.85°N, Long. 74.34–76.32°E) sampled during the SW monsoon of 1995, surface concentrations and saturations were 11.2–62.5 nM (mean ± SD = 28.5 ± 14.7) and 193–953% (458 ± 223), respectively<sup>31</sup>. These values, among the highest observed in oceanic surface waters, were associated with low sea surface temperatures (minimum 22.8°C) and high NO<sub>3</sub><sup>-</sup> (maximum 16 μM) indicating intense upwelling. The accumulation of N<sub>2</sub>O in very high concentration in areas such as the Arabian Sea is because its cycling is greatly affected by ambient O<sub>2</sub> levels in the low range (< 0.5 ml l<sup>-1</sup>). While its concentration peaks as the O<sub>2</sub> levels approach but do not reach suboxia, in strongly reducing environments such as those found within the core of the denitrifying zone, N<sub>2</sub>O itself is reduced to N<sub>2</sub> by bacteria<sup>28</sup>. Thus, the vertical profiles of N<sub>2</sub>O in the Arabian Sea exhibit two maxima separated by a minimum; the minimum coincides with the secondary nitrite maximum while the maxima are located at the peripheries of this feature (Figure 10)<sup>32</sup>. Since the upper N<sub>2</sub>O maximum is located just below the surface mixed layer, it sustains fairly large inputs of N<sub>2</sub>O to the surface layer, in turn supporting a large atmospheric flux from this region<sup>32,33</sup>. The occurrence of intense sources and sinks in close proximity of each other is expected to lead to a turnover rate which may be the most rapid on our planet<sup>31,32</sup>.

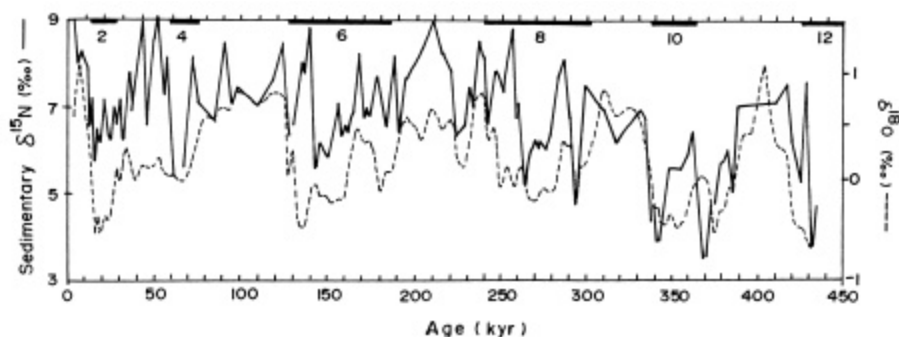
The cause of the unusually large N<sub>2</sub>O buildup in oceanic OMZs is still not fully understood. This is because N<sub>2</sub>O is an intermediate or a byproduct of both the oxidative (nitrification) and reductive (denitrification) pathways of nitrogen transformations<sup>28</sup>. These pathways are expected to lead to different isotopic signatures and therefore a study of natural abundance of nitrogen and oxygen isotopes in dissolved N<sub>2</sub>O may provide insights into its production mechanisms<sup>34,35</sup>.



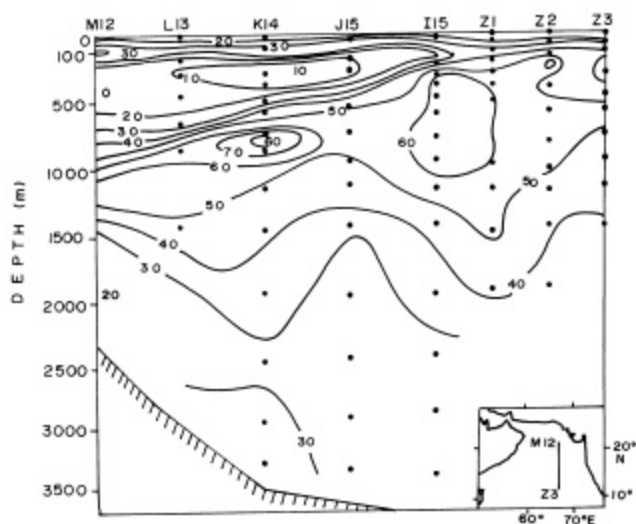
**Figure 8.** Nitrogen isotopic composition (expressed as ‰ δ<sup>15</sup>N relative to atmospheric N<sub>2</sub>) of NO<sub>3</sub><sup>-</sup> (solid circles) and N<sub>2</sub> (open circles) plotted vs depth in the Arabian Sea suboxic zone (from Brandes et al. 2013)

**Table 2.** <sup>15</sup>N/<sup>14</sup>N ratio in sinking organic matter (from Schafer and Ittekkot<sup>22</sup>)

Site	Depth (m)	δ <sup>15</sup> N settling particles (‰)		δ <sup>15</sup> N sediment (‰)
		Range	Mean	
<i>Bay of Bengal</i>				
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		
<i>Arabian Sea</i>				
Western	3000	5.3–8.8	7.1	9.2
Central	2900–3100	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	



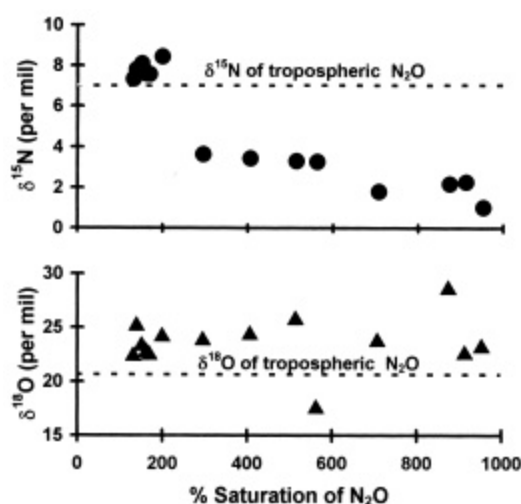
**Figure 9.** Downcore profiles of isotopic compositions of nitrogen in organic matter and oxygen in the shells of planktonic foraminifera in RC27-61 raised from the Owen Ridge (16°39.5'N, 59°31.4'E). Solid bars at the top of the figure marked by even numbers represent cold oxygen isotope stages (modified from Altabet *et al.*<sup>23</sup>).



**Figure 10.** Vertical (north-south) section of N<sub>2</sub>O (nM) in the Arabian Sea. Station locations are shown in the inset (from Naqvi *et al.*<sup>32</sup>).

Results of recent measurements of  $^{15}\text{N}/^{14}\text{N}$  and  $^{18}\text{O}/^{16}\text{O}$  in N<sub>2</sub>O in surface waters of the Arabian Sea reveal a negative correlation between  $\delta^{15}\text{N}$  and per cent saturation with N<sub>2</sub>O in the upwelled waters off south-west India being the most depleted in  $^{15}\text{N}$  (Figure 11)<sup>31</sup>. Although these  $\delta^{15}\text{N}$  values are the lowest ever reported for sea water [also substantially lower than the  $\delta^{15}\text{N}$  of tropospheric N<sub>2</sub>O (7‰, ref. 35)], these are much higher than the expected  $\delta^{15}\text{N}$  of N<sub>2</sub>O produced through nitrification<sup>34</sup>. By contrast,  $\delta^{18}\text{O}$  does not exhibit a discernible relationship with per cent saturation, and with the exception of one sample, all  $\delta^{18}\text{O}$  values are consistently higher than the  $\delta^{18}\text{O}$  of tropospheric N<sub>2</sub>O (20.7‰, ref. 35).

Vertical profiles of carbon and oxygen isotope ratios at two stations in the central Arabian Sea are shown in Figure 12. 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<sub>2</sub>O minimum observed at 200–500 m at SS 3201 coincided with an intense SNM and a pronounced peak of  $\delta^{15}\text{N}$ -NO<sub>3</sub>. Preferential loss of lighter N<sub>2</sub>O to N<sub>2</sub> within this layer



**Figure 11.** Nitrogen and oxygen isotopic composition of N<sub>2</sub>O vs per cent saturation at the sea surface (depth < 5 m). Horizontal dashed lines indicate the composition of N<sub>2</sub>O in marine air<sup>35</sup>. Values with moderate saturation and  $\delta^{15}\text{N}$  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.*<sup>31</sup>).

evidently led to enrichments of  $^{15}\text{N}$  and  $^{18}\text{O}$  in residual N<sub>2</sub>O which are by far the greatest reported from any natural environment<sup>31</sup>. The N<sub>2</sub>O concentration minimum was embedded between two maxima, but the isotopic compositions of these N<sub>2</sub>O-rich layers were very different. Going upward from the OMZ, the  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  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  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  also decreased below SNM, their levels remained much higher than the tropospheric values down to 1500 m. A similar pattern was also seen at the mildly reducing SS 3204 although the  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  increases within the OMZ were smaller. An important aspect of the data is that the  $\delta^{15}\text{N}$  of NO<sub>3</sub> is consistently lower than that of N<sub>2</sub>O at depths exceeding ~ 200 m, and higher at shallower depths at both stations. This indicates that the intense N<sub>2</sub>O accumulation in the upper and lower parts of the



OMZ may be through different mechanisms. Greater enrichment of  $\delta^{15}\text{N}$  in  $\text{N}_2\text{O}$  relative to  $\text{NO}_3^-$  appears to be characteristic of denitrification. This pattern is most pronounced within  $\text{N}_2\text{O}$ -depleted SNM at SS 3201. Its persistence even below SNM at SS 3204 and at depths exceeding  $\sim 200$  m at SS 3204 suggests significant  $\text{N}_2\text{O}$  production through denitrification. This observation is consistent with the view that denitrification may lead to a net  $\text{N}_2\text{O}$  accumulation under certain conditions<sup>36</sup>.

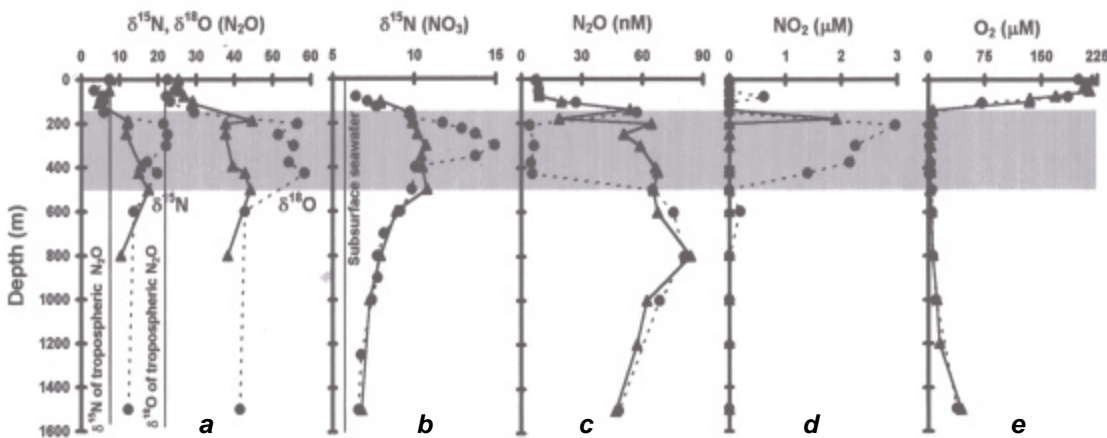
While the isotopically lighter  $\text{N}_2\text{O}$  in waters above the suboxic zone is apparently not produced by denitrification, the pathway  $\text{NH}_4^+ \rightarrow \text{NO}_2^- \rightarrow \text{N}_2\text{O}$  also cannot fully explain the observed data for two reasons. Firstly, the  $\delta^{15}\text{N}$  values are much higher than that reported for nitrification<sup>34</sup>. Secondly, the observed  $\delta^{18}\text{O}$  is much higher than the value for nitrification ( $< -3\text{‰}$ ) expected from  $\delta^{18}\text{O}$  of  $\text{H}_2\text{O}$  and  $\text{O}_2$  (ref. 37). A more likely pathway of  $\text{N}_2\text{O}$  production in the upper layer which can account for both the isotope and concentration data is a nitrification–denitrification coupling ( $\text{NH}_4^+ \rightarrow \text{NH}_2\text{OH} \rightarrow \text{NO} \rightarrow \text{N}_2\text{O}$ )<sup>38</sup>. Whatever be the mechanism of enhanced  $\text{N}_2\text{O}$  production in low  $\text{O}_2$  waters, the large temporal changes in the extent of the oxygen-deficient zones imply that the  $\text{N}_2\text{O}$  production rate in the Arabian Sea and in other similar areas may vary greatly with time, and this could have contributed significantly to changes in the atmospheric  $\text{N}_2\text{O}$  content revealed by the ice core data<sup>39</sup>.

Isotopic data from the Arabian Sea also have an important implication for the atmospheric  $\text{N}_2\text{O}$  budget. Analysis of stratospheric  $\text{N}_2\text{O}$  has shown large enrichments of heavier isotopes ( $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  values of  $\sim 21$  and  $35\text{‰}$ , respectively),

departures from tropospheric isotopic composition observed in the surface waters of the Arabian Sea clearly indicate that air–sea exchange cannot – given the heavy isotopic signature of  $\text{N}_2\text{O}$  derived from the stratosphere – allow the tropospheric budget of  $\text{N}_2\text{O}$  to be closed without invoking hitherto-unknown  $\text{N}_2\text{O}$  sources and sinks.

### Other trace gases

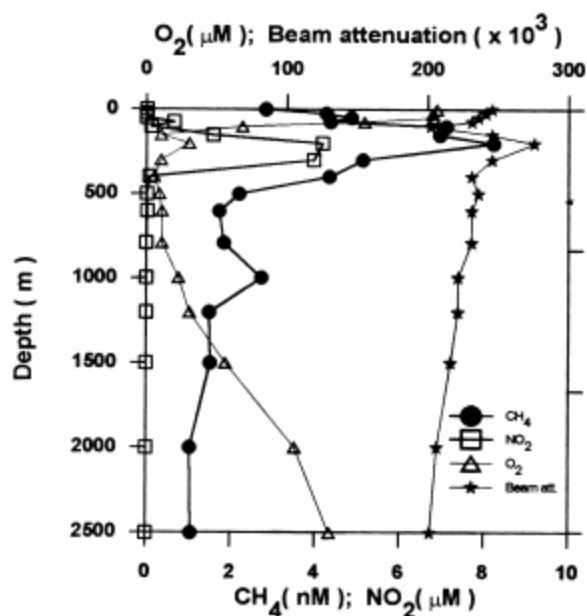
The Arabian Sea is also a region where the emission rate of  $\text{CH}_4$ , the second most important greenhouse gas, is several times higher than the global average<sup>41–43</sup>. However, unlike  $\text{N}_2\text{O}$  these emissions are not large enough to affect the global  $\text{CH}_4$  budget (the estimated flux of  $\sim 0.04 \text{ Tg C y}^{-1}$  is merely 0.01% of  $\text{CH}_4$  emission rate to the atmosphere from all sources<sup>44</sup>). A pronounced subsurface maximum in  $\text{CH}_4$  concentration, observed in most oceanic areas, is also found in the Arabian Sea. However, it seems to be intensified by the acute  $\text{O}_2$  deficiency (Figure 13), and may be formed *in situ* due to  $\text{CH}_4$  production within anoxic interiors of particles<sup>43</sup>. The coastal waters of the eastern Arabian Sea have generally high  $\text{CH}_4$  concentrations particularly close to the river mouths. But large near-bottom anomalies, such as those observed in areas of known hydrocarbon seepage, are not seen even in the inner shelf region, where the presence of gas charged sediments is shown by geophysical data<sup>45</sup>, indicating that sedimentary supply



**Figure 12.** Vertical profiles of  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  (‰ relative to air) of  $\text{N}_2\text{O}$  (a);  $\delta^{15}\text{N}$  of  $\text{NO}_3^-$  (b); and concentrations of  $\text{N}_2\text{O}$  (c),  $\text{NO}_2^-$  (d) and  $\text{O}_2$  (e) at stations SS 3201 ( $17^\circ\text{N}$ ,  $68^\circ\text{E}$ ; circles joined by dotted lines) and SS 3204 ( $19^\circ45'\text{N}$ ,  $64^\circ37'\text{E}$ ; triangles, joined by continuous lines). The shaded region represents secondary nitrite maximum at SS 3201. Vertical lines indicate  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  of tropospheric  $\text{N}_2\text{O}$  (a) and mean  $\delta^{15}\text{N}$  of  $\text{NO}_3^-$  in subsurface sea water<sup>27</sup> (b) (from Naavi *et al.*<sup>31</sup>).

and it is believed that the resultant large fluxes of  $^{15}\text{N}$  and  $^{18}\text{O}$  (400 and  $500 \text{ Tg N‰ y}^{-1}$ , respectively) from the stratosphere to the troposphere are balanced largely through exchange with the ocean where isotopically light  $\text{N}_2\text{O}$  may be produced by nitrifying bacteria<sup>26,40</sup>. However, opposing trends in  $^{15}\text{N}$  and  $^{18}\text{O}$  and modest

does not dominantly control  $\text{CH}_4$  distribution in coastal waters. Instead, the available data strongly suggest that coastal wetlands, particularly mangrove swamps, generate large amounts of  $\text{CH}_4$ , and probably make an important contribution through freshwater discharge to  $\text{CH}_4$  cycling in the coastal region<sup>43</sup>.



**Figure 13.** Vertical profiles of  $\text{CH}_4$  in relation to  $\text{NO}_2$ ,  $\text{O}_2$  and beam attenuation at SS 3441 ( $15^\circ\text{N}$ ,  $69^\circ\text{E}$ ) (from Jayakumar *et al.*<sup>43</sup>).

The Arabian Sea is also expected to contribute substantially to the fluxes of dimethyl sulphide (DMS) from oceans due to the presence of large coccolithophorid populations<sup>46</sup>. Being the main source of non sea salt sulphate in the atmosphere, DMS provides cloud condensation nuclei. Currently there is no published report on its cycling in the Arabian Sea. However, this deficiency is expected to be remedied soon with information generated during the JGOFS Arabian Sea Process Study.

### Concluding remarks

With an extremely delicate biogeochemical balance that exists in the oceanic  $\text{O}_2$ -deficient zones, areas such as the Arabian Sea will perhaps be among the first to react to potential anthropogenic perturbations such as global warming and increased nutrient/organic loading. Because of this it has been suggested that the Arabian Sea could serve as an ocean scale barometer of global climate change<sup>47</sup>. Any alterations in the rate of mid-depth water renewal or in subsurface oxygen demand may bring about large changes in chemical fluxes including those of the climatically important gases, thus providing a climatic feedback. Similarly, an expansion of the OMZ, particularly towards the coastal zone, may also have deleterious consequences on biological resources as evident from mass mortality of fish reported from the south-west coast of India<sup>48</sup>. It is still not clear as to how the suboxic ecosystem in the Arabian Sea will respond to changes induced by man. Future work must therefore focus on prediction of the magnitude and direction of these impacts.

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