

2.1.12 Carbon-Nitrogen Cycling in Northern Indian Ocean

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Introduction

Oceanography of the northern Indian Ocean is greatly influenced by the Asian landmass which bounds the Indian Ocean at rather low latitudes. The unique six-monthly reversals of the atmospheric and oceanic circulations, and the asymmetric distribution of the monsoon winds, rainfall and river runoff, bring about extremely large chemical and biological changes in the region in both space and time. For example, the Arabian Sea experiences excessive evaporation over precipitation and runoff, whereas in the case of the Bay of Bengal it is the other way around. Also, the strong summer monsoon winds cause extensive upwelling of nutrient-rich subsurface waters in the coastal regions of Somalia, Oman and Southwest India as well as in the open northwestern Arabian Sea. This supports a high rate of biological production. By contrast, upwelling is much weaker in the Bay of Bengal due to freshwater influx. Furthermore, while both the regions experience a pronounced oxygen (O_2) deficiency below the surface mixed

layer in the upper kilometer or so, the O₂ depletion is far more severe in the Arabian Sea. This leads to the development of reducing conditions under which bacteria carry out extensive conversion (denitrification) of the oxidized forms of nitrogen [mainly nitrate (NO₃⁻) ions] to molecular nitrogen (N₂). Indeed the Arabian Sea is one of only three sites in the open ocean where denitrification occurs in the water column on a large scale. The presence of several diverse biogeochemical regimes within a small area makes the northern Indian Ocean, particularly the Arabian Sea, a natural laboratory to investigate oceanic biogeochemical processes. Consequently, it has been recently subjected to extensive process studies by the international scientific community under JGOFS (Joint Global Ocean Flux Study). Results obtained during these surveys have made very significant additions to what had been known about this region previously, mostly as a result of efforts by scientists of the National Institute of Oceanography (NIO), Goa. In addition, investigations under LOICZ (Land-Ocean Interactions in the Coastal Zone) have also been initiated recently to study the role of continental margins in biogeochemical cycling in the Arabian Sea. This report highlights some results of the research carried out at NIO on carbon-nitrogen cycling in the northern Indian Ocean.

Oxygen-deficiency and Denitrification

Spectrophotometric measurements show that O₂ levels between approximately 150 and 1000m depths in the northern and central parts of the Arabian Sea are lower than 5 μM (~0.1 ml/l corresponding to ~2% of surface-water concentrations). The entire O₂-deficient layer is not strongly reducing, however, as evident from the distribution of nitrite (NO₂⁻), an intermediate which accumulates in the water column during denitrification. An abrupt build-up

of NO_2^- occurs when the O_2 concentrations fall below $1 \mu\text{M}$ ($\sim 0.02 \text{ ml/l}$) (Figure 1). Such a strong dependence of redox processes to minor changes in ambient O_2 levels implies an extremely sensitive ecosystem with a delicately-poised biogeochemical balance which is expected to react rapidly to anthropogenic perturbations.

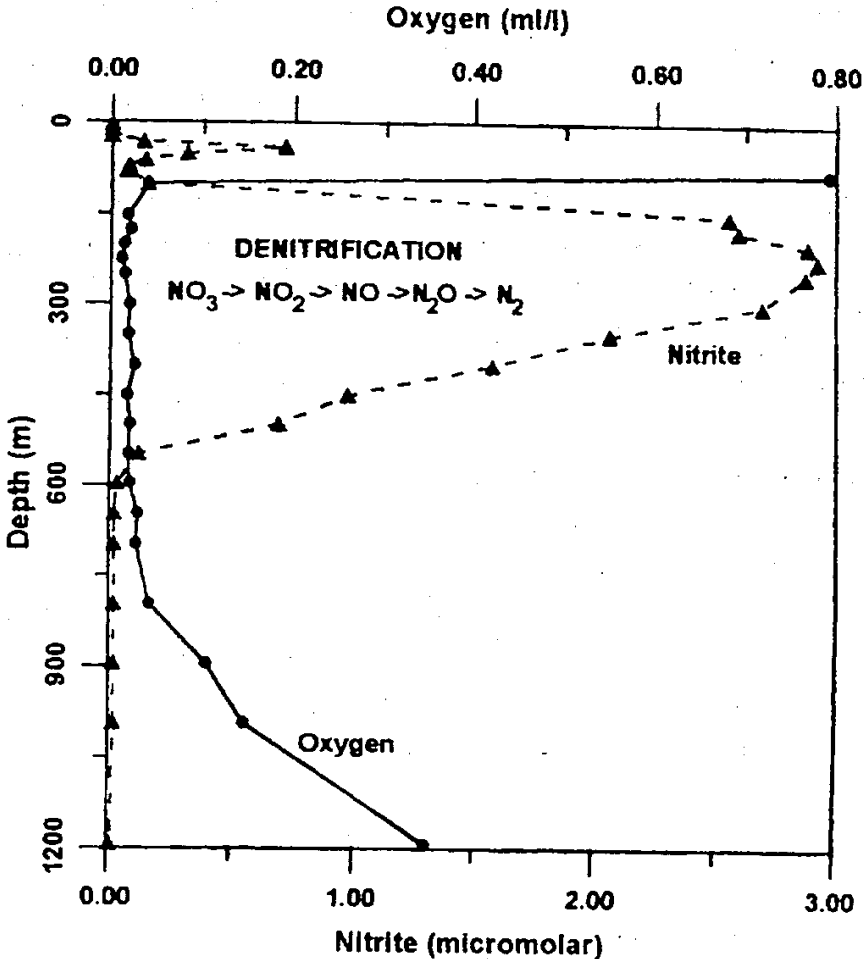


Figure 1: Vertical profiles of dissolved oxygen and nitrite at the US JGOFS Sta. N7 (19°N , 67°E , R. V. Thompson Cruise 39)

Quantification of denitrification rates in the Arabian Sea, needed for global budgeting of nitrogen, has been made following physico-chemical and biochemical techniques. In the first approach, deficiencies in NO_3^- concentration relative to those expected from some other chemical tracers (such as O_2) are estimated, and these "nitrate deficits" are combined with computed current field and with suitable

diffusion coefficients to work out the rate at which the deficits are exported out of the reducing zone. Assuming a steady state this should be the same as the rate at which the deficits are produced [1]. In the biochemical method, the activity of the enzymes which control respiration [electron transport system (ETS)] is measured by extracting the enzymes from microplankton and incubating them with an electron acceptor and with the natural substrates of the enzyme system. The potential rate so obtained is then converted into denitrification rate using suitable factors. In spite of the differences between and the uncertainties inherent in the two methods, they have yielded remarkably similar denitrification rates - around 30 Tg N y⁻¹ (1Tg=10¹² g). This is about 1/3 of the estimated global water column denitrification rate.

An anomalous feature of the Arabian Sea oxygen minimum zone (OMZ) is that the zones of the highest primary production and the most vigorous denitrification are geographically separated here [2]. Estimates of the water-column respiration rate based on ETS data also show that the highest rates occur in the oligotrophic central Arabian Sea and that these 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 [3-5]. Another related paradox is that the respiration rates are counter-intuitively higher in the suboxic than in the oxic parts of the water column in the Arabian Sea. In fact, the rates of respiration within the denitrifying layer are so high and the bacteria that carry out degradation proliferate to such an extent that there is a marked increase in water turbidity (Figure 2). It is still not clear as to what produces this bacterial biomass maximum under energetically less favourable conditions, and what is the source of carbon that sustains

the observed high respiration rates, but two possible explanations have been offered: (a) Denitrifiers may efficiently utilize the dissolved organic matter supplied to the OMZ [3,4] either quasi-horizontally from the continental margins [6] or vertically through diurnal migrations of organisms particularly the mesopelagic fish such as myctophids [7]. Significantly, the Arabian Sea contains huge stocks (~100 million tonnes) of myctophids which are specially adapted to low ($<0.1 \text{ ml l}^{-1}$) ambient O_2 levels [8], but 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 [9]. 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.

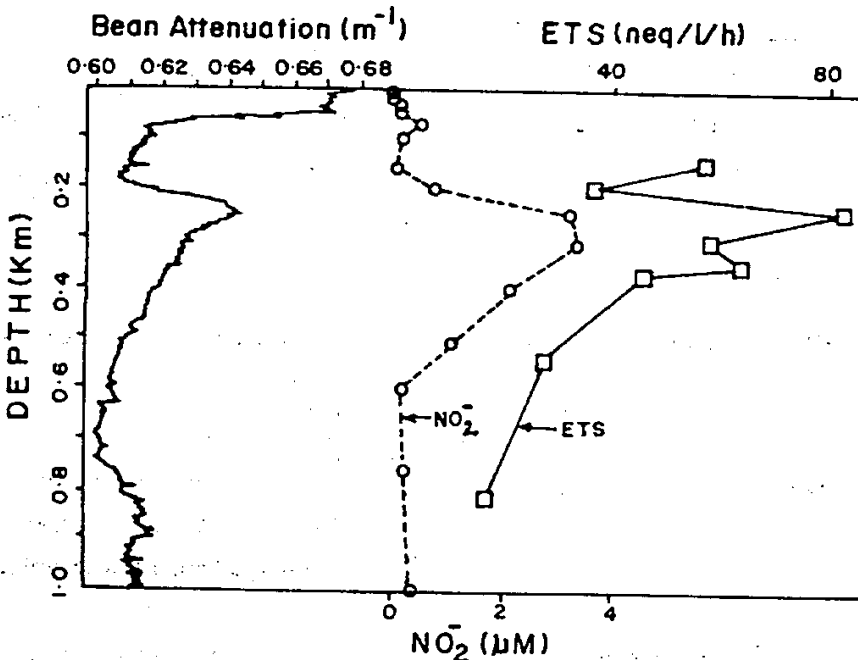


Figure 2: Vertical profiles of nitrite and ETS activity in relation to beam attenuation at $18^{\circ}14'N$, $70^{\circ}25'E$.

In addition to the perennial denitrifying layer found in the central Arabian sea, reducing conditions also develop in near-bottom waters of the inner continental shelf along the central and southwestern coasts of India, as revealed by observations recently conducted under LOICZ (Figure 3). However, this is a seasonal phenomenon, confined to the southwest monsoon when the nutrient-rich, O_2 -poor waters upwell and cover large parts of the shelf. Fertilization of euphotic zone leads to very high rates of primary production which, in turn, cause a complete O_2 consumption in the upwelled water. And as the latter is capped by a thin (~10 m) lid of fresher water originating from river runoff and local precipitation, the organic matter decay involves denitrification not seen at such shallow depths anywhere else in the ocean.

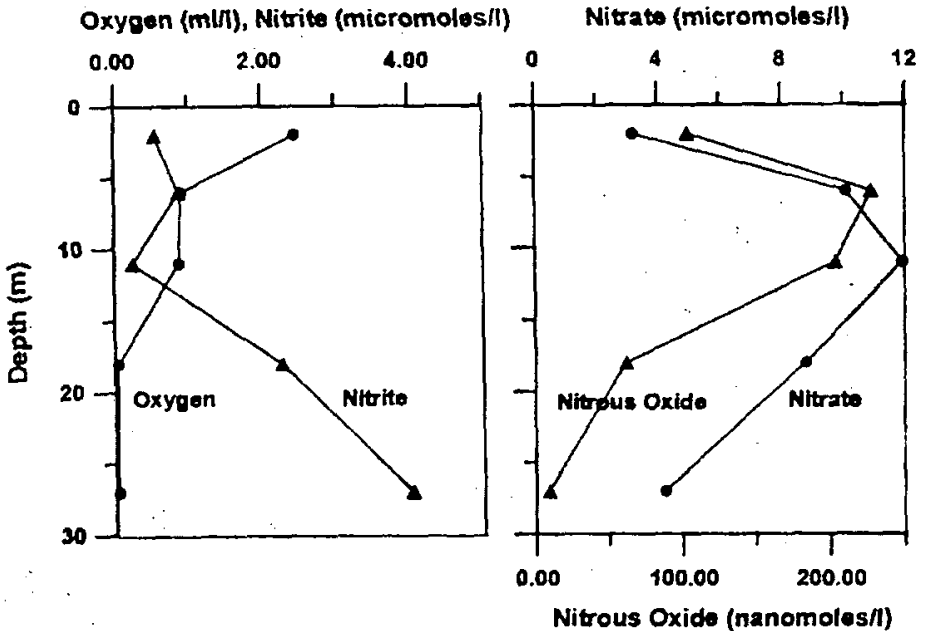


Figure 3: Vertical profiles of oxygen, nitrite, nitrate and nitrous oxide indicating the occurrence of shallow-water denitrification at a station ($13^{\circ}07.6'N$, $73^{\circ}37.9'E$) located off Mangalore during the southwest monsoon.

Unlike the Arabian Sea, the Bay of Bengal does not appear to be an active water-column denitrification site even though the concentrations of O_2 at its minimum are only slightly lower as compared to the Arabian Sea [10]. Interestingly, in spite of the lower biological productivity the sinking flux of particulate organic matter, as measured by sediment traps [11], is significantly higher in the Bay of Bengal relative to the Arabian Sea, but the subsurface respiration rates are lower as indicated by the ETS data [5]. An important inference that can be drawn from these apparently contradictory data sets is that the interaction of biogenic matter with the abundant terrigenous particles of fluvial origin may lead to an incorporation of organic matter into dense particles resulting in its rapid removal to the seafloor and lower decomposition rates in the water column. This may also account for weak north-south gradients in O_2 and carbon dioxide (CO_2) [12].

Nitrous Oxide (N_2O) 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 [$O(^1D)$], which should be equal to the natural flux of N_2O to the atmosphere from all sources, is about 12 Tg N_2O-N y^{-1} . Of this at least half seems to come from the oceans [13]. 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. Large supersaturations of N_2O have been observed in the surface waters of the Arabian Sea, especially within the three

upwelling zones, resulting in a very high rate of N_2O emission [14, 15]. 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 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 (Figure 4). Thus, the Arabian Sea contains sites located very close to each other, vertically as well as horizontally, which serve both as strong sources and strong sinks of N_2O leading to a turnover which may be the most rapid on our planet [14, 15].

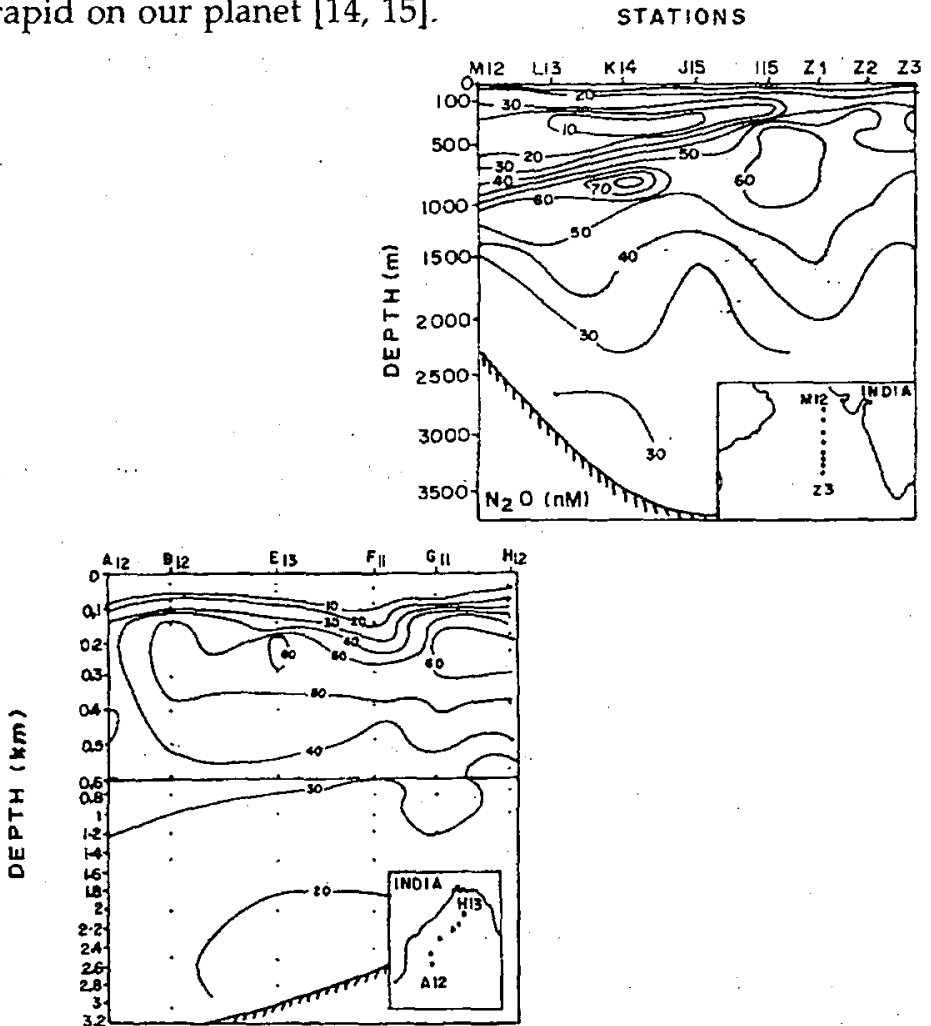


Figure 4: Vertical sections of nitrous oxide (nM) in the Arabian Sea (upper panel) and Bay of Bengal (insets show the station locations).

The rate of N_2O turnover is particularly high in the coastal upwelling zone off southwestern India during the southwest monsoon, where some of the highest concentrations of N_2O as well as the steepest vertical gradients in the world have been observed (Figure 3). As will be shown later the isotopic signatures of N_2O in this region are also quite different from those generally seen in the oceans [15].

As compared to the Arabian Sea, the surface saturation and consequently sea-to-air flux of N_2O in the Bay of Bengal are substantially smaller due to the strong thermohaline stratification (Figure 4). Moreover, due to the absence of bulk water-column denitrification, there is no water-column sink of N_2O . And since the mid-depth O_2 levels are most conducive for N_2O build-up, this region serves as one of the largest oceanic reservoirs of N_2O [16].

Isotopic Fractionation During Denitrification

Measurement of natural abundance of stable isotopes of nitrogen and oxygen has provided extremely useful information for understanding pathways of biogeochemical transformations and quantifying their rates. 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 the heavier isotopes. For example, of the two natural isotopes of nitrogen with mass numbers of 14 and 15 (^{14}N and ^{15}N), NO_3^- ions containing ^{14}N are lost more easily than those containing ^{15}N during denitrification. Consequently N_2 , the end product of denitrification, gets depleted with ^{15}N while an enrichment of this isotope takes place in the residual NO_3^- (Figure 5). These data can be used to calculate the isotopic fractionation factor (ϵ)

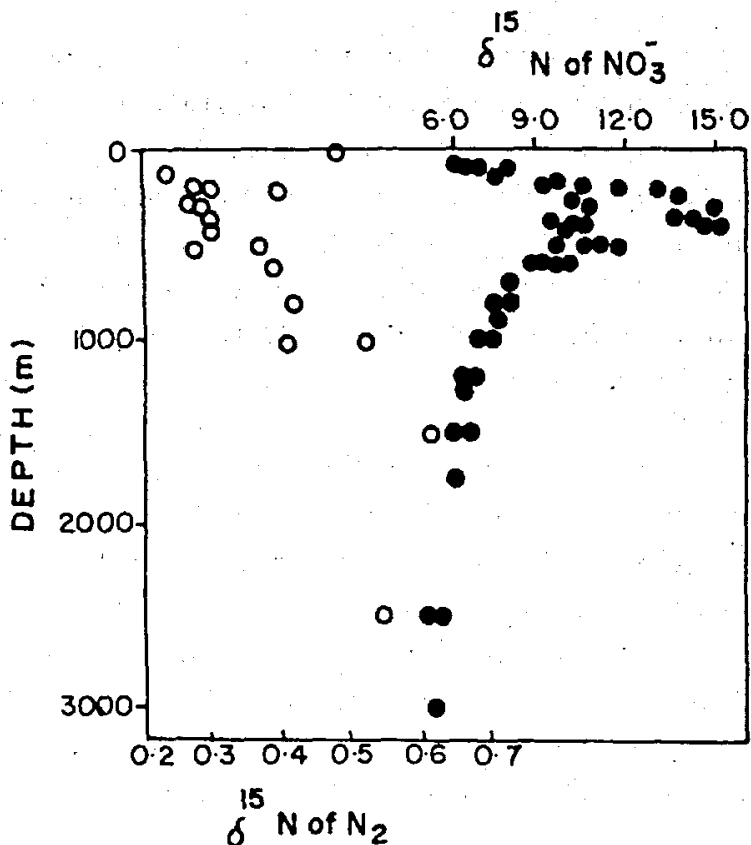


Figure 5: Nitrogen isotopic composition (expressed as ‰ $\delta^{15}\text{N}$ relative to atmospheric N_2) of nitrate (solid circles) and of molecular nitrogen (open circles) plotted versus depth in the Arabian Sea suboxic zone.

during denitrification from simple advection-reaction and diffusion-reaction models, yielding ϵ values of 22 and 25 per mil, respectively [17]. 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.

Another very interesting aspect of the isotopic data is the steep decrease in $\delta^{15}\text{N}$ of NO_3^- observed above the denitrifying layer (Figure 5), a trend which is exactly opposite to that seen outside the suboxic zone. Although this feature can result from an input of unaltered NO_3^- horizontally advected from outside the suboxic zone, this is an unlikely scenario, and a more plausible source of

isotopically light NO_3^- to the surface layer may be nitrogen fixation. Assuming this to be the case, the extent of nitrogen fixation could be estimated from simple isotope mass balance. The results suggest that a whopping 40% of the NO_3^- present at the bottom of the surface mixed layer might be derived through fixation. The estimated nitrogen fixation rate for the suboxic Arabian sea ($\sim 6 \text{ Tg N y}^{-1}$) is roughly 1/4 of the water-column denitrification rate [17]. Thus, in spite of a high rate of nitrogen fixation, the Arabian Sea still serves as a net sink of combined nitrogen.

Changes in the isotopic compositions of nitrogen and oxygen [that has two major isotopes with mass numbers of 16(^{16}O) and 18(^{18}O)] in N_2O are even more dramatic: Within the core of the denitrifying layer $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ exhibit the highest values observed in any natural environment; however, just above this layer, isotopically light N_2O accumulates in high concentrations (Figure 6), implying that N_2O emitted to the atmosphere from this region cannot be very heavy [15,18]. Analysis of the N_2O -rich upwelled water off the southwest coast of India reveals contrasting isotopic 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. This implies that some other hitherto poorly understood sources of N_2O must exist on land. The contrasting isotopic trends and modest departures from the tropospheric composition in the N_2O -rich upwelled waters off the Indian coast also indicate that N_2O production in this region cannot be through either nitrification or denitrification alone. Instead, a novel coupling between these processes represented by the pathway $\text{NH}_4^+ \text{NH}_2\text{OH} \text{NO} \text{N}_2\text{O}$ can explain both the concentration and isotopic data [15].

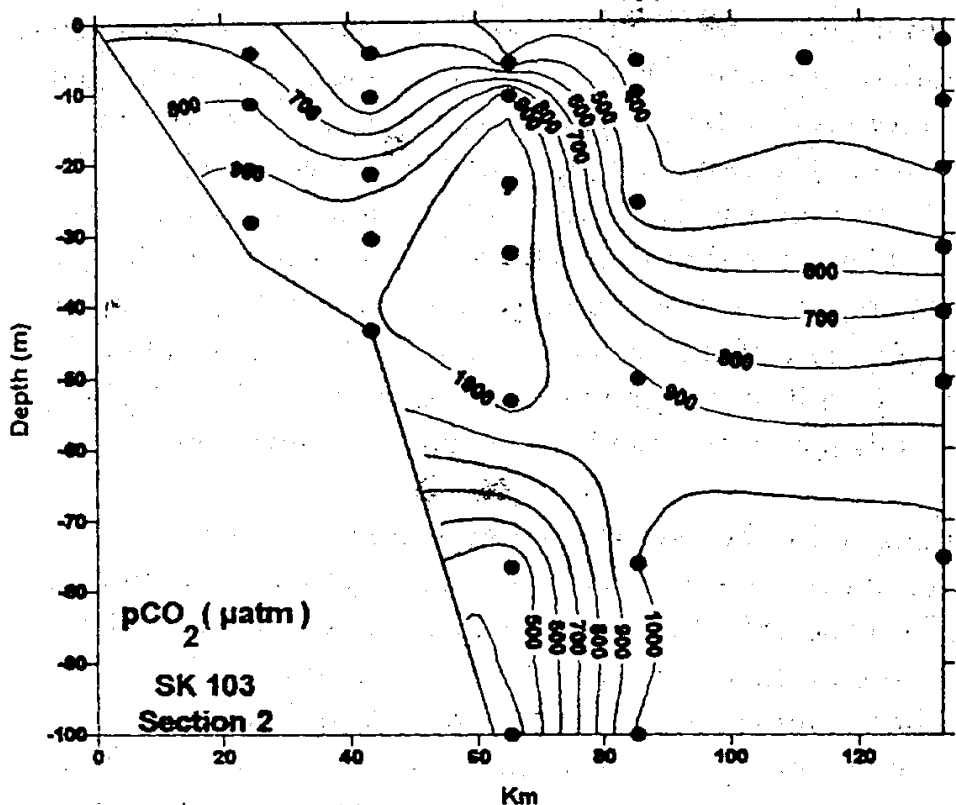


Figure 6: Vertical profiles of $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ (‰ relative to air) in nitrous oxide (a), and concentrations of nitrous oxide (b) and nitrite (c) at 17°N , 68°E (circles joined by dotted lines) and $19^\circ 45'\text{N}$, $64^\circ 37'\text{E}$ (triangles, joined by continuous lines).

Distributions and Fluxes of Carbon Dioxide (CO_2) and Methane (CH_4)

The oceans play an extremely important role in regulating the atmospheric CO_2 content. The "biological pump", involving the fixation of inorganic carbon by plants into particulate organic matter, which undergoes sedimentation, leads to an export of carbon from the surface to the deep sea. It makes the deep sea the repository of the bulk (>90%) of carbon in the biosphere-atmosphere-hydrosphere system, and keeps the atmospheric CO_2 at moderately low levels: in the absence of this mechanism the atmospheric CO_2 content would have been several fold higher and consequently the earth would have been much warmer.

The rate of such biological removal of CO_2 is expected to be the highest in oceanic areas of high primary production. However, the process which is predominantly responsible for the fertilization of the surface ocean with essential nutrients enhancing biological production, viz. upwelling of deep waters, also pumps CO_2 to the surface waters. Therefore, whether a given area acts as a net sink or a net source of atmospheric CO_2 depends upon the balance between the two opposing effects.

In the Arabian Sea, supply of CO_2 through upwelling of deep waters greatly overwhelms biological removal. Indeed the partial pressure of carbon dioxide ($p\text{CO}_2$) in surface waters within the three upwelling zones is among the highest reported from the oceans (e.g. Figure 7). Even outside the upwelling zone, the surface water $p\text{CO}_2$ is

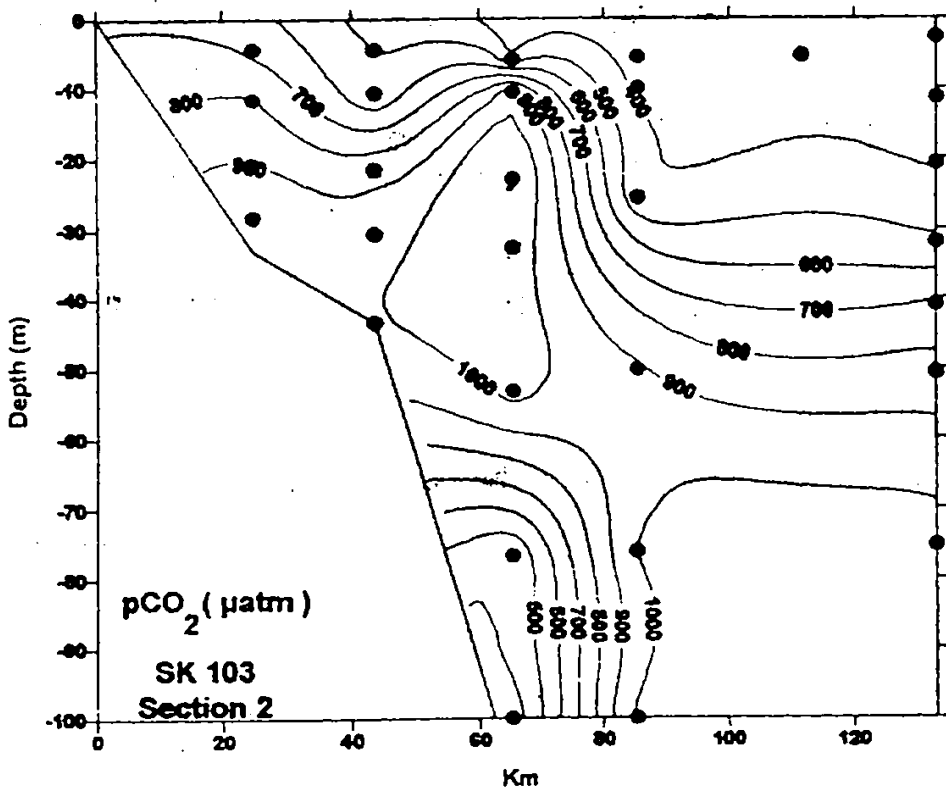


Figure 7: Vertical section of $p\text{CO}_2$ across the shelf off Cochin during the southwest monsoon.

always higher than that in the atmosphere, leading to a net flux of CO_2 from the ocean to the atmosphere. This has been quantified as 45 Tg C y^{-1} [19]. On the other hand, in the Bay of Bengal, which experiences nearly-estuarine conditions, the strong thermohaline stratification suppresses pumping of CO_2 from the deep sea to the surface layer. And as the euphotic zone is substantially fertilized through river discharge and atmospheric inputs of nutrients (a significant fraction of which is of anthropogenic origin), there is a net removal of CO_2 through biological activity making the Bay of Bengal a unique sink of atmospheric CO_2 of an estimated strength of 20 Tg C y^{-1} [20].

In addition to the contrasting surface water CO_2 fields, there are three other important differences between the CO_2 distributions in subsurface waters of the two arms of the northern Indian Ocean [12]. First, the mid-depth $p\text{CO}_2$ maximum is more pronounced in the Arabian Sea due to the more acute O_2 deficiency and resultant denitrification. Second, as stated earlier, the north-south gradients in total CO_2 are very weak in the Bay as a result of lower subsurface respiration rates (Figure 8). Third, the deep-water total CO_2 concentrations are somewhat higher in the Bay, reflecting different routes of deep water supply to the two basins.

The Arabian Sea has also been found to be a region where the emission rate of CH_4 , the second most important greenhouse gas, is several times higher than the global average. However, unlike N_2O these emissions are not large enough to affect the global CH_4 budget (the estimated flux of $\sim 0.04 \text{ Tg C y}^{-1}$ is merely 0.01% of CH_4 emission rate to the atmosphere from all sources [21]). A pronounced subsurface maximum in CH_4 concentration, observed in most oceanic areas, is also found in the Arabian Sea. However, it seems to be intensified by the acute O_2

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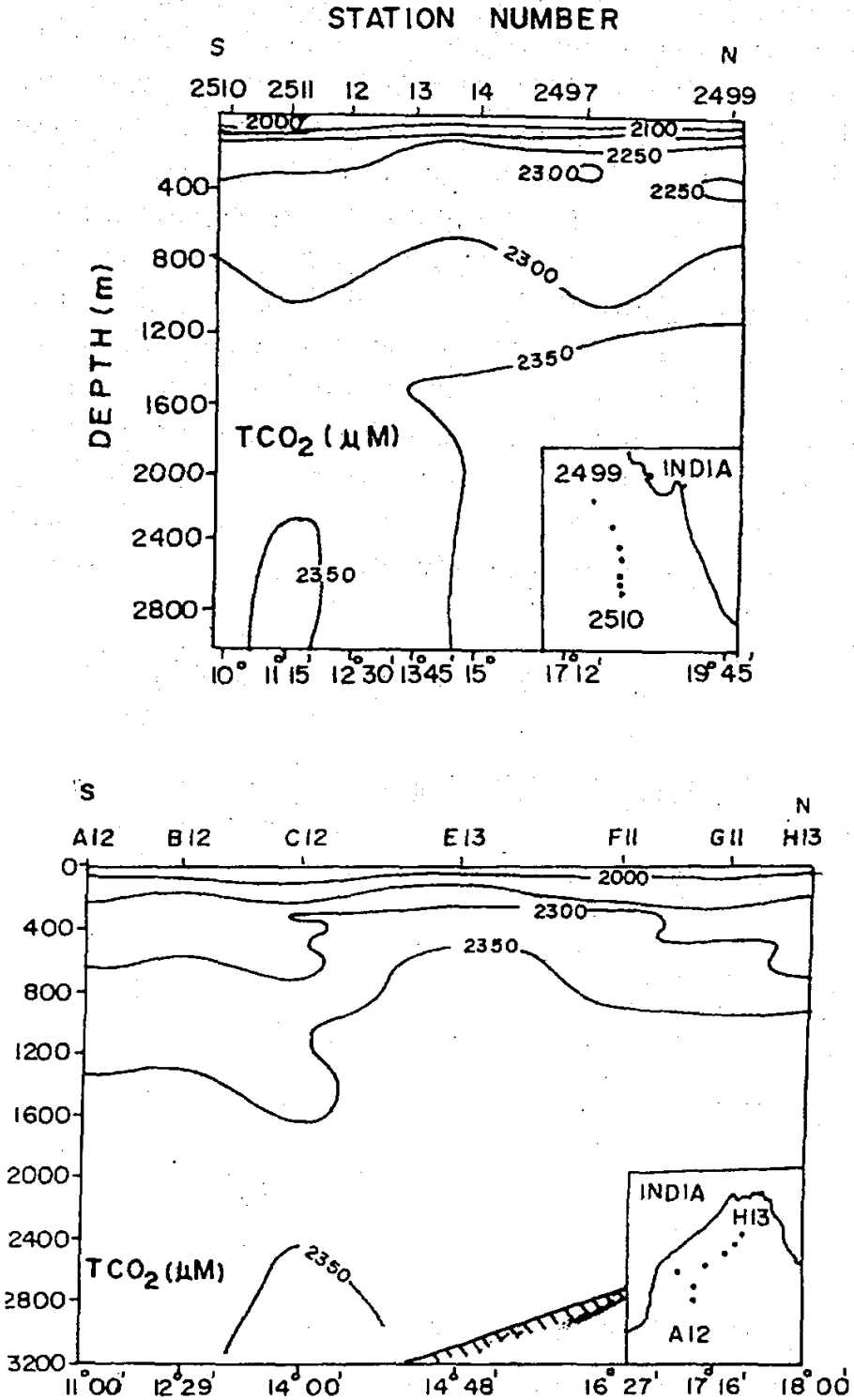


Figure 8: A comparison of vertical sections of total carbon dioxide in the Arabian Sea (upper panel) and Bay of Bengal (lower panel).

deficiency (Figure 9), and may be formed in situ due to CH_4 production within anoxic interiors of particles [22]. The coastal waters of the eastern Arabian Sea have generally high 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 indicated by geophysical data [23], indicating that the sedimentary supply does not dominantly control CH_4 distribution in coastal waters. Instead, the available data strongly suggest that the coastal wetlands, particularly mangrove swamps, generate large amounts of CH_4 , and probably make an important contribution through freshwater discharge to CH_4 cycling in the coastal region [22].

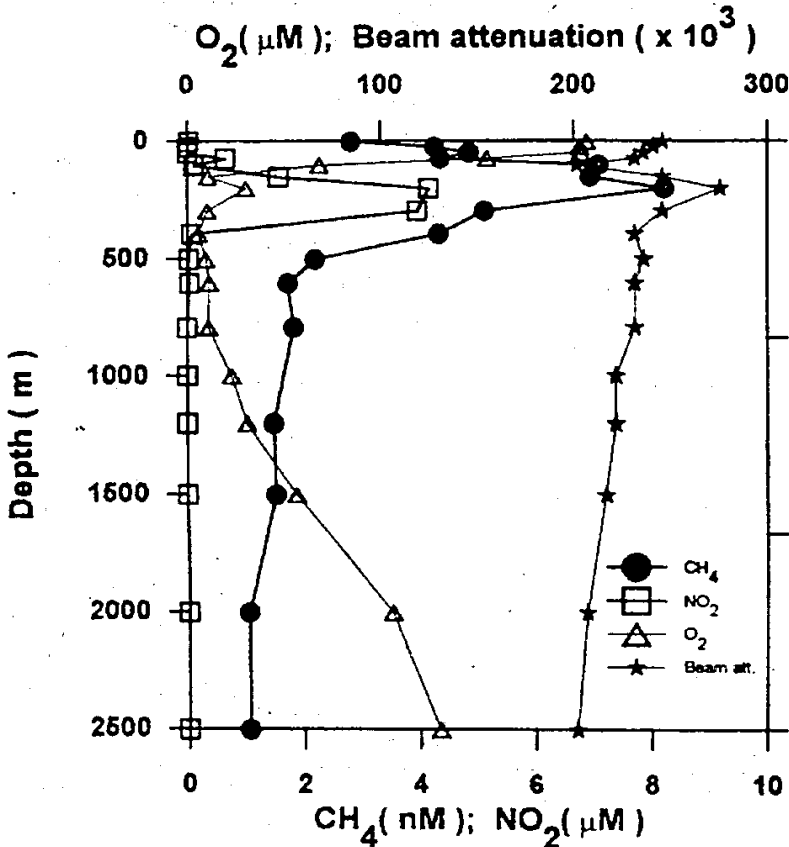


Figure 9: Vertical profiles of methane in relation to nitrite, oxygen and beam attenuation at 19°N, 69°E.

Conclusion

The unique geographical setting and climate of the Arabian Sea make the biogeochemical cycling in this region globally significant. The most important feature is the acute O₂ deficiency at intermediate depths and the resultant denitrification estimated to occur at a rate of 30 Tg N h⁻¹. This process has the potential to alter the oceanic combined nitrogen inventory, biological productivity and atmospheric CO₂ content on the geological time scale. The O₂ deficiency also affects the production and consumption of other climatically important gases such as N₂O and CH₄. However, there are several important issues concerning the Arabian Sea biogeochemistry which are yet to be adequately resolved. One of these is the poorly-constrained carbon budget of the OMZ. The greatest uncertainty in this budget is perhaps due to the unknown fluxes associated with diurnal vertical 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, which is extremely relevant in the context of the Arabian Sea but has attracted little attention so far, is the microbiology of the suboxic ecosystem. The microbial community apparently bring about extremely large changes in chemical fluxes in response to minor changes in ambient environmental conditions (particularly O₂ levels), but the mechanisms of this response are not known. These aspects should be investigated using modern immunological and molecular techniques. Similarly, while the limited isotopic studies carried out so far have yielded some very intriguing results, the full potential of this approach is yet to be realized. Experimental work involving isotopic tracers may help in gaining insights into the mechanisms of biogeochemical transformations and in constraining their rates. In particular, the extent of nitrogen

fixation in this area needs to be more precisely quantified. Another poorly-understood aspect of biogeochemistry of 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 (including time series) measurements in the water column and sediments. The ultimate goal of future research should be the development of realistic models. At present we only have limited budget models. The next step should be the development of 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 region 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.

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