

# OXYGEN DEFICIENCY IN THE NORTH INDIAN OCEAN

## *DEFICIENCIA DE OXIGENO EN EL OCEANO INDICO NORTE*

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### ABSTRACT

The Indian Ocean contains one of the oceans' most pronounced oxygen minimum zones (OMZ), which, anomalously, is the most intense in the northwestern sector (Arabian Sea). It also contains the majority of the area of oceanic continental margins in contact with oxygen-depleted waters. Impacts of the oxygen deficiency on regional biogeochemistry, especially anaerobic nitrogen transformations, are described. A comparison of the perennial, mesopelagic OMZ in the open Northwestern Indian Ocean is made with a shallower oxygen deficient system that develops seasonally (during late summer and autumn) over the western Indian shelf. The latter appears to have intensified in recent years presumably due to anthropogenic nutrient loading from land.

KEYWORDS: Indian Ocean, nitrogen cycling, denitrification, N<sub>2</sub>O, eutrophication

### RESUMEN

El Océano Índico alberga una de las zonas de mínimo oxígeno (ZMO) más pronunciadas, siendo más intensa en el sector nor-occidental (Mar de Arabia). También presenta la mayor parte del área del margen continental en contacto con aguas carentes de oxígeno. Se describen los impactos de la deficiencia de oxígeno sobre la biogeoquímica, especialmente sobre las transformaciones anaeróbicas del nitrógeno. Se realiza una comparación entre la ZMO mesopelágica permanente del Océano Índico nor-occidental y un sistema deficiente en oxígeno más somero que se desarrolla estacionalmente (durante el final del verano y el otoño) sobre la plataforma continental de la India occidental. Este último parece intensificarse en los últimos años debido a la carga de nutrientes antropogénicos provenientes del continente.

PAI ABRAS CLAVES: Océano Índico, ciclo del nitrógeno, denitrificación, N<sub>2</sub>O, eutrofización.

Unlike the Atlantic and Pacific Oceans, the most intense Oxygen Minimum Zone (OMZ) in the Indian Ocean is not located along its eastern boundary, but in the north. This anomaly, like other distinguishing features of the Indian Ocean, arises from its unusual geography, i.e., mainly the presence of the Asian landmass that restricts its northern expanse to the tropics, not allowing adequate ventilation of the thermocline from the north and, to a smaller extent, a porous eastern boundary (openings between the Indonesian islands), which facilitates exchange of water with the Pacific Ocean at low latitudes. The two northern basins - the Arabian Sea and the Bay of Bengal - are characterized by O<sub>2</sub> levels below 0.1 ml L<sup>-1</sup> (~4 mM) within a wide depth range (~100/150 to 1,000 m) with the former experiencing *slightly* more severe O<sub>2</sub>-depletion. In fact, minimum O<sub>2</sub> concentration in the Arabian Sea is lower by <2 M as compared to that in the Bay of Bengal. However, even such a minute difference results in starkly contrasting biogeochemical cycling in the two basins (Fig. 1). This is because O<sub>2</sub> concentrations within the OMZ often fall below the threshold (<1 mM) required for denitrification (microbial reduction of NO<sub>3</sub> to N<sub>2</sub>) and reduction of other polyvalent elements in the Arabian Sea, but not in the Bay of Bengal (Naqvi *et al.* 2006a).

The perennial suboxic (=denitrifying) zone of the Arabian Sea (shaded area in Fig. 1; Naqvi 1991) also differs from the other open-ocean suboxic zones in that it is located well away from the sites of the most intense upwelling in the western Arabian Sea (off Somalia and Oman), and is the best developed in the least productive central Arabian Sea. Suboxic (even anoxic) conditions do develop over the western Indian shelf, but this happens only

seasonally (during late summer and autumn) and the two zones are not contiguous as they are separated by a slightly oxygenated pole-ward undercurrent (Naqvi *et al.* 2000, 2006b). Nevertheless, 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<sub>2</sub> <0.5 ml L<sup>-1</sup> (22 μM) and <0.2 ml L<sup>-1</sup> (9 μM), are estimated to cover about 1.15 × 10<sup>6</sup> and

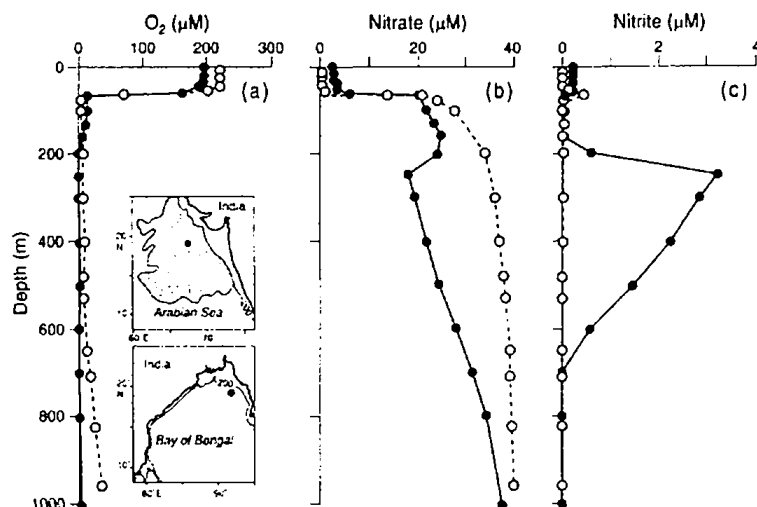


FIGURE 1. Comparison of vertical profiles of (a)  $O_2$  (b)  $NO_3$  and (c)  $NO_2$  in the Arabian Sea (filled circles) and the Bay of Bengal (open circles). The insets show the station locations and the geographical extent of perennial open-ocean denitrification zone (shaded area). From Naqvi *et al.* (2006a).

$0.76 \times 10^6$  km<sup>2</sup> of marginal seafloor in the region, which amount to 59 and 63%, of the corresponding global areas (Helly & 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  $O_2$ -deficient environments highly vulnerable to human impact.

As in the suboxic zones of the eastern tropical Pacific Ocean, a particle maximum, also called the intermediate nepheloid layer (INL), occurs within the denitrification-indicator secondary nitrite maximum (SNM) in the Arabian Sea as well (Naqvi *et al.* 1993). The confinement of the INL only to the SNM, and its offshore intensification and shoaling preclude the advection of particle-rich layers from the continental margin; instead its association with the maxima in the activity of the electron transport system (ETS), particulate protein, and bacterial biomass point to an in situ biological origin. The ubiquitous, relatively-sterile 'clear zone' overlying the suboxic zone in the oceanic OMZs may be unsuitable for microbial heterotrophs because of the ambient  $O_2$  levels being slightly too low for the aerobic and slightly too high for the anaerobic respirations. However, once the  $O_2$  falls below the threshold for the anaerobes to be able to utilize other more abundant oxidants (mainly  $NO_3$ ), the environment becomes conducive for them to proliferate. It implies that respiration in the 'clear

zone' is limited by  $O_2$  rather than organic matter. Within the OMZ, however, the sinking flux of particulate organic carbon (POC) appears to be inadequate to sustain respiration rates derived from the ETS activity as well as bacterial production (Naqvi & Shailaja 1993, Ducklow 1993). This calls for additional supply of organic matter to the OMZ - either quasi-horizontally from the continental margins, or vertically through diurnal migration of organisms particularly myctophiids and episodic injections of transparent exopolymer particles.

Measured  $N_2/Ar$  profiles exhibit a well-defined maximum within the SNM, but the computed amounts of excess  $N_2$  relative to the levels observed outside the SNM are almost twice the 'nitrate deficits' calculated from the classical (Redfield) stoichiometry (Fig. 2; Codispoti *et al.* 2001; Devol *et al.* in press; Naqvi *et al.* 2006c). This mismatch may result from incorrect stoichiometric assumptions inherent in the nitrate deficit calculation, inputs of new nitrogen through  $N_2$ -fixation,  $N_2$  contributions from sedimentary denitrification along continental margins, anaerobic ammonia oxidation (anammox), and metal-catalyzed denitrification reactions. Recent results from the suboxic waters of TNamibia and Chile have demonstrated that, relative to canonical denitrification, anammox may be a more important process of  $N_2$  formation (*e.g.*, Kuypers *et al.* 2005). However, the significance of this process in the Arabian Sea water column is yet to be evaluated.

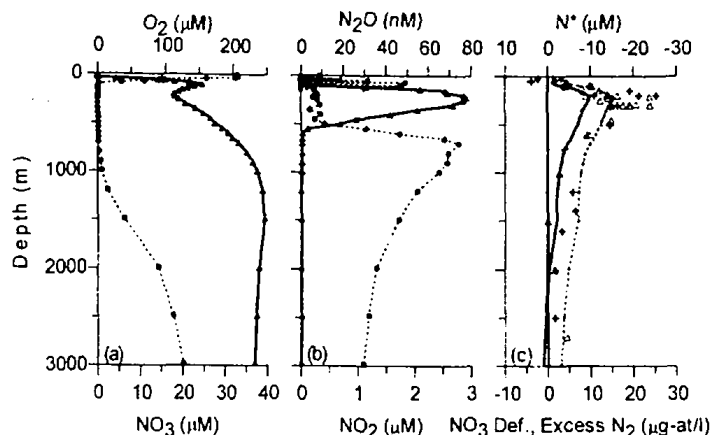


FIGURE 2: Vertical profiles of properties at 19°N, 67°E (all data except for N<sub>2</sub> collected on TN039 cruise of US JGOFS on 1-2/10/1994). (a) O<sub>2</sub> (circles) and NO<sub>3</sub> (triangles); (b) N<sub>2</sub>O (circles) and NO (triangles); (c) NO<sub>3</sub> deficit (dots connected by the solid line), N\* (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 from this site and triangles for those from other stations also located within the denitrification zone). From Naqvi *et al.* (2006c).

Incubation experiments involving production of <sup>29</sup>N<sub>2</sub> in samples spiked with <sup>15</sup>NO<sub>3</sub> yielded N<sub>2</sub> production rates averaging 9.1 ± 1.0 nmol N l<sup>-1</sup> d<sup>-1</sup>, which when extrapolated to the entire Arabian Sea indicate an overall denitrification rate of 41 ± 18 Tg N y<sup>-1</sup> (Devol *et al.* in press). This is within the range (10–44 Tg N y<sup>-1</sup>) of previous estimates for canonical denitrification in the region based on stoichiometric calculations and ETS measurements. While the reasons for the above-mentioned mismatch between excess N, and nitrate losses are not clear, it may nevertheless be concluded that, if denitrification is defined as the conversion of combined nitrogen to N<sub>2</sub> then current estimate of its rate in the Arabian Sea needs an upward revision.

Like other regions containing intense OMZs, the North Indian Ocean is an important area for N<sub>2</sub>O production and emission to the atmosphere. Where the SNM is absent (Bay of Bengal, southern and western Arabian Sea), vertical N<sub>2</sub>O profiles exhibit a single maximum coinciding with the O<sub>2</sub> minimum. Reduction of N<sub>2</sub>O to N<sub>2</sub> keeps its concentration suppressed within the SNM with high concentrations found at its peripheries, thereby accounting for the double maxima observed within the sub-oxic zone (Naqvi & Noronha, 1991; Naqvi *et al.* 2006a).

Large mass-dependent fractionation of stable isotopes occurs during sub-oxic transformations of nitrogen. Preferential reduction of <sup>14</sup>NO<sub>3</sub> by denitrifiers results in marked (15–18‰ relative to air) enrichment of <sup>15</sup>N in the residual NO<sub>3</sub> (Brandes *et*

*al.* 1998) Even larger variations in both <sup>15</sup>N/<sup>14</sup>N and <sup>18</sup>O/<sup>16</sup>O in N<sub>2</sub>O (3 to 81‰, for d<sup>15</sup>N and 17 to 95‰ for d<sup>18</sup>O) have been observed within the open-ocean suboxic zone, the heaviest and the lightest values coming from the core of the SNM and the upper portion of the thermocline, respectively. The isotopic data are indicative of multiple pathways of N<sub>2</sub>O production (nitrification, denitrification and the coupling of the two processes; Yoshinari *et al.* 1997; Naqvi *et al.* 1998).

The suboxic zone occurring seasonally over the western Indian shelf occupies a two orders of magnitude smaller volume than its perennial open-ocean counterpart, but it experiences more extreme conditions and exhibits some unexpected trends (Naqvi *et al.* 2000, 2006b). The development of this system is closely related to the seasonally changing coastal circulation and hydrography. During the SW monsoon the circulation is conducive for upwelling off the Indian west coast, which brings low-O<sub>2</sub> water over the shelf. But this water is generally prevented from surfacing due to the presence of a thin (<10 m) warm, fresher layer formed as a result of intense rainfall in the coastal zone. Respiration of organic matter coupled with strong near-surface stratification leads to the development of very intense O<sub>2</sub> depletion at perhaps the shallowest depth (sometimes within 10 m) of the sea surface anywhere in the world. Off Goa, near-bottom O<sub>2</sub> concentrations reach suboxic levels in August, and complete denitrification is followed by the SO<sub>4</sub><sup>2-</sup> reduction in September-

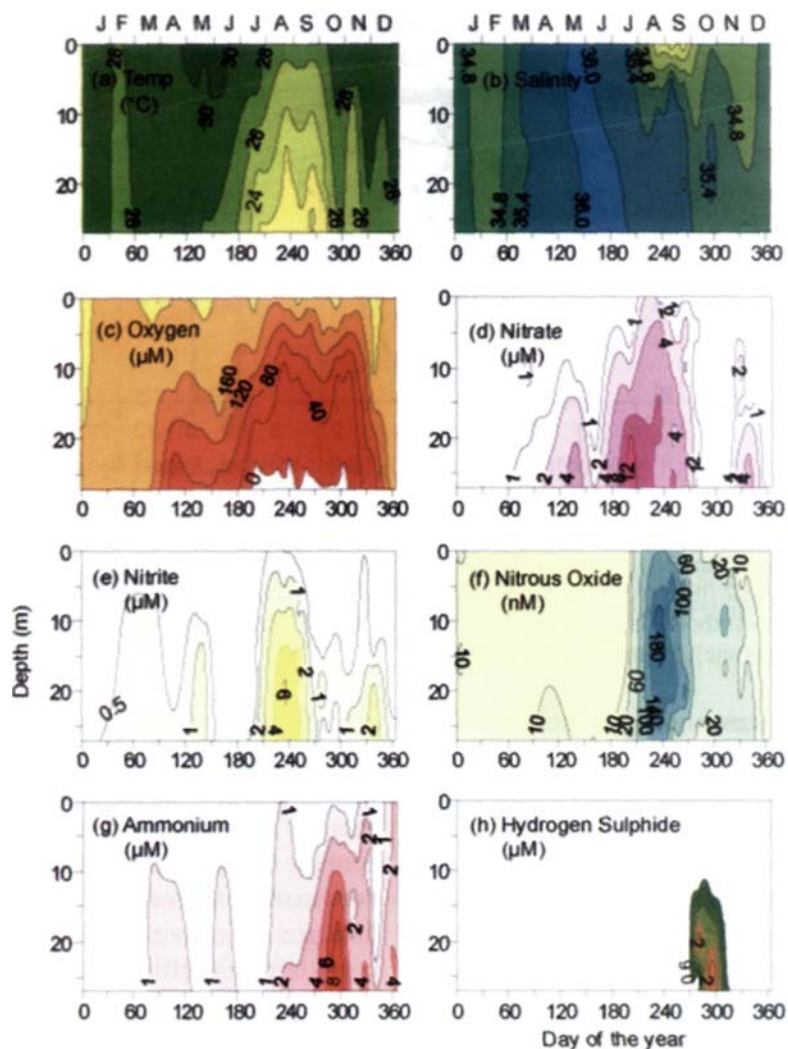


FIGURE 3: Monthly-/fortnightly-averaged records showing annual cycle of (a) temperature, (b) salinity, (c) oxygen, (d-g) inorganic nitrogen species, and (h) hydrogen sulfide at the Candolim Time Series (CATS) site (15°31'N, 73°39'E) based on observations from 1997 to 2004. From Naqvi *et al.* (2006c).

October (Fig. 3). With the reversal of surface currents, oxic conditions are reestablished in November-December. When the reducing conditions are at their peak in September-October, the cross-shelf sections north of about 12°N latitude show the classical sequence of utilization of electron acceptors: O<sub>2</sub> over and beyond the outer shelf, NO<sub>3</sub><sup>-</sup> over the mid-shelf and SO<sub>4</sub><sup>2-</sup> over the inner shelf. This coastal O<sub>2</sub>-deficient zone, the largest of its kind in the world (area ~200,000 km<sup>2</sup>), is primarily of natural origin, but it appears to have intensified in recent years, presumably in response to enhanced inputs of inputs from land, since there are no indications of water column SO<sub>4</sub><sup>2-</sup> reduction in the region, now recurring every year, in the historical data sets.

The rate of denitrification in the coastal hypoxic zone is an order of magnitude smaller than that in the open ocean OMZ, but the former is distinguished by uncommon accumulation of N<sub>2</sub>O (the highest recorded in the ocean), making this region a significant source of atmospheric N<sub>2</sub>O (Naqvi *et al.* 2000, 2006b). The extents of heavier isotope enrichment in the combined NO<sub>3</sub><sup>-</sup> and NO<sub>2</sub><sup>-</sup> pool and in N<sub>2</sub>O in reducing waters appear to be considerably smaller in the coastal region than in the open ocean, reflecting more varied sources/sinks and/or different isotopic fractionation factors (Naqvi *et al.* 2006c). The distributions of two other major redox-sensitive elements, iron (Fe) and manganese (Mn), reveal prominent mid-depth maxima within the SNM due to their reductive solubilization from particulate

matter (Saggar *et al.* 1989). Enhanced availability of Fe<sup>2+</sup> within suboxic waters probably helps the growth of denitrifiers (J.W. Moffett *et al.*, unpublished manuscript). Even greater dissolution of particulate Fe seems to occur over the wide Indian shelf that is seasonally exposed to suboxic waters, but not over the Omani shelf, and this in conjunction with atmospheric deposition pattern makes primary productivity in some parts of the western Arabian Sea Fe-limited (S.W.A. Naqvi *et al.* unpublished manuscript).

The O<sub>2</sub>-deficiency makes a profound impact on biological processes (Morrison *et al.* 1999). The quality and quantity of primary production are affected when suboxic waters ascend to euphotic zone (Naqvi *et al.* 2006b). The O<sub>2</sub>-deficiency alters the diurnal migration pattern of most zooplankton. However, some organisms that are adapted to tolerate suboxic conditions are amazingly abundant (*e.g.*, myctophiids whose estimated biomass in the Arabian Sea alone is ~100 million tonnes). Exclusion of demersal fish from the shallow suboxic zone and frequent episodes of fish mortality, presumably caused by the surfacing of O<sub>2</sub>-depleted water, affect fishery resources (Banse 1959, Naqvi *et al.* 2006b). The impact on the benthic community is particularly strong, which within the OMZ is largely composed of surface-feeding polychaetes, some having undergone morphological modifications in order to adapt to low O<sub>2</sub> levels. Interestingly, while the diversity and evenness of benthic fauna is reduced, the total biomass may be higher within the sediments in contact with the OMZ than those exposed to more oxygenated waters (Levin *et al.* 2000). Sulfur bacteria such as *Thiomargarita*, *Thioploca* and *Beggiatoa* have not been reported from the Indian shelf so far, but *Thioploca* mats have been observed along the continental slope off Pakistan (Schmaljohann *et al.* 2001).

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