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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 (N_2O) production: In the open-ocean suboxic zone, an accumulation of secondary nitrite (NO_2^-) is invariably accompanied by depletion of N_2O whereas in the coastal suboxic zone high NO_2^- and very high N_2O concentrations frequently co-occur, indicating, respectively, net consumption and net production of N_2O by denitrifiers. The extents of heavier isotope enrichment in the combined nitrate and nitrite (NO_3^-+NO_2^-) pool and in N_2O 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 greatly affected by the ambient oxygen (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 (NO_3^-), and it is only in sediments and in parts of the water column in a few well-demarcated regions that dissolved O_2 gets almost completely depleted to allow microbial conversion of NO_3^- to molecular nitrogen (N_2); this process, denitrification, is the most important pathway of losses of fixed nitrogen, and thus a key player in the nitrogen budget (Deuser, 1975; 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). Moreover, 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

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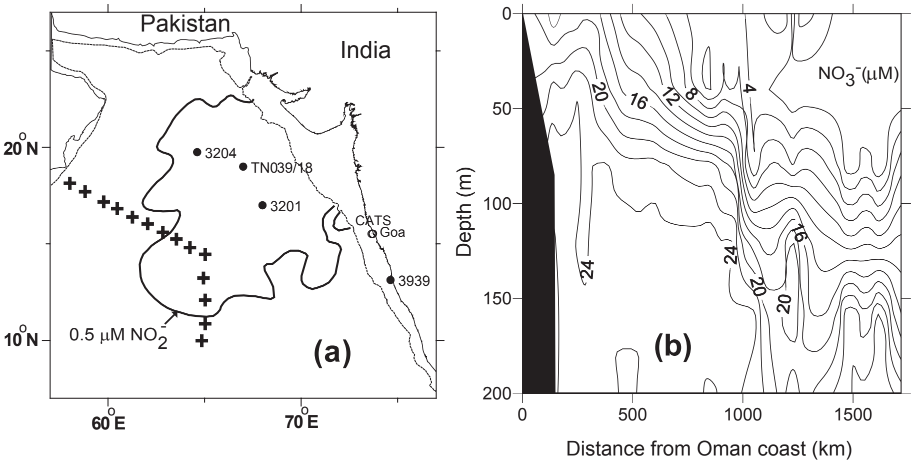

Fig. 1. **(a)** Geographical limits of the offshore suboxic zone as demarcated by the 0.5 μM NO_2^- contour (redrawn from Naqvi, 1991). Also shown are the stations (marked by crosses) worked during the U.S. JGOFS cruise TN050 (August–September 1995), whose data have been used to construct the NO_3^- section shown in **(b)**, as well as some other stations (marked by circles) mentioned elsewhere in the paper. Isopleths in (b) and Figs. 2–4 were drawn using Surfer® for Windows version 8 by Golden Software, Inc.

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 $O_2 < 0.1\,\mathrm{mL\,L^{-1}}$; $\sim 4\,\mu$M) within a very wide depth range ($\sim$100/150 to 1000 m) in the north, particularly in the Northwestern Indian Ocean (Wyrtki, 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 $O_2 < 0.5\,\mathrm{mL\,L^{-1}}$ (22 μM) and $< 0.2\,\mathrm{mL\,L^{-1}}$ (9 μM), are estimated to cover about 1.15×10^6 and $0.76 \times 10^6\,\mathrm{km^2}$, respectively, 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_2-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[1] zones

As stated above, the most intense ODZ, as inferred from the occurrence of a secondary nitrite (NO_2^-) 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 off 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 mesoscale 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_2 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 of nutrients by phytoplankton and the subsequent vertical flux of organic matter must also contribute to the observed O_2

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[1] 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_2 is below $\sim 0.015\,\mathrm{mL\,L^{-1}}$ ($\sim 0.7\,\mu$M) (Winkler $O_2 < \sim 0.1\,\mathrm{mL\,L^{-1}}$ ($\sim 4\,\mu$M); Cline and Richards, 1972; Morrison et al., 1999).

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 region 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_3^-; Fig. 1b) do indeed indicate long-distance ($\geq$1000 km) transport of the upwelled water reaching well within the region of the most intense O_2 deficiency, but the generally-observed gradual offshore decrease in surface nutrient concentration is not supportive of this view. Moreover, the sediment trap data clearly show that the flux of particulate organic matter to the deep sea is higher in the western Arabian Sea than in the central and eastern Arabian Sea (Rixen et al., 2005).

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. Aerosol analysis during the SW monsoon also revealed very low (below detection limit) concentrations of the labile-Fe(II) off the central Omani coast, presumably because the air masses during this season come from the pristine southern hemisphere (Sierfert et al., 1999). 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_3^-. 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_3^- 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 material 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).

It must, however, be pointed out that despite the absence of the SNM in the western Arabian Sea, high concentrations of elements that are more soluble in the reduced states (e.g. Fe and Mn) and of the reduced species (such as I^-) can still occur within the core of the O_2 minimum (Saager et al., 1989; Farrenkopf et al., 1997; Farrenkopf and Luther, 2002). Farrenkopf et al. (1997) and Farrenkopf and Luther (2002) ascribed the elevated I^- levels, at least in part, to heterotrophic iodate (IO_3^-) reduction and Bange et al. (2001) postulated that the associated thermodynamically-feasible oxidation of ammonium (NH_4^+) by IO_3^- could produce N_2O. N_2O is probably also formed through nitrifier denitrification in these waters (Shailaja et al., 2006). However, it is unlikely that the production of N_2 and N_2O through canonical denitrification is quantitatively very important outside the SNM zone.

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 northward 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 35 400 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° 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 denitrifying off the continental margin probably as far north as 17° N latitude. Consequently, as reflected by the distribution of NO_2^- (Fig. 2d), denitrification intensifies away from the coast. This pattern is opposite to 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 owes to a lower respiration rate within the WIUC, which, in turn, may be caused by two factors. Firstly, 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 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

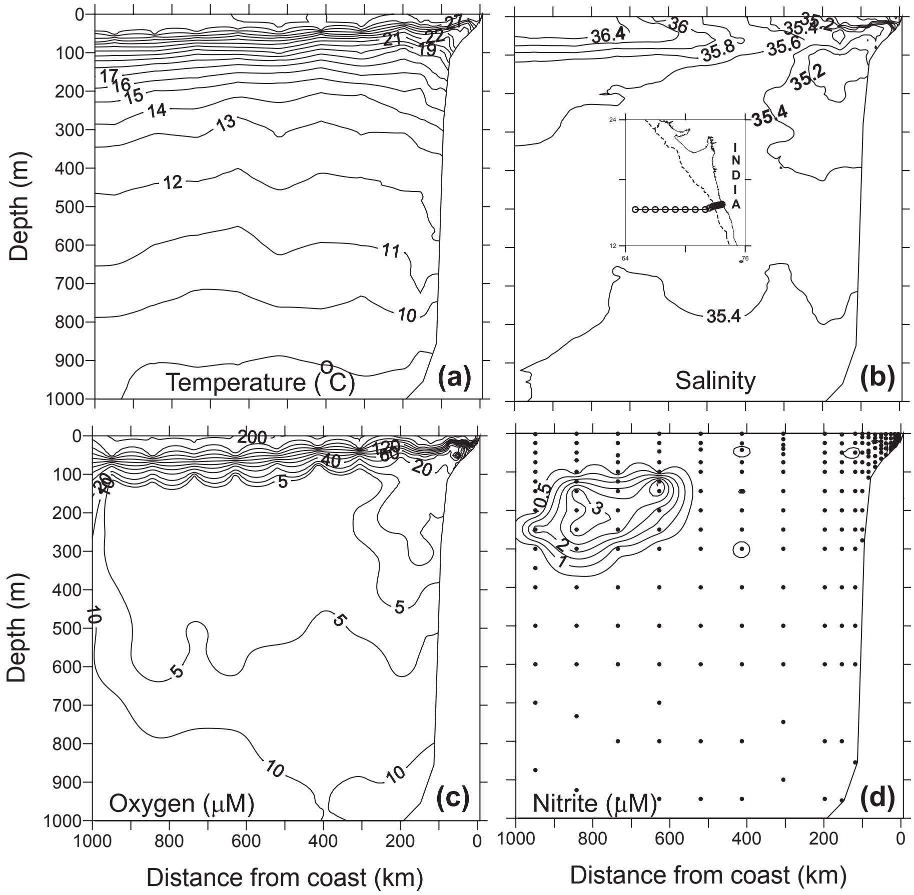

Fig. 2. Variations in **(a)** temperature, **(b)** salinity, **(c)** O_2, and **(d)** NO_2^- in the upper 1 km off Goa (see inset in (b) for station locations) during 1–6 December 1998. Modified from Naqvi et al. (2006a).

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 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 –

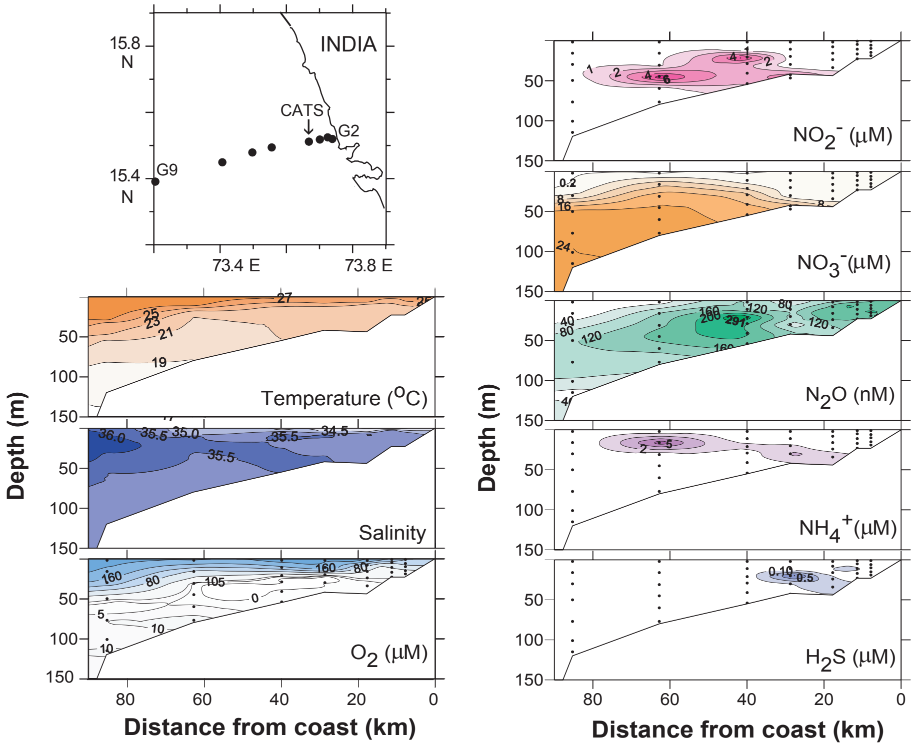

Fig. 3. Vertical sections of temperature, salinity, O_2, inorganic nitrogen species and hydrogen sulphide off Goa during 9 to 10 October 1999. Station locations are shown in the accompanying map for this frequently-sampled, shallower part of the Goa transect also shown in Fig. 2. These data are hitherto unpublished.

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 the 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° 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±3.8 nmol N L^{-1} d^{-1}; n=15) are lower than those for the shallower system (21.6±46.8 nmol N L^{-1} d^{-1}; n=15). Although the overall rate for the offshore suboxic zone (~41 Tg N y^{-1}) derived from these data is within the range (10 to 44 Tg N y^{-1}) of previous estimates for denitrification in the region based on stoichiometric calculations (Naqvi, 1987; Mantoura et al., 1993) and electron transport system (ETS) activity (Naqvi and Shailaja, 1993), it still suffers from considerable uncertainty for the following reasons. Firstly, recent research has demonstrated that, in addition to canonical denitrification, the anaerobic ammonium oxidation (anammox; the reaction of NH_4^+ with NO_2^-) is an important process of 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). Thus, incubations with $^{15}NO_3^-$ alone might lead to an underestimation of N_2 production. Secondly, measurements of the N_2/Ar ratio in seawater have yielded estimates of "excess" N_2 that are up to twice the corresponding NO_3^- deficits

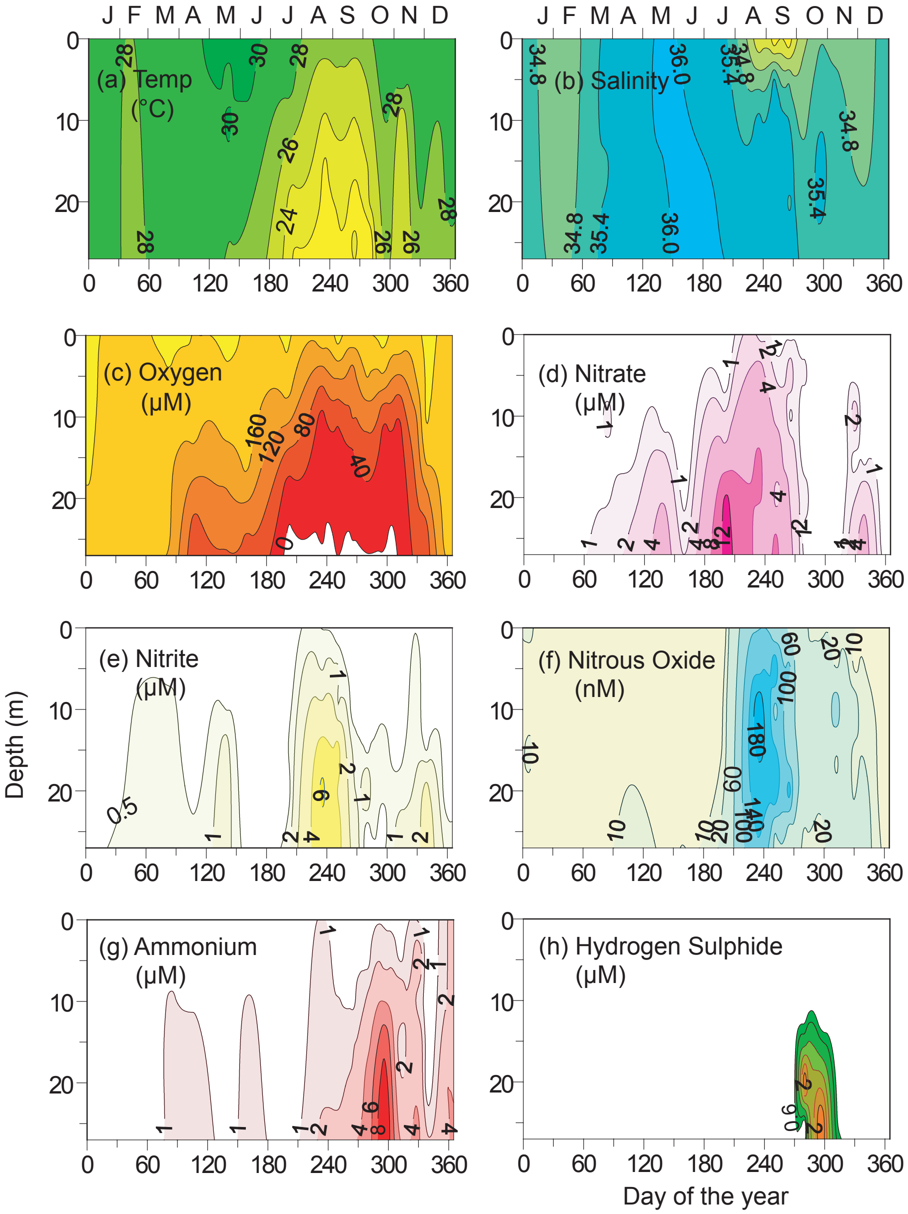

Fig. 4. Monthly-/fortnightly-averaged records showing annual cycle of **(a)** temperature, **(b)** salinity, **(c)** oxygen, **(d–g)** inorganic nitrogen species, and **(h)** hydrogen sulphide at the Candolim Time Series (CATS) site (15°31′ N, 73°39′ E; Fig. 3) based on observations from 1997 to 2004. Modified from Naqvi et al. (2006a).

(the deficiency in NO_3^- with reference to the concentration expected from the Redfield stoichiometry; Codispoti et al., 2001; Devol et al., 2006a, b; Fig. 5). Although it is possible that sedimentary denitrification contributes to some extent to the observed N_2 excess, the two potentially more important processes causing the discrepancy are anammox and mineralization within the OMZ of organic matter produced by nitrogen fixers that has non-Redfieldian elemental composition (N:P≫16) (Codispoti et al., 2001; Devol et al., 2006a, b; Codispoti, 2006). It would thus appear that the current estimates for N_2 production in the open-ocean suboxic zone should be conservative. This is probably also true, perhaps even more so, for estimates from the coastal suboxic zone. The upwelled water has a NO_3^- content in excess of 20 μM, and it takes about a month for the NO_3^- to be completely lost after the onset of denitrification, indicating that the actual NO_3^- consumption rate should be far in excess of that measured by the $^{15}NO_3^-$ incubation method. Repeat observations at several sites over the inner shelf off the central west coast of India suggested an average NO_3^- consumption rate of 0.83 μmol L^{-1} d^{-1}, and applying this rate to an estimated volume of 1.2 to $3.6 \times 10^{12}\,\mathrm{m}^3$ yields an overall loss of 1.3 to 3.8 Tg N y^{-1} (Naik, 2003[2]). 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_4^{2-}) reduction has been found to recur every year at the CATS site ever since the monitoring began in 1997. The data show substantial intra-seasonal as well as inter-annual variations, the latter without a clear secular trend. 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_2 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_2 data from these cruises with those generated by us from 1997 to 2004 shows a significant decrease in near-bottom O_2 over the inner- and mid-shelf (depth <60 m) for the period August–October (Naqvi et al., 2006a). Even though hydrogen sulphide (H_2S) was not measured on the IFP cruises, the absence of zero Winkler oxygens 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_4^{2-} reducing, at least until the 1980s (Naqvi et al., 2000). Thus, the subsurface O_2 deficiency over the Indian shelf seems to have intensified significantly since the 1970s. Although the cause of this change cannot be pinpointed with absolute certainty, it is 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^{-1}) of dissolved inorganic nitrogen (DIN) to the Arabian Sea (Naqvi et al., 2006b). The deposition rate from the atmosphere is perhaps relatively more important. Bange et al. (2000) estimated a total DIN deposition of ∼1.6 Tg y^{-1} for the region north of 6° N latitude, and although this is based on observations offshore, the flux density is expected to be higher over the Indian shelf. It would be reasonable to assume that most of the aeolian and riverine inputs are of anthropogenic origin, which could 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 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 NO_3^- can be removed at depth if the additional organic matter produced is oxidized by NO_3^-, thereby making subsurface denitrification very sensitive to the external DIN loading.

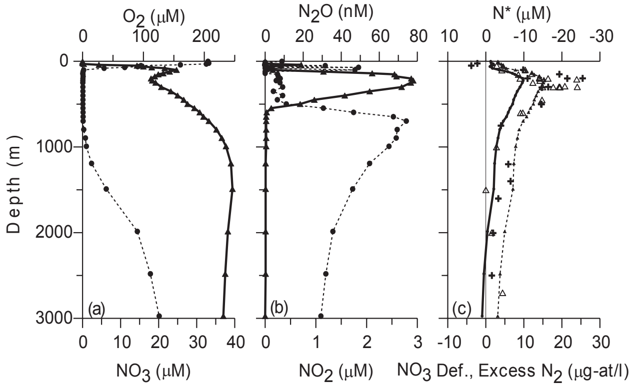

Fig. 5. Vertical profiles of properties at 19° N, 67° E (all data except for N_2/Ar collected on TN039 cruise of U.S. JGOFS (Sta. 18; Fig. 1) on 1–2 October 1994). **(a)** O_2 (circles) and NO_3^- (triangles); **(b)** N_2O (circles) and NO_2^- (triangles); **(c)** NO_3^- deficit according to Codispoti 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_2" calculated from the N_2/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). N_2/Ar data are from Devol et al. (2006a).

5 Nitrous oxide cycling

The distribution pattern of N_2O in the water column in the open Arabian Sea is similar to that observed in other areas containing intense ODZs: Within the denitrifying zone N_2O concentrations are invariably below ∼10 nM with peak values exceeding 40 nM occurring at the oxic-suboxic interfaces; outside the denitrification zone a single broad N_2O maximum is associated with the O_2 minimum (Law and Owens, 1990; Naqvi and Noronha, 1991; Bange et al., 2001, 2005). The N_2O minimum associated with the SNM can only result from the conversion of N_2O to 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 N_2O 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 $\delta^{15}N$ and $\delta^{18}O$[3] that are coincident with

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[2] Naik, H.: Benthic nitrogen cycling with special reference to nitrous oxide in the coastal and continental shelf environments of the eastern Arabian Sea, Ph.D. thesis, Goa University, unpublished, 147 pp., 2003.

[3] Nitrogen and oxygen isotope ratios of N_2O throughout this paper are expressed as per mil deviations from atmospheric N_2 and O_2, respectively. In the case of oxygen the values against air can

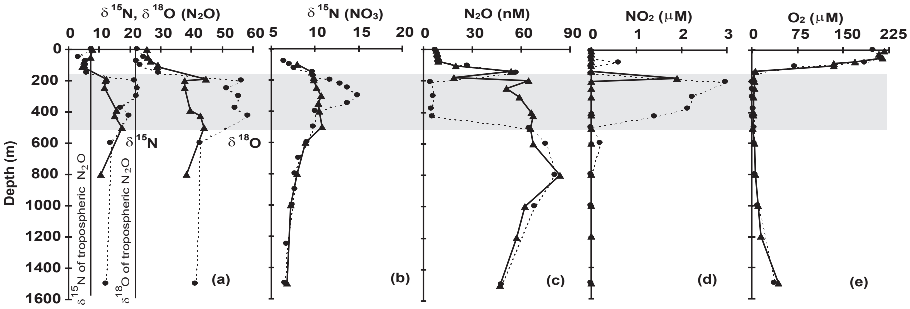

Fig. 6. Vertical profiles of δ^{15}N and δ^{18}O (‰ relative to air; see footnote #3) of N_2O **(a)**, δ^{15}N of NO_3^- **(b)**, and concentrations of N_2O **(c)**, NO_2^- **(d)** and O_2 **(e)** at stations SS 3201 (17° N, 68° E; filled circles, joined by dotted lines) and SS 3204 (19.75° N, 64.62° E; filled triangles, joined by continuous lines). The shaded region represents the secondary NO_2^- maximum at SS 3201. Vertical lines give δ^{15}N and δ^{18}O of tropospheric N_2O. Station locations shown in Fig. 1. After Naqvi et al. (1998a).

the upper N_2O 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 N_2O is isotopically lighter, both for nitrogen and oxygen, than the tropospheric N_2O. 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 N_2O is preferentially utilized by denitrifiers). Intriguingly, the δ^{15}N values for N_2O exceed those for NO_3^-[4], going against the trend exhibited by cultures of *Paracoccus denitrificans* grown under steady-state conditions (Barford et al., 1999), which suggested greater fractionation during the reduction of NO_3^- to N_2O (~16‰) than of N_2O to N_2 (~13‰). The higher δ^{15}N of N_2O seems to imply that the natural bacterial populations should have a larger isotopic effect for the final reduction sequence. Moreover, as this trend persists also in the N_2O-rich waters below the SNM (Fig. 6), it necessitates the involvement of denitrification at least in channeling the lighter nitrogen isotope to N_2, if not in N_2O production, well outside the SNM. Based on the analysis of N_2O isotopomer ratios (site preference of ^{15}N in the linear N_2O molecule), Yamagishi et al. (2005) also identified denitrification to be the dominant process responsible for N_2O production in the 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 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 N_2O.

The coastal suboxic zone in the Arabian Sea is distinguished by much higher concentrations of N_2O (reaching up to ~0.8 μM) as compared to the open ocean. The highest values are unexpectedly associated with very high NO_2^- (reaching up to 16 μM) and low (near exhaustion) NO_3^- levels often at mid-depths. This trend, observed in most cross-shelf sections (e.g. Fig. 3), has also been recurring at the CATS site (Fig. 4) where peak N_2O values invariably coincide with rapidly declining NO_3^- and the build-up of NO_2^-. The N_2O concentrations decrease rapidly as the system turns sulphate reducing. This indicates that the observed high concentrations cannot be due to inhibition of N_2O reductase activity by H_2S (Senga et al., 2006). The oxygen concentrations are too low for nitrification to occur in these waters, leaving denitrification as the principal pathway of N_2O production. These results are completely different from those from the open ocean SNM (Fig. 6). Incubations of water samples collected from the Indian shelf, that were O_2-poor but not denitrifying to begin with, revealed transient N_2O 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 N_2O-reductase leading to a large fraction of nitrogen undergoing bacterial reduction ending up as N_2O (Naqvi et al., 2000). Because such production occurs within a few metres of the sea surface, the observed surface N_2O concentrations (5 to 436 nM, mean 37.3 nM, n=241) and the computed emission to the atmosphere (0.05 to 0.38 Tg N_2O 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 N_2O are relatively narrow (−2 to 13‰ for δ^{15}N and 17 to 60‰ for δ^{18}O) over the shelf as compared to the open ocean (3 to 81‰ for δ^{15}N and 17 to 95‰ for δ^{18}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

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be converted to the more commonly used SMOW (standard mean ocean water) scale utilizing the equation (Kim and Craig, 1990):

$\delta^{18}O_{AIR}=-23.0+\delta^{18}O_{SMOW}/1.0235$

[4] Analysis of isotopic composition of nitrate generally involves its chemical reduction to NH_4^+, during which process nitrite, if present, is also similarly reduced. The data being reported here, as in all previous studies, thus pertain to the combined NO_3^- and NO_2^- pool, but will still be denoted by δ^{15}N of NO_3^- for convenience hereafter.

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 N_2O concentration (decrease from the pronounced maximum from the top of the suboxic zone to near-zero concentration close to the sea floor), the δ^{15}N and δ^{18}O values did not vary greatly. While, the aforementioned exchange of intermediates between 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 N_2O 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 NO_3^-, as we shall see in the following section.

6 Nitrogen isotopic fractionation during denitrification

Water column distributions of δ^{15}N in NO_3^- and 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 $^{14}NO_3^-$ over $^{15}NO_3^-$) in seawater (Cline and Kaplan, 1975), leading to an enrichment of ^{15}N in the NO_3^- pool and its depletion in the N_2 pool. In the central Arabian Sea, the δ^{15}N of NO_3^- increases from ∼6‰ 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 δ^{15}N of N_2 concurrently decreases from ∼0.6‰ to ∼0.2‰ (Brandes et al., 1998). Brandes et al. combined their isotopic data with NO_3^- deficits (computed from the relationship between the tracer "NO" with potential temperature) and used advection-reaction (Rayleigh distillation) and diffusion-reaction models to compute the isotope fractionation factor (ε) of 22‰ and 25‰, respectively. Altabet et al. (1999) obtained a somewhat higher (∼30‰), value for ε using −N* (cf. Gruber and Sarmiento, 1997) and Rayleigh fractionation. The estimates of ε are about the same for the suboxic 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 (ε=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.

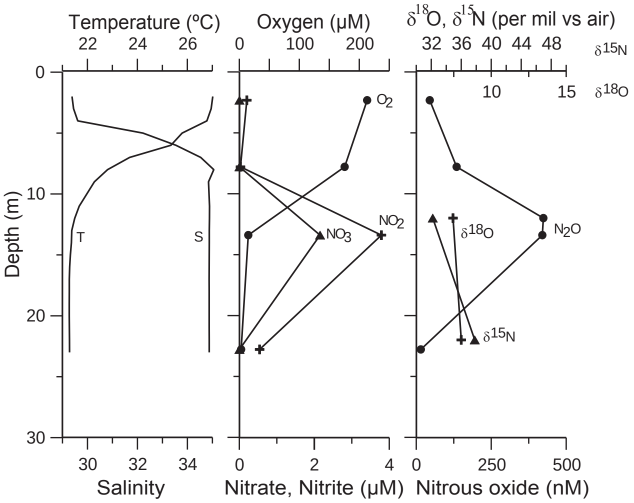

Fig. 7. Vertical profiles of temperature, salinity, dissolved O_2, inorganic nitrogen species and δ^{15}N and δ^{18}O of N_2O at Sta. SK 137/39 (9.950° N; 76.017° E; Fig. 1) sampled on 8 August 1998. These data are hitherto unpublished.

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 δ^{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 deficit increased with depth reaching the peak value of just under 15 μM in the deepest sample. While all the above parameters exhibited expected depthwise changes, the profile of δ^{15}N-NO_3^- deviated greatly from the one expected in a closed system where Rayleigh distillation may be assumed to apply. That is, given the high NO_3^- deficit in subsurface waters, the δ^{15}N-NO_3^- values should have ranged between 17 and 26‰ if the

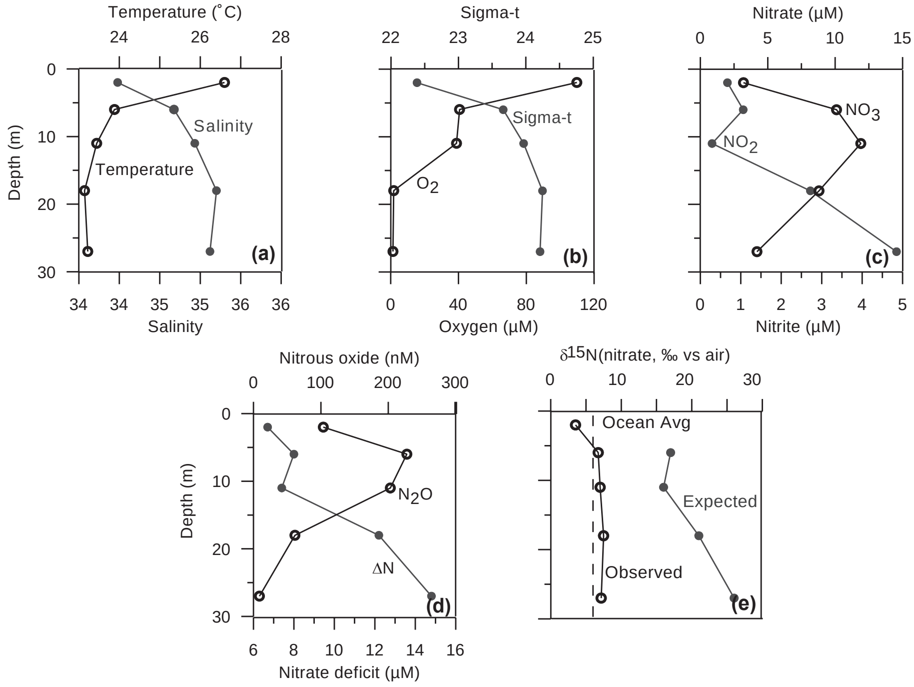

Fig. 8. Vertical profiles of temperature, salinity, density, dissolved O_2, inorganic nitrogen species and δ^{15}N of NO_3^- (observed as well as expected from the computed NO_3^- deficits and the reported fractionation factor for the open ocean) at Sta. SS 3939 (13.126° N; 74.631° E; Fig. 1) sampled on 30 August 1997. These data are hitherto unpublished.

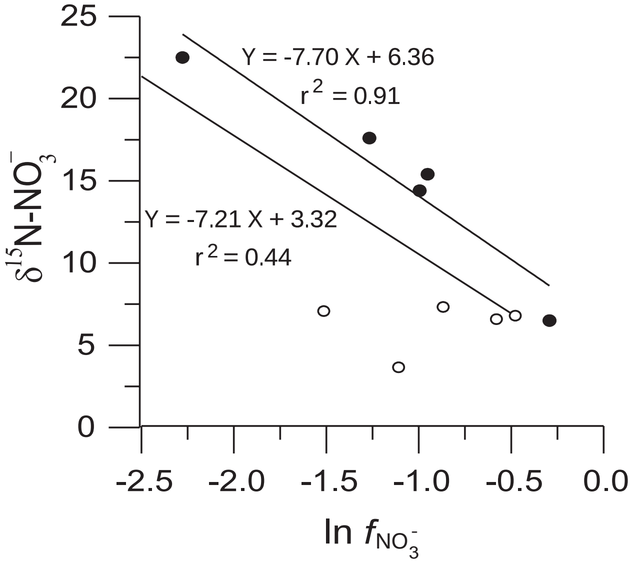

Fig. 9. δ^{15}N of NO_3^- versus natural log of fraction of the original NO_3^- remaining for samples from Sta. SS 3939 (open circles) and Stas. G3–G5 (filled circles). The two regression lines with slopes of −7.70 and −7.21 are for data from Stas. G3–G5 only and those from all stations, respectively. Station locations are shown in Fig. 1. These data are hitherto unpublished.

isotopic fractionation factor reported for the open ocean suboxic zone (∼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 δ^{15}N-NO_3^- values (6.65 to 7.41‰) that were quite close to the oceanic average with no depthwise variability. 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 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 δ^{15}N-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 mmol NO_3^- m^{-2} 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., 2006c[5]). These rates by themselves appear to be inadequate to account for the observed NO_3^- loss in the water column. The other processes that may bring about NO_3^- removal are anammox,

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[5] Naqvi, S. W. A., Naik, H., Lavik, G., and Kuypers, M. M. M.: Sedimentary denitrification rates over the western Indian continental shelf, in preparation, 2006c.

dissimilatory reduction of NO_3^- to NH_4^+ (which may also be coupled to anammox) and/or autotrophic denitrification (e.g. reduction of NO_3^- by species such as S^{2-}/HS^-, Fe^{2+} and 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 NO_2^- concentrations (maximum 16 μM) are expected to be matched by a high rate of diffusive supply of NH_4^+ from the sediments (Naqvi et al., 2000). (2) Apparently low $\delta^{15}N\text{-}NO_3^-$ relative to the NO_3^- deficit could be produced by mixing of waters. In order to 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 $^{15}NO_3^-$ and $^{14}NO_3^-$, followed by rapid 1:1 mixing with the freshly-upwelled water having a NO_3^- content and $\delta^{15}N$ of, say, 24 μM and 7‰, respectively. The resultant mixture would possess the isotopic characteristics of the upwelled water ($\delta^{15}N$=7‰), but it would show a NO_3^- deficit of 12 μM. Alternatively, continuous mixing (the open system behaviour) could also result in an underestimation of the fractionation factor. (3) It has been found recently that the reduction of NO_3^- to NO_2^- involves huge isotopic discrimination, such that $\delta^{15}N$ of NO_2^- in the suboxic zone of the eastern tropical North Pacific is quite low (K. Casciotti, personal communication). As pointed out, the procedures followed by us actually yields the isotopic composition of NO_3^- plus NO_2^-, and so the measured values would be dependent on the ratio between concentrations of the two species. The NO_2^- : NO_3^- ratio is generally much higher in the coastal zone than in the open ocean, and that could contribute to lower $\delta^{15}N$ of the combined NO_3^- and NO_2^- pool. (4) Finally, it is also possible that if and when the NO_3^- loss is 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 NO_3^- (Fig. 9). For these samples the fractionation factor was computed using a simple advection-reaction model that ignores mixing. As the sampling sites were located very close to each other along a coast-perpendicular transect, and the 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):

$$\delta^{15}N{-}NO_3{=}10^3(\alpha-1)\log_e f_{NO3} + (\delta^{15}N{-}NO_3)_{init}$$

where f_{NO3} is the ratio between the observed and expected NO_3^-+NO_2^- concentrations, the latter equaling AOU/8.65, and $(\delta^{15}N\text{-}NO_3)_{init}$ gives the isotopic composition of the initial (unaltered) material.

The plot of $\delta^{15}N\text{-}NO_3$ versus $\log_e f_{NO3}$ (Fig. 9) indicates a good linear correlation (r^2=0.91) with the slope of the regression line (value for ε_{denit}) 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 $\delta^{15}N$ value of 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 pathways of oceanic nitrogen cycling.

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