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# Coastal versus open-ocean denitrification in the Arabian Sea

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## Abstract

The Arabian Sea contains one of the three major open-ocean denitrification zones in the world. In addition, pelagic denitrification also occurs over the inner and mid-shelf off the west coast of India. The major differences between the two environments are highlighted using the available data. The perennial open-ocean system occupies two orders of magnitude larger volume than the seasonal coastal system, however, the latter offers more extreme conditions (greater nitrate consumption leading to complete anoxia). Unlike the open-ocean system, the coastal system seems to have undergone a change (i.e., it has intensified) over the past few decades presumably due to enhanced nutrient loading from land. The two systems also differ from each other with regard to the modes of nitrous oxide ( $\text{N}_2\text{O}$ ) production: in the open-ocean suboxic zone, an accumulation of secondary nitrite ( $\text{NO}_2^-$ ) is invariably accompanied by depletion of  $\text{N}_2\text{O}$  whereas in the coastal suboxic zone high  $\text{NO}_2^-$  and very high  $\text{N}_2\text{O}$  concentrations frequently co-occur, indicating, respectively, net consumption and net production of  $\text{N}_2\text{O}$  by denitrifiers. The extents of heavier isotope enrichment in the combined nitrate and nitrite ( $\text{NO}_3^- + \text{NO}_2^-$ ) pool and in  $\text{N}_2\text{O}$  in reducing waters appear to be considerably smaller in the coastal region, reflecting more varied sources/sinks and/or different isotopic fractionation factors.

## 1 Introduction

Being a polyvalent element, the speciation, transformations and fluxes of nitrogen in aquatic environments are controlled by the ambient oxygen ( $\text{O}_2$ ) concentration. As seawater is generally oxygenated, fixed nitrogen in the ocean largely ends up in the most oxidized (+5) state, viz. nitrate ions ( $\text{NO}_3^-$ ), and it is only in a few well-demarcated regions that a part of the water column gets almost completely stripped of  $\text{O}_2$  to allow the microbial conversion of  $\text{NO}_3^-$  to molecular nitrogen ( $\text{N}_2$ ); this process, denitrification, is the most important pathway of losses of fixed nitrogen, and thus a key player in

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the nitrogen budget (Deuser, 1973; Hattori, 1983; Codispoti and Christensen, 1985). In the Atlantic and Pacific Oceans, such  $O_2$ -deficient zones (ODZs) occur at mid-depths beneath the productive tropical eastern boundary upwelling zones. What distinguishes the Indian Ocean from the two other oceans is that the most intense ODZ here is located in the northern region, especially in the Arabian Sea. This anomaly, like other distinguishing features of the Indian Ocean, arises from its unusual geography, i.e. mainly the presence of Asian landmass that restricts its northern expanse to the tropics and, to a smaller extent, a porous eastern boundary (openings between the Indonesian islands) which allows exchange of water with the Pacific Ocean at low latitudes. The resultant circulation is not conducive for the development of biologically productive upwelling centres off the coasts of Myanmar and Australia similar to those found off the west coasts of Africa and the Americas. Instead, the most intense upwelling and consequently the highest rates of primary production (PP) at the surface and associated remineralization at depth occur along the northwestern boundary of the Indian Ocean (the Somali and Arabian coasts). Secondly, despite some production of intermediate waters in the Persian Gulf and the Red Sea, subsurface water renewal in the Indian Ocean occurs largely through advection from the south. The waters derived from the Southern Hemisphere gradually lose  $O_2$  and accumulate products of metabolism ( $CO_2$ , nutrients) during their northward flow. Thus, a lower supply and an enhanced  $O_2$  demand combine to produce very intense  $O_2$  deficiency (Winkler  $O_2 < 0.1 \text{ mL L}^{-1}$ ;  $\sim 4 \mu\text{M}$ ) within a very wide depth range ( $\sim 100/150$  to  $1000 \text{ m}$ ) in the north, particularly in the Northwestern Indian Ocean (Wyrski, 1971; Sen Gupta and Naqvi, 1984; Naqvi, 1987).

Due to the semi-enclosed nature of the North Indian Ocean, the OMZ impinges upon a very large area of the continental margin: bottom waters with  $O_2 < 0.5 \text{ mL L}^{-1}$  ( $22 \mu\text{M}$ ) and  $< 0.2 \text{ mL L}^{-1}$  ( $9 \mu\text{M}$ ), are estimated to cover about  $1.15 \times 10^6$  and  $0.76 \times 10^6 \text{ km}^2$  of the marginal seafloor in the region, which amount to as much as 59 and 63%, of the corresponding global areas (Helly and Levin, 2004). Moreover, littoral countries of the North Indian Ocean approximately account for a quarter of the world's human population, which in conjunction with the ongoing rapid economic growth makes the

region's coastal environments experiencing O<sub>2</sub>-deficiency highly vulnerable to human impact. Despite this vulnerability, most previous studies on nitrogen transformations in suboxic waters focused on the open ocean (Bange et al., 2005, and references therein), and it is only in recent years that significance of coastal processes is increasingly being appreciated (Naqvi et al., 2000, 2006a). We describe here factors that differentiate the open-ocean and coastal suboxic zones making use of a variety of new and some published data.

## 2 Processes of formation of coastal and open-ocean suboxic<sup>1</sup> zones

As stated above, the most intense ODZ, as inferred from the occurrence of a secondary nitrite (NO<sub>2</sub><sup>-</sup>) maximum (SNM), is located in the generally most productive northwestern part of the Indian Ocean. However, within the Arabian Sea itself, suboxic conditions are not associated with the upwelling systems of Somalia and Arabia; instead, the SNM zone extends toward the southwest into the central Arabian Sea from the northwestern Indian shelf, a region of relatively low PP (Fig. 1a; Naqvi, 1991). This is believed to arise from a more effective subsurface-water renewal along the Arabian Sea's western boundary through advection from the south (given that the cross-equatorial exchange of subsurface waters is largely confined in the western Indian Ocean – Swallow, 1984) as well as from the Red Sea and the Persian Gulf. Moreover, the dominance of upper-layer flow by meso-scale eddies, which account for the bulk of the kinetic energy (Flagg and Kim, 1998) and extend to the core of the suboxic zone, may facilitate greater downward diffusion of O<sub>2</sub> from the surface in the west. In contrast, the SNM coincides with the zone of the lowest kinetic energy and reduced vertical penetration of the eddy field (Kim et al., 2001). In addition to these physical factors, the availability and utilization

<sup>1</sup>We consider “suboxic” to be synonymous with “denitrifying”, operationally defined by the existence of the SNM. In the Arabian Sea, as in the eastern Pacific, the SNM is confined to the depth range where colorimetric O<sub>2</sub> is below ~0.015 mL L<sup>-1</sup> (~0.7 μM) (Winkler O<sub>2</sub> < ~0.1 mL L<sup>-1</sup> (~4 μM); Cline and Richards, 1972; Morrison et al., 1999).

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tion of nutrients by phytoplankton and the subsequent vertical flux of organic matter must also contribute to the observed O<sub>2</sub> distribution. Kim et al. (2001) opined that the route of offshore transport of the nutrient-rich upwelled water (occurring predominantly through filaments and plumes) is such that the denitrification zone receives more nutrients/organic matter than the regions located to its south and west. They emphasized the importance of the Ras al Hadd Jet that transports upwelled water first along the northeast Omani coast and then away from the coast off the cape it has been named after. Nutrient distributions during the upwelling season (e.g. for NO<sub>3</sub><sup>-</sup>; Fig. 1b) do indeed indicate long-distance (≥1000 km) transport of the upwelled water reaching well within the region of the most intense O<sub>2</sub> deficiency, but the generally-observed gradual offshore decrease in surface nutrient concentration is not supportive of this view.

Recent results of modeling (Wiggert et al., 2006) as well as observations (Naqvi et al., unpublished manuscript) suggest that, contrary to the prevalent belief, PP in the western Arabian Sea might sometimes be limited by iron instead of nitrogen during the southwest (SW) monsoon. These results have important implications for the composition of phytoplankton and the vertical scale of organic matter degradation. Iron deficiency has been known to cause an increase in ratio of Si:N uptake by diatoms (Hutchins and Bruland, 1998) facilitating greater offshore transport of NO<sub>3</sub><sup>-</sup>. A more rapid depletion of silicate is expected to cause a shift in phytoplankton community structure with increasing abundance of smaller autotrophs offshore, which is in accordance with observations (Garrison et al., 1998). During the northeast (NE) monsoon the central Arabian Sea experiences convective mixing that penetrates, at the most, to a depth of 125 m (Banse, 1984, 1987). The depthwise nutrient distribution in the region is such that vertical mixing brings up substantial amounts of NO<sub>3</sub><sup>-</sup> to the euphotic zone but not much silicate, thereby limiting diatom productivity (Naqvi et al., 2002). Thus, PP in the open central Arabian Sea seems to be dominated by small, non-diatomaceous autotrophs during both the SW and NE monsoons. The organic matter produced by these organisms would be degraded at shallower depths relative to that produced by diatoms. Therefore, one would expect the average depth of remineralization of ma-

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terial exported from the surface layer to shoal up with increasing distance from the coast, such that more material is degraded close to the core of the  $O_2$  minimum zone in the offshore region. This is consistent with the observed  $O_2$  distribution (Naqvi et al., unpublished manuscript).

5 The development of suboxic conditions over the Indian shelf is related in a general way to the prevalence of large-scale, mesopelagic, open-ocean  $O_2$  deficiency, because the latter is the source of water that upwells over the Indian shelf during the SW monsoon. Nevertheless, the open-ocean and coastal suboxic zones are not contiguous. This is due to the presence of the West India Undercurrent (WIUC) that flows north-  
10 ward while the surface flow is toward the south. The WIUC may be identified just off the continental shelf/slope from the distribution of temperature (upward sloping of isotherms at the top of this feature and downward tilt close to its bottom; Fig. 2a), and even more clearly from those of salinity and  $O_2$  (Figs. 2b, c). Note that the water derived from the south has lower salinity and slightly higher  $O_2$  content. As judged by the  
15 35.4 salinity contour, the influence of the undercurrent, at its peak, extends vertically down to approximately 400 m depth and horizontally up to 200 km from the continental slope at  $15^\circ$  N latitude (Fig. 2b). Even though seasonally variable, the WIUC is very important for determining the redox status of subsurface waters since it is a source of  $O_2$  to the otherwise suboxic mesopelagic zone that prevents the water from turning  
20 denitrifying off the continental margin probably as far north as  $17^\circ$  N latitude. Consequently, as reflected by the distribution of  $NO_2^-$  (Figs. 2d), denitrification intensifies away from the coast. This pattern is opposite of that observed in the two other major oceanic suboxic zones, especially off Peru-Chile, where the poleward undercurrents, in fact, support bulk of the denitrification (Codispoti et al., 1989). This difference probably  
25 owes to a lower respiration rate within the WIUC, which, in turn, may be caused by two factors. First, unlike its counterpart off Peru-Chile the WIUC does not occur over the shelf but along the continental slope, and secondly, except in the most southern part, upwelling along the west coast of India is by and large confined to a narrow strip over the inner shelf such that surface waters directly overhead of the WIUC are not very

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productive. As the water upwells and moves shoreward, rapid increase in respiration depletes its already low  $O_2$  content, culminating in the seasonal development of reducing conditions (denitrification followed by sulphate ( $SO_4^{2-}$ ) reduction) over the mid- and inner-shelf regions (e.g. Fig. 3) covering a wide latitudinal range (between at least 12 and 20° N, probably extending further north to the Pakistani coast).

### 3 Seasonality of $O_2$ deficiency

The main difference between the open-ocean and coastal suboxic zones is that while the former is perennial, the latter occurs only during and shortly after the SW monsoon. The open-ocean suboxic zone is also influenced by monsoonal changes, albeit to a smaller extent, that should be related to both the  $O_2$  supply and consumption within the ODZ. For example, surveys carried out during consecutive SW and NE monsoon seasons (1987 to 1988) led Naqvi et al. (1990) to suggest a more vigorous denitrification (inferred from higher  $NO_2^-$  concentrations) during the latter season, a finding subsequently supported by the observations of de Sousa et al. (1996) made in 1996. Morrison et al. (1998, 1999) also found substantial variability in the depth profiles of  $NO_2^-$  but without a clear seasonal trend within 100 to 600 m at stations occupied repeatedly during the U.S. JGOFS expedition in 1994–1995. In any case, the substantial short-term changes evident in these data sets imply that the intermediate waters in the Arabian Sea must be quickly renewed (Swallow, 1984; Naqvi, 1987; Somasundar and Naqvi, 1988; Naqvi and Shailaja, 1993).

The temporal evolution of suboxic conditions over the western Indian shelf is intimately linked to the seasonal reversal of surface circulation. During the NE monsoon, the West India Coastal Current (WICC) carries warmer, fresher waters of equatorial origin toward the north. The low concentrations of nutrients coupled with downwelling associated with this flow result in low productivity and relatively deep mixed layers so that the shelf waters are generally well oxygenated. In contrast, circulation during the SW monsoon is characterized by an equatorward surface current, the above-mentioned

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5 poleward WIUC and coastal upwelling typical of oceanic eastern boundaries. However, upwelling along the Indian west coast is nowhere as vigorous as along the coasts of Somalia, Yemen and Oman in the western Arabian Sea. Moreover, due to the presence of a warm, low-salinity lens – formed through intense precipitation in the coastal zone – the upwelled water rarely comes in contact with the atmosphere, and the resultant strong thermohaline stratification contributes to the sustenance of very severe  $O_2$ -depletion very close (within few metres) to the sea surface. The  $O_2$  deficiency begins with the advent of upwelling sometime in April–May and intensifies gradually with time. Off Goa, where sufficient data exist due to quasi-time series monitoring of a station (the Candolim Time Series, CATS) over the inner shelf since 1997, near-bottom  $O_2$  concentrations reach suboxic levels in August as evident by the accumulation of  $NO_2^-$  and the depletion of  $NO_3^-$  (Fig. 4). Complete loss of the oxidized nitrogen species is followed by  $SO_4^{2-}$  reduction in September–October. With the reversal of surface currents, oxic conditions are re-established in November–December. When the reducing conditions are at their peak in September–October, the cross-shelf sections north of about  $12^\circ$  N latitude (e.g. Fig. 3) show the classical sequence of utilization of electron acceptors:  $O_2$  over and beyond the outer shelf,  $NO_3^-$  over the mid-shelf and  $SO_4^{2-}$  over the inner shelf. This is perhaps the only known region along an open coast where all three types of redox environments are found on the same shelf segment in such an organized manner.

#### 4 Denitrification rates

Rates of water-column denitrification in the Arabian Sea have been determined recently by Devol et al. (2006a) through on-deck and in-situ incubations of water samples spiked with  $^{15}NO_3^-$  and measuring the production of  $^{15}N$ -labelled  $N_2$ . As expected, the rates for the offshore suboxic zone ( $8.8 \pm 3.8 \text{ nmol N L}^{-1} \text{ d}^{-1}$ ;  $n=15$ ) are lower than those for the shallower system ( $21.6 \pm 46.8 \text{ nmol N L}^{-1} \text{ d}^{-1}$ ;  $n=15$ ). Although the overall rate for

the offshore suboxic zone ( $\sim 41 \text{ Tg N y}^{-1}$ ) derived from these data is within the range (10 to  $44 \text{ Tg N y}^{-1}$ ) of previous estimates for denitrification in the region based on stoichiometric calculations and electron transport system (ETS) activity, it still suffers from considerable uncertainty for the following reasons. Recent research has demonstrated that, in addition to canonical denitrification, the anaerobic ammonium ( $\text{NH}_4^+$ ) oxidation (anammox; the reaction of  $\text{NH}_4^+$  with  $\text{NO}_2^-$ ) is an important process of  $\text{N}_2$  formation; in fact, in most of the cases examined so far, the latter pathway has been found to be dominant (Kuypers et al., 2003, 2005; Thamdrup et al., 2006<sup>2</sup>). Thus, incubations with  $^{15}\text{NO}_3^-$  are expected to lead to an underestimation of the extent of  $\text{N}_2$  production. Secondly, measurements of the  $\text{N}_2/\text{Ar}$  ratio in seawater have yielded estimates of “excess”  $\text{N}_2$  which are up to twice the corresponding  $\text{NO}_3^-$  deficits (the deficiency in  $\text{NO}_3^-$  with reference to the concentration expected from the Redfield stoichiometry; Codispoti et al., 2001; Devol et al., 2006a, b; Fig. 5). Some of this discrepancy might arise from the above-mentioned contribution from anammox, with the rest mostly caused by the non-Redfieldian ( $\text{N:P} \gg 16$ ) composition of organic matter, produced by nitrogen fixers, that is supplied to and degraded within the OMZ (Codispoti et al., 2001; Devol et al., 2006a, b). In any case, it would appear that the current estimates for  $\text{N}_2$  production in the open-ocean suboxic zone should be conservative. This is probably also true, perhaps even more so, for the estimates from the coastal suboxic zone. The upwelled water has a  $\text{NO}_3^-$  content in excess of  $20 \mu\text{M}$ , and it takes about a month for the  $\text{NO}_3^-$  to be completely lost after the onset of denitrification, indicating that the actual  $\text{NO}_3^-$  consumption rate should be far in excess of that measured by the  $^{15}\text{NO}_3^-$  incubation method. Repeat observations at several sites over the inner shelf off the central west coast of India suggested an average  $\text{NO}_3^-$  consumption rate of  $0.83 \mu\text{mol L}^{-1} \text{d}^{-1}$ , and applying this rate to an estimated volume of  $1.2$  to  $3.6 \times 10^{12} \text{ m}^3$  yields an overall loss

<sup>2</sup>Thamdrup, B., Dalsgaard, T., Jensen, M. M., Ulloa, O., Farias, L., and Escribano, R.: Anaerobic ammonium oxidation in the oxygen-deficient waters off northern Chile, *Limnol. Oceanogr.*, in review, 2006.

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of 1.3 to 3.8 Tg N y<sup>-1</sup> (Naik, 2003). This is only 3 to 9% of the denitrification rate estimated for the perennial suboxic zone of the open Arabian Sea.

It is very likely that even the relatively modest rate over the Indian shelf has been anthropogenically enhanced over the past few decades. Sulphate (SO<sub>4</sub><sup>2-</sup>) reduction has been found to recur every year at the CATS site ever since the monitoring began in 1997. However, there is no indication of occurrence of this process in the historical data sets from anywhere along the Indian west coast. For example, an extensive set of hydrocast data for salinity, temperature and O<sub>2</sub> along numerous cross-shelf sections was generated under the UNDP/FAO-sponsored Integrated Fisheries Project (IFP) during 1971–1975 covering different seasons. In the region off Karwar (just south of Goa), a comparison of the O<sub>2</sub> data from these cruises with those generated by us from 1997 to 2004 shows a significant decrease in near-bottom O<sub>2</sub> over the inner- and mid-shelf (depth <60 m) for the period August–October. Even though hydrogen sulphide (H<sub>2</sub>S) was not measured on the IFP cruises, the absence of zero Winkler oxygens, characteristic of anoxic waters, in the IFP data set indicates that it was probably not present. Other data taken subsequently also suggest that the subsurface environment was denitrifying, but not SO<sub>4</sub><sup>2-</sup> reducing, at least until the 1980s. Thus, the subsurface O<sub>2</sub> deficiency over the Indian shelf seems to have intensified significantly since the 1970's. Although the cause of this regime shift cannot be pinpointed with absolute certainty, it was most likely related to an increased nitrogen loading from land (Naqvi et al., 2000). Indeed, fertilizer consumption in the region has undergone an order of magnitude increase over the past few decades, and this is expected to have affected river runoff. However, the available data suggest a modest riverine flux (0.1 Tg N y<sup>-1</sup>) of dissolved inorganic nitrogen (DIN) to the Arabian Sea (Naqvi et al., 2006b), and a similar rate of deposition of from the atmosphere (Bange et al., 2000). Nevertheless, assuming that most of these inputs are of anthropogenic origin, they could potentially account for a significant fraction of denitrification rate over the shelf estimated above, and the shift from natural suboxic to anthropogenic anoxic conditions. This is because the stoichiometries of primary production (C:N=6.6) and denitrification (C:N=1.1) are such

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that new inputs of DIN into suboxic waters get amplified by a factor of up to 6 (Codispoti et al., 2001). That is, for each unit of DIN added to the surface waters up to 6 units of  $\text{NO}_3^-$  can be removed at depth if the additional organic matter produced is oxidized by  $\text{NO}_3^-$ , thereby making subsurface denitrification very sensitive to the external DIN loading.

## 5 Nitrous oxide cycling

The distribution pattern of nitrous oxide ( $\text{N}_2\text{O}$ ) in the water column in the open Arabian Sea is similar to that observed in other areas containing intense ODZs: Within the denitrifying zone  $\text{N}_2\text{O}$  concentrations are invariably below  $\sim 10$  nM with peak values exceeding 40 nM occurring at the oxic-suboxic interfaces; outside the denitrification zone a single broad  $\text{N}_2\text{O}$  maximum is associated with the  $\text{O}_2$  minimum (Law and Owens, 1990; Naqvi and Noronha, 1991; Bange et al., 2001, 2005). The  $\text{N}_2\text{O}$  minimum associated with the SNM can only result from the conversion of  $\text{N}_2\text{O}$  to  $\text{N}_2$  by denitrifiers; in contrast, there are several possible pathways – nitrification, denitrification and a coupling between the two processes – that can produce the greatly elevated  $\text{N}_2\text{O}$  concentrations at the peripheries of the SNM zone. The natural isotope abundance of nitrogen and oxygen provide a measure of the relative importance of these various possibilities. These data reveal minima in both  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  that are coincident with the upper  $\text{N}_2\text{O}$  concentration peak (Fig. 6). Such minima, also reported from the Pacific Ocean, are consistent with the nitrification being the major production pathway (Dore et al., 1998). Incidentally, this is the only level where the dissolved  $\text{N}_2\text{O}$  is isotopically lighter, both for nitrogen and oxygen, than the tropospheric  $\text{N}_2\text{O}$ . The values are understandably heavy – indeed the heaviest reported yet from any oceanic setting – within the SNM zone due to fractionation associated with denitrification (i.e., lighter  $\text{N}_2\text{O}$  is preferentially utilized by denitrifiers). Intriguingly, the  $\delta^{15}\text{N}$  values for  $\text{N}_2\text{O}$  exceed those for  $\text{NO}_3^-$ , going against the trend exhibited by cultures of *Paracoccus denitrificans* grown under steady-state conditions (Barford et al., 1999), which suggested greater fraction-

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ation during the reduction of  $\text{NO}_3^-$  to  $\text{N}_2\text{O}$  (~16‰) than of  $\text{N}_2\text{O}$  to  $\text{N}_2$  (~13‰). The higher  $\delta^{15}\text{N}$  of  $\text{N}_2\text{O}$  implies that the natural bacterial populations should have a larger isotopic effect for the final reduction sequence. Moreover, as this trend persists also in the  $\text{N}_2\text{O}$ -rich waters below the SNM (Fig. 6), it necessitates the involvement of denitrification at least in channeling the lighter nitrogen isotope to  $\text{N}_2$ , if not in  $\text{N}_2\text{O}$  production, well outside the SNM. Based on the analysis of  $\text{N}_2\text{O}$  isotopomer ratios (site preference of  $^{15}\text{N}$  in the linear  $\text{N}_2\text{O}$  molecule), Yamagishi et al. (2005) also identified denitrification to be the dominant process responsible for  $\text{N}_2\text{O}$  production in the  $\text{O}_2$  minimum zone of the North Pacific. However, since nitrification and denitrification involve common intermediates and occur in close proximity of each other in  $\text{O}_2$ -depleted waters, both in the spatial and temporal domains, the exchange of these intermediates (nitrification-denitrification coupling) are expected to greatly affect the isotopic composition of  $\text{N}_2\text{O}$ . The coastal suboxic zone in the Arabian Sea is distinguished by much higher concentrations of  $\text{N}_2\text{O}$  (reaching up to  $\sim 0.8 \mu\text{M}$ ) as compared to the open ocean. The highest concentrations are unexpectedly associated with very high  $\text{NO}_2^-$  (reaching up to  $16 \mu\text{M}$ ) and low (near exhaustion)  $\text{NO}_3^-$  levels often at mid-depths (Fig. 3) indicating net production through denitrification, in stark contrast to observations within the open ocean SNM (Fig. 6). Incubations of water samples collected from the Indian shelf, that were  $\text{O}_2$ -poor but not denitrifying to begin with, revealed transient  $\text{N}_2\text{O}$  accumulation at micromolar levels once the system turned reducing, and it was hypothesized that frequent aeration due to turbulence in shallow, rapidly-denitrifying systems might suppress the activity of  $\text{N}_2\text{O}$ -reductase leading to a large fraction of nitrogen undergoing bacterial reduction ending up as  $\text{N}_2\text{O}$  (Naqvi et al., 2000). Because such production occurs within a few metres of the sea surface, the observed surface  $\text{N}_2\text{O}$  concentrations (5 to 436 nM, mean 37.3 nM,  $n=241$ ) and the computed emission to the atmosphere (0.05 to 0.38 Tg  $\text{N}_2\text{O} \text{ y}^{-1}$ ) are unusually high (Naqvi et al., 2006a).

In spite of the more extreme redox conditions prevailing in the coastal suboxic zone, the ranges of isotopic values for  $\text{N}_2\text{O}$  are relatively narrow ( $-2$  to  $13\%$  for  $\delta^{15}\text{N}$  and  $17$  to  $60\%$  for  $\delta^{18}\text{O}$ ) over the shelf as compared to the open ocean ( $3$  to  $81\%$  for  $\delta^{15}\text{N}$  and

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17 to 95‰ for  $\delta^{18}\text{O}$ ) (Yoshinari et al., 1997; Naqvi et al., 1998a, b). This is exemplified by data from a typical coastal site presented in Fig. 7. The isothermal, isohaline sub-pycnocline waters at this site had lost most of the oxidized nitrogen (especially in the deepest sample where the loss was almost complete). However, despite large vertical gradient in  $\text{N}_2\text{O}$  concentration (decrease from the pronounced maximum from the top of the suboxic zone to near-zero concentration close to the sea floor), the  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  values did not vary greatly. While, the aforementioned exchange of intermediates between the nitrification and denitrification, which is expected to occur to a much larger degree in the more spatially and temporally variable coastal environment, makes the interpretation of isotopic data from the coastal region less straightforward with regard to the pathways of  $\text{N}_2\text{O}$  cycling, it is quite likely that the observed differences arise from a different fractionation pattern from that observed in the open ocean suboxic zone, as in the case of  $\text{NO}_3^-$ , as we shall see in the following section.

## 6 Nitrogen isotopic fractionation during denitrification

Water column distributions of  $\delta^{15}\text{N}$  in  $\text{NO}_3^-$  and  $\text{N}_2$  in the open Arabian Sea exhibit large changes brought about by the microbial consumption/production of these species (Brandes et al., 1998; Naqvi et al., 1998a, b; Altabet et al., 1999). Denitrification has been known to involve pronounced mass-dependent fractionation (preferential reduction of  $^{14}\text{NO}_3^-$  over  $^{15}\text{NO}_3^-$ ) in seawater (Cline and Kaplan, 1975), leading to an enrichment of  $^{15}\text{N}$  in  $\text{NO}_3^-$  pool and its depletion in the  $\text{N}_2$  pool. In the central Arabian Sea, the  $\delta^{15}\text{N}$  of  $\text{NO}_3^-$  increases from  $\sim 6\text{‰}$  in deep waters (2500 to 3000 m), comparable with values from other areas (Wu et al., 1997; Sigman et al., 1997), to 15 to 18‰ within the core of the denitrifying layer (Fig. 6; Brandes et al., 1998; Altabet et al., 1999); the  $\delta^{15}\text{N}$  of  $\text{N}_2$  concurrently decreases from  $\sim 0.6\text{‰}$  to  $\sim 0.2\text{‰}$  (Brandes et al., 1998). Brandes et al. combined their isotopic data with  $\text{NO}_3^-$  deficits (computed from the relationship between the tracer “NO” with potential temperature) and used

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advection-reaction (Rayleigh fractionation) and diffusion-reaction models to compute the isotope fractionation factor ( $\epsilon$ ) of 22‰ and 25‰, respectively. Altabet et al. (1999) obtained a somewhat higher ( $\sim 30\%$ ), value for  $\epsilon$  using  $-N^*$  (cf. Gruber and Sarmiento, 1997) and Rayleigh fractionation. The estimates of  $\epsilon$  are about the same for the sub-oxic zones of the Arabian Sea and the eastern tropical North Pacific (Brandes et al., 1998; Altabet et al., 1999), implying relative constancy of isotopic fractionation in the open ocean. These estimates are also well within the range of those obtained earlier through laboratory cultures of heterotrophic denitrifiers ( $\epsilon=17$  to 29‰; Delwiche and Steyn, 1970; Mariotti et al., 1981; Barford et al., 1999). One important implication of these results is that for anammox to be a major producer of  $N_2$  in the open ocean, its effect on isotopic composition of  $NO_3^-$ , about which not much is known at present, should not be too different from that of heterotrophic denitrification.

The isotopic distribution pattern observed in the coastal suboxic zone is quite different, and more variable, from that described above, even though the data are rather limited. These data come from two sets of observations – in August 1997 off Mangalore (Sta. SS 3939; isotopic analysis carried out following Brandes et al., 1998) and in September 2000 off Goa (Stas. G3, G4 and G5; isotopic analysis carried out following Tanaka and Saino, 2002). On both occasions the water column had experienced significant losses of  $NO_3^-$ . Hydrographic and chemical data at Sta. SS 3939 along with the  $\delta^{15}N-NO_3^-$  values are plotted against depth in Fig. 8. Temperatures and salinity profiles are typical of this region for the survey period, showing strong near-surface thermohaline stratification and isothermal and isohaline conditions below the shallow pycnocline. Similarly, the two deepest samples experienced near-complete  $O_2$  depletion that is characteristic of the sampling period. The  $NO_3^-$  profile exhibited a mid-depth maximum below which concentrations decreased while the  $NO_2^-$  concentrations showed a concomitant increase with depth.  $NO_3^-$  deficit was calculated as the difference between the expected and observed  $NO_3^-$  concentrations (the former was approximately quantified by dividing the apparent oxygen utilization (AOU) with 8.65, the ratio between  $O_2$  consumption and  $NO_3^-$  regeneration for aerobic respiration; Richards, 1965). This

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deficit increased with depth reaching the peak value of just under  $15 \mu\text{M}$  in the deepest sample. While all the above parameters exhibited expected depthwise changes, the profile of  $\delta^{15}\text{N}-\text{NO}_3^-$  deviated greatly from the expected one. That is, given the high  $\text{NO}_3^-$  deficit in subsurface waters, the  $\delta^{15}\text{N}-\text{NO}_3^-$  values should have ranged between 17 and 26‰ if the isotopic fractionation factor reported for the open ocean suboxic zone ( $\sim 25\%$ ) was also applicable to the shallow suboxic zone. The values measured were consistently lower. In fact, all the four samples taken from within or below the pycnocline yielded  $\delta^{15}\text{N}-\text{NO}_3^-$  values (6.65 to 7.41‰) that were quite close to the oceanic average with no depthwise variability.  $\text{NO}_3^-$  in the only sample taken from the surface layer was distinctly lighter (3.43‰).

Several possibilities could be invoked to explain the above observations: (1) Processes responsible for the observed  $\text{NO}_3^-$  losses in the coastal suboxic zone may be different from those in its open ocean counterpart. A likely scenario is that a substantial fraction of the loss may occur within the sediments, and the much smaller isotopic fractionation associated with sedimentary denitrification (Brandes and Devol, 2002) could then account for the low  $\delta^{15}\text{N}-\text{NO}_3^-$  values. The few data on sedimentary denitrification, measured mostly during the upwelling period following the acetylene block technique, have yielded values ranging from 0.23 to  $1.25 \text{ mmol NO}_3^- \text{ m}^{-2} \text{ d}^{-1}$ , which are generally within the range of values from other areas (Naik and Naqvi, 2002). Estimates based on the isotope pairing method are comparable with these values (Naqvi et al., unpublished manuscript). These rates by themselves appear to be inadequate to account for the observed  $\text{NO}_3^-$  loss in the water column. The other processes that may bring about  $\text{NO}_3^-$  removal are anammox, dissimilatory reduction of  $\text{NO}_3^-$  to  $\text{NH}_4^+$  (which may also be coupled to anammox) and/or autotrophic denitrification (e.g. reduction of  $\text{NO}_3^-$  by species such as  $\text{S}^{2-}/\text{HS}^-$ ,  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$ ; Luther et al., 1997). Of these at least anammox is expected to be quite important in view of the above-mentioned results from other regions, more so over the Indian shelf where very high  $\text{NO}_2^-$  concentrations (maximum  $16 \mu\text{M}$ ) are expected to be matched by a high rate of diffusive supply of  $\text{NH}_4^+$  from the sediments (Naqvi et al., 2000). (2) Apparently low  $\delta^{15}\text{N}-\text{NO}_3^-$  relative to

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the  $\text{NO}_3^-$  deficit could be produced by mixing involving anoxic water. In order to further illustrate this possibility the following hypothetical scenario may be considered: A parcel of water is subjected to complete denitrification, thereby resulting in the removal of both  $^{15}\text{NO}_3^-$  and  $^{14}\text{NO}_3^-$ , followed by rapid 1:1 mixing with the freshly-upwelled water having a  $\text{NO}_3^-$  content and  $\delta^{15}\text{N}$  of, say,  $24\ \mu\text{M}$  and  $7\text{‰}$ , respectively. The resultant mixture would possess the isotopic characteristics of the upwelled water ( $\delta^{15}\text{N}=7\text{‰}$ ), but it would show a  $\text{NO}_3^-$  deficit of  $12\ \mu\text{M}$ . (3) It has been found recently that the reduction of  $\text{NO}_3^-$  to  $\text{NO}_2^-$  involves huge isotopic discrimination, such that  $\delta^{15}\text{N}$  of  $\text{NO}_2^-$  in the suboxic zone of the eastern tropical North Pacific is quite low (K. Casciotti, personal communication). The procedures followed by us to measure isotopic composition of  $\text{NO}_3^-$  did not differentiate between  $\text{NO}_3^-$  and  $\text{NO}_2^-$ , and therefore the measured values would be dependent on the ratio between  $\text{NO}_2^-$  and  $\text{NO}_3^-$  concentrations. This ratio is generally much higher in the coastal zone than in the open ocean, and that could contribute to lower  $\delta^{15}\text{N}$  of the combined  $\text{NO}_3^-$  and  $\text{NO}_2^-$  pool. (4) Finally, it is also possible that if and when the  $\text{NO}_3^-$  loss occurs through heterotrophic denitrification, the fractionation factor associated with the process may not be the same in the coastal and offshore regions. There is some experimental evidence suggesting that the degree of isotopic discrimination may indeed vary with denitrification rate (K.-K. Liu, personal communication).

Unlike the above-mentioned observations off Mangalore, isotopic data off Goa do reveal substantial enrichment of the heavier isotope in residual  $\text{NO}_3^-$  (Fig. 9). For these samples the fractionation factor was computed using a simple advection-reaction model that ignores diffusion. As the sampling sites were located very close to each other along a coast-perpendicular transect, and the  $\text{NO}_3^-$  loss occurred in the upwelled water as it ascended over the shelf, this assumption seems justifiable. The isotopic distribution could thus be modelled with a simple Rayleigh equation (Bender, 1990):

$$\delta^{15}\text{N}-\text{NO}_3=10^3(\alpha-1)\log_e f_{\text{NO}_3}+(\delta^{15}\text{N}-\text{NO}_3)_{\text{init}}$$

where  $f_{\text{NO}_3}$  is the ratio between the observed and expected  $\text{NO}_3^-+\text{NO}_2^-$  concentrations

and  $(\delta^{15}\text{N}-\text{NO}_3)_{\text{init}}$  gives the isotopic composition of the initial (unaltered) material.

The plot of  $\delta^{15}\text{N}-\text{NO}_3$  versus  $\log_e f_{\text{NO}_3}$  (Fig. 9) indicates a good linear correlation ( $r^2=0.91$ ) with the slope of the regression ( $-\varepsilon_{\text{denit}}$ ) line being  $-7.70$ . Inclusion of data from Sta. SS 3939 leads to a little change in the slope ( $-7.21$ ), but the correlation is deteriorated ( $r^2=0.44$ ). At the first glance these results appear to support the notion of lower fractionation factor in the coastal suboxic zone. However, as discussed above, the possibility of other factors being also responsible for pulling down the  $\delta^{15}\text{N}$  value of  $\text{NO}_3^-$  of coastal waters cannot be ruled out. In fact, it is quite likely that all the factors mentioned above may be in operation, their relative importance varying in space and time. Such a dynamic environment which contrasts the relatively more stable conditions of the open ocean system offers both challenges and opportunities to gain further insights into the pathways of oceanic nitrogen cycling.

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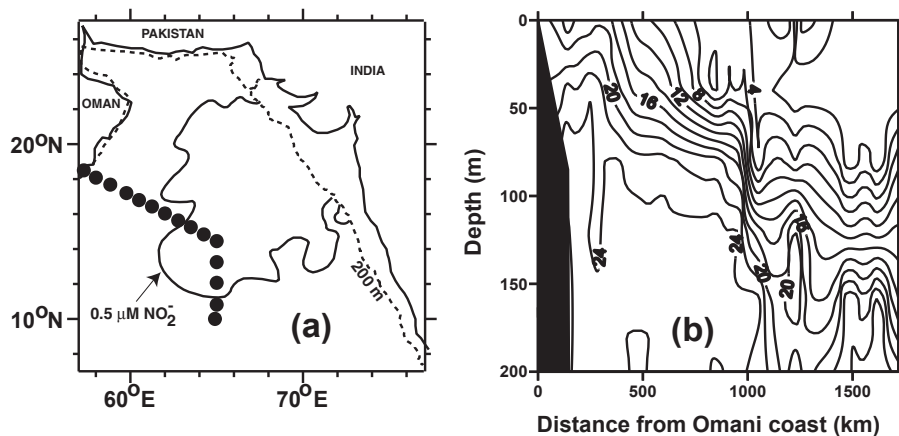
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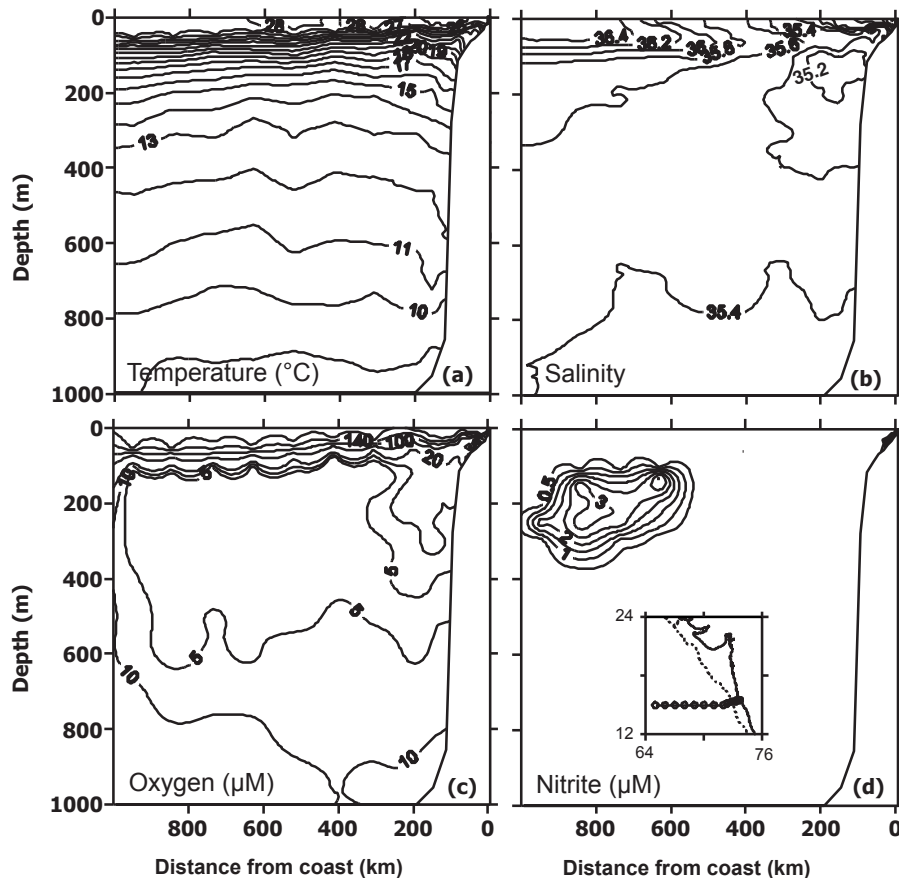
**Fig. 1.** (a) Geographical limits of the offshore suboxic zone as demarcated by the  $0.5 \mu\text{M NO}_2^-$  contour (redrawn from Naqvi, 1991). Also shown are the stations worked during the U.S. JGOFS cruise TN050 (August–September, 1995) whose data have been used to construct the  $\text{NO}_3^-$  section shown in (b).

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**Fig. 2.** Variations in (a) temperature, (b) salinity, (c)  $O_2$ , and (d)  $NO_2^-$  in the upper 1 km off Goa (see inset in (d) for station locations) during 1–6 December 1998.

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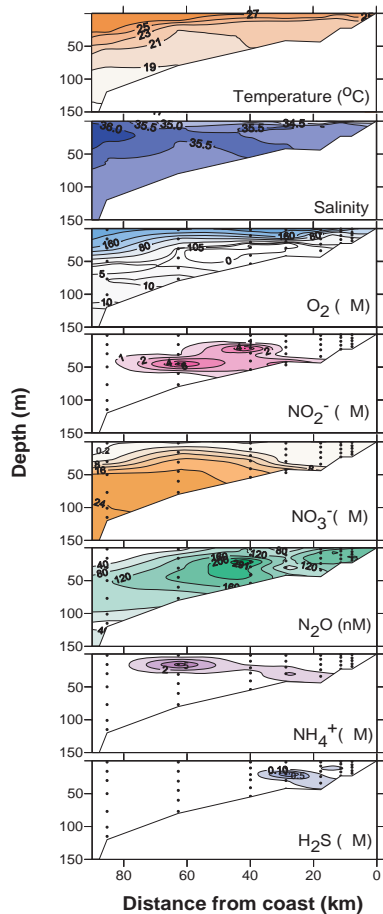
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**Fig. 3.** Vertical sections of temperature, salinity,  $O_2$ , inorganic nitrogen species and hydrogen sulphide off Goa (part of the same transect as in Fig. 2) during 9 to 10 October 1999.

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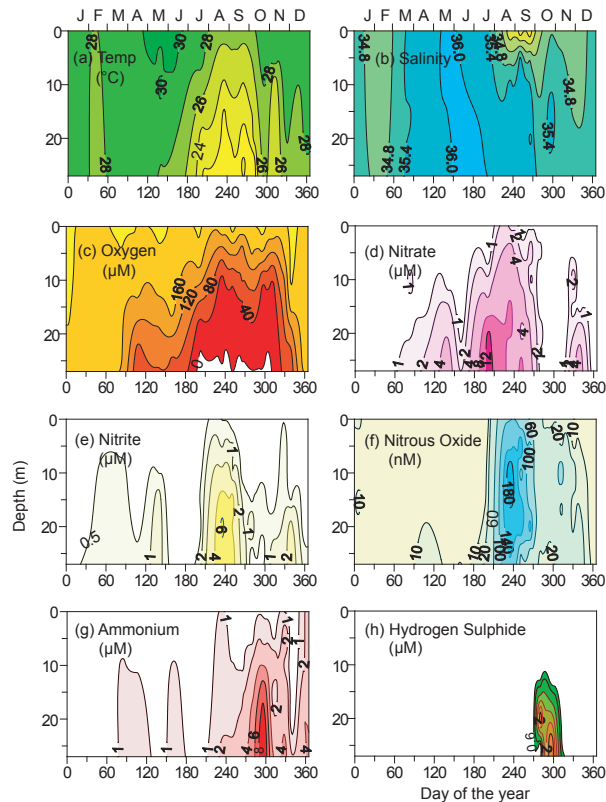
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**Fig. 4.** Monthly/fortnightly-averaged records showing annual cycle of **(a)** temperature, **(b)** salinity, **(c)** oxygen, **(d–g)** inorganic nitrogen species, and **(h)** hydrogen sulphide at the Candolim Time Series (CATS) site ( $15^{\circ}31' N$ ,  $73^{\circ}39' E$ ) based on observations from 1997 to 2004.

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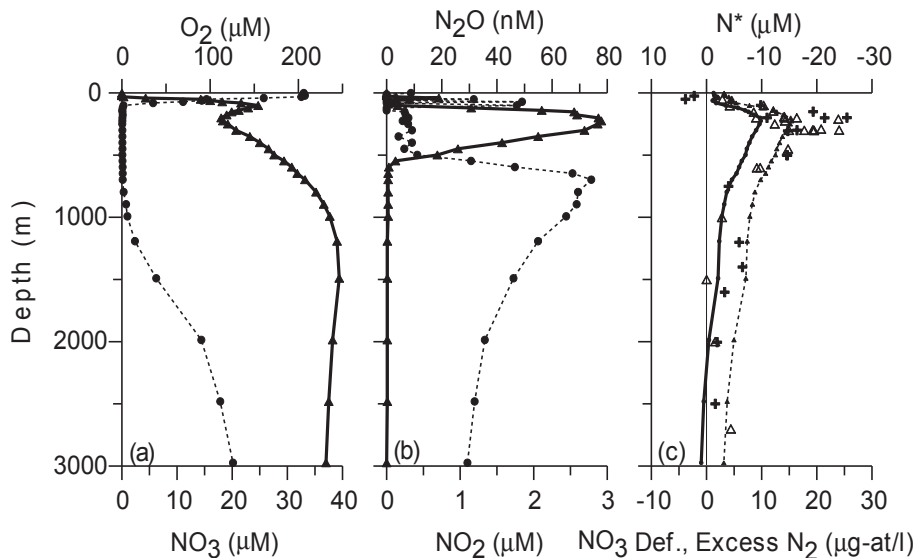
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**Fig. 5.** Vertical profiles of properties at 19° N, 67° E (all data except for N<sub>2</sub> collected on TN039 cruise of U.S. JGOFS on 1–2 October 1994). **(a)** O<sub>2</sub> (circles) and NO<sub>3</sub><sup>-</sup> (triangles); **(b)** N<sub>2</sub>O (circles) and NO<sub>2</sub><sup>-</sup> (triangles); **(c)** NO<sub>3</sub><sup>-</sup> deficit according to Codispoti et al. (2001) (dots connected by the solid line), N\* according to Gruber and Sarmiento (2002) (small filled triangles connected by the dashed line), and “excess N<sub>2</sub>” calculated from the N<sub>2</sub>/Ar ratio (larger unconnected symbols – crosses for data collected on two different cruises from this station and triangles for those from other stations also located within the denitrification zone).

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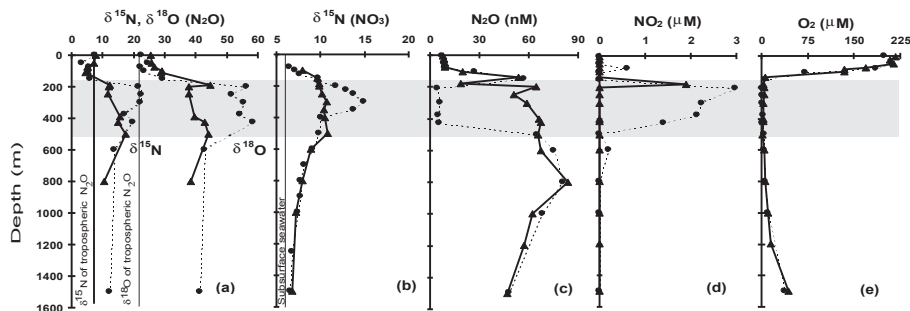
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**Fig. 6.** Vertical profiles of  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  (‰ relative to air) of  $\text{N}_2\text{O}$  (**a**)  $\delta^{15}\text{N}$  of  $\text{NO}_3^-$  (**b**), and concentrations of  $\text{N}_2\text{O}$  (**c**),  $\text{NO}_2^-$  (**d**) and  $\text{O}_2$  (**e**) at stations SS 3201 ( $17^\circ\text{N}$ ,  $68^\circ\text{E}$ ; filled circles, joined by dotted lines) and SS 3204 ( $19.75^\circ\text{N}$ ,  $64.62^\circ\text{E}$ ; filled triangles, joined by continuous lines). The shaded region represents the secondary  $\text{NO}_2^-$  maximum at SS 3201. Vertical lines give  $\delta^{15}\text{N}$  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 seawater (b) (from Naqvi et al., 1998a).

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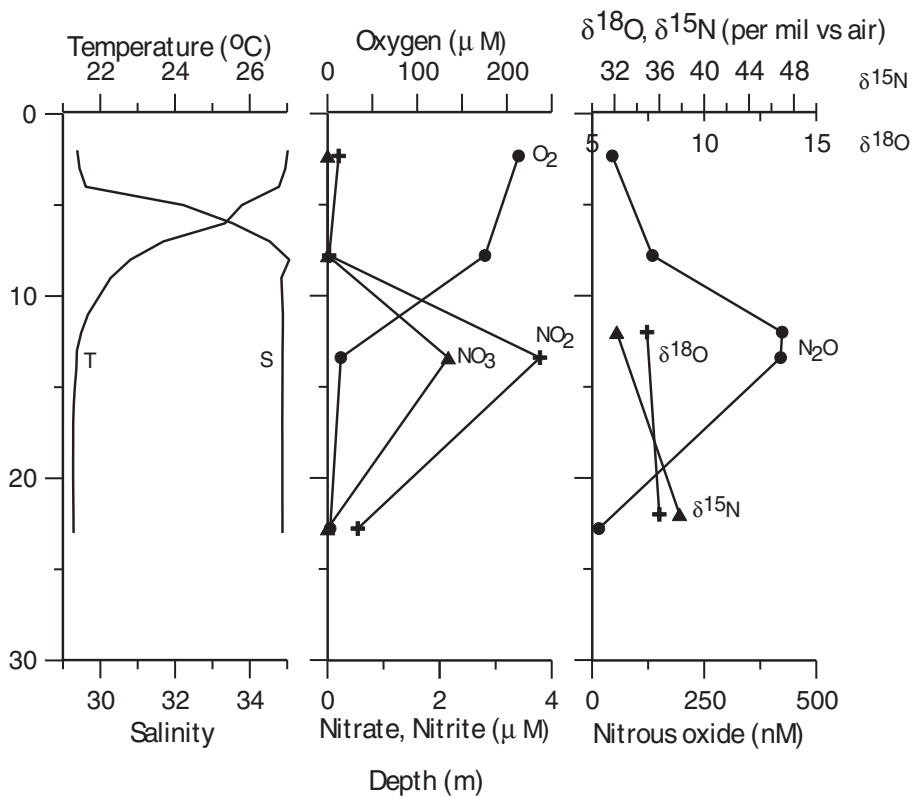
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**Fig. 7.** Vertical profiles of temperature, salinity, dissolved O<sub>2</sub>, inorganic nitrogen species and δ<sup>15</sup>N and δ<sup>18</sup>O of N<sub>2</sub>O at Sta. SK 137/39 (9.950° N; 76.017° E) sampled on 8 August 1998.

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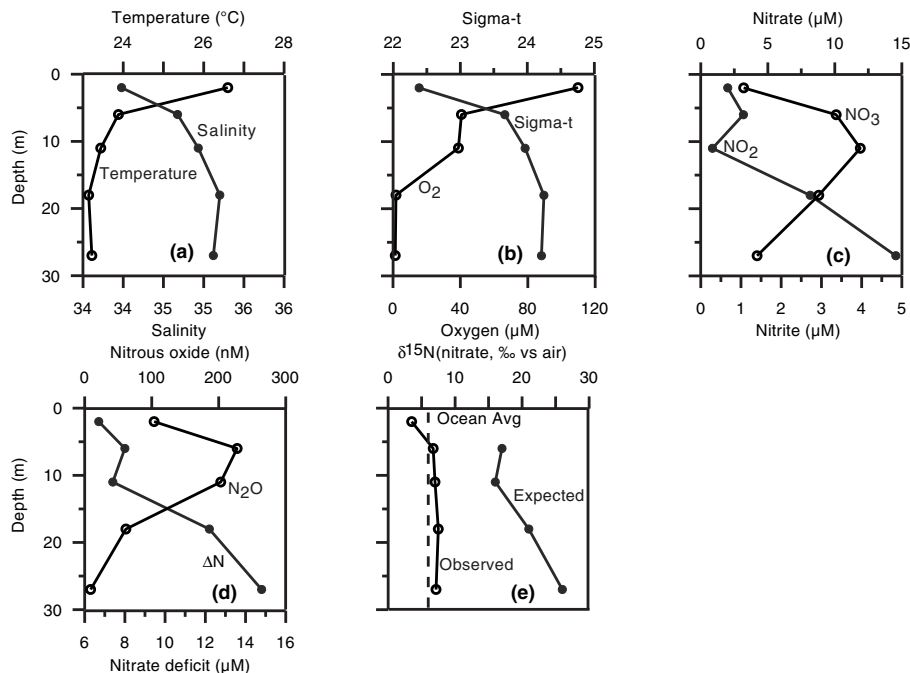
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**Fig. 8.** Vertical profiles of temperature, salinity, density, dissolved O<sub>2</sub>, inorganic nitrogen species and δ<sup>15</sup>N of NO<sub>3</sub><sup>-</sup> (observed as well as expected from the computed NO<sub>3</sub><sup>-</sup> deficits and the reported fractionation factor for the open ocean) at Sta. SS 3939 (13.126° N; 74.631° E) sampled on 30 August 1997.

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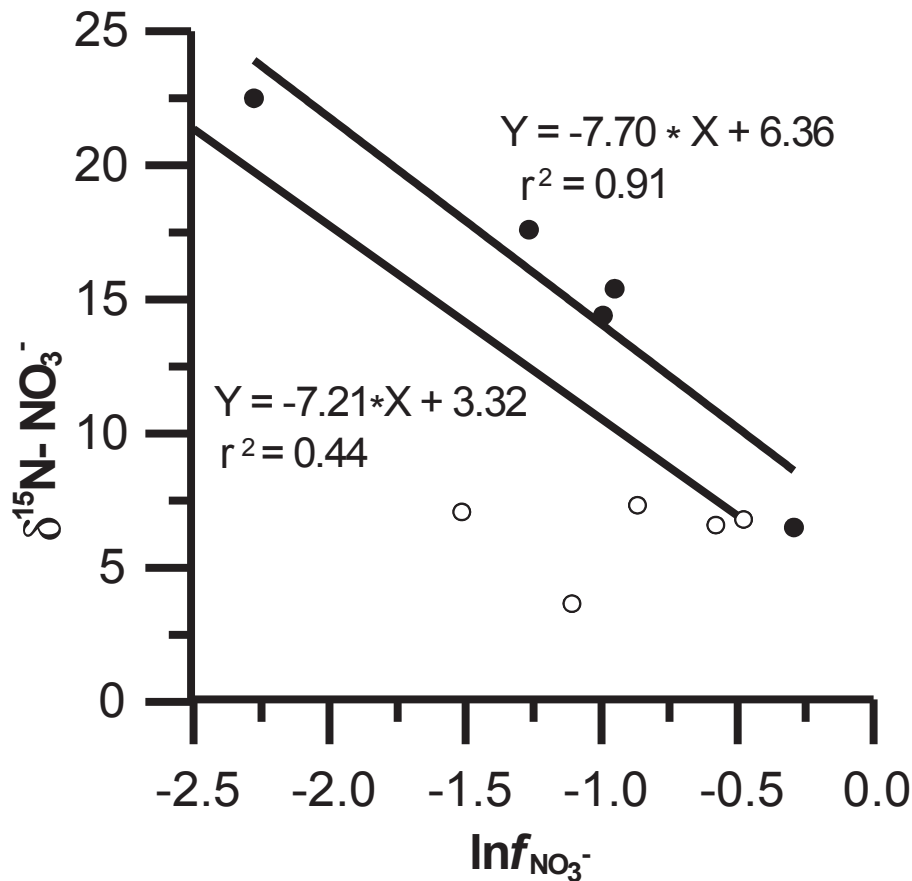
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**Fig. 9.**  $\delta^{15}\text{N}$  of  $\text{NO}_3^-$  versus natural log of fraction of the original  $\text{NO}_3^-$  remaining for samples from Sta. SS 3939 (open circles) and Sta. SK 137/39 (filled circles). The two regression lines with slopes of  $-7.70$  and  $-7.21$  are for data from Sta. SK 137/39 only and those from both stations, respectively.

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