## Some aspects of the nitrogen cycling in the Arabian Sea

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Abstract - Extensive observations made in the Arabian Sea establish it as one of the largest oceanic reducing sites accounting for approximately 1/3 of the global water column denitrification. Evidence for large short-term (seasonal) variations in the intensity of the oxygen-deficient conditions is provided by data on the nitrogen system as well as the activity of the electron transport system (ETS). The results imply a quick renewal of the oxygen-depleted waters. Denitrification in the Arabian Sea is unique in that it does not occur beneath centres of most intense seasonal upwelling; instead, it is most intense in (offshore) areas of relatively low primary productivity. This anomaly could arise from a combination of several factors: (1) An important role of region-wide mixing in providing nutrients to the euphotic zone. This is supported by the relatively uniform offshore particle fluxes to the deep sea as well as the high nitrous oxide saturations at the sea surface and consequently large atmospheric fluxes. (2) A dominant effect of the re-oxygenation of subsurface layers through the supply of oxygen from the surface; this seems to be dependent on the vertical stratification which is closely linked to surface circulation that is most intense close to the coast. (3) An additional (quasi-horizontal) mode of input of biodegradable organic matter, probably in the form of the dissolved and suspended organic matter to the oxygen-poor waters. The ETS data strongly support this view as only 2/3 of the observed respiration rates can possibly be fuelled by the particle flux.

Estimates of some important terms in the nitrogen cycling are evaluated. The available data suggest that the Arabian Sea probably serves as a large sink of inorganic combined nitrogen ( $\sim$ 3 x 10<sup>13</sup> g N y<sup>-1</sup>). This quantity should be supplied by the flow of deep waters that upwell to the upper layers. Changes in the deep-sea circulation pattern through geological times might cause fluctuations in this vital supply, affecting the upper and mid-depth chemical composition and consequently the primary productivity of the North Indian Ocean.

#### INTRODUCTION

Marine oxygen-deficient zones (where the dissolved oxygen content of some subsurface waters falls to near-zero levels) cover < 2% of the total area of the oceans. However, they make very important contributions to global nitrogen cycling. Through denitrification, which occurs within the near-anoxic waters as well as in marine sediments, these environments have the potential for altering the oceanic combined nitrogen inventory. This may in turn affect the biological productivity and therefore the climate through controls on atmospheric carbon dioxide (MCELROY, 1983; KNOX and MCELROY, 1984). These environments might exert a more direct control on the climate through nitrous oxide (N<sub>2</sub>O). This is because the oxygen-deficient and surrounding low-oxygen waters are perhaps the most important media for the biochemical transformations involving this important greenhouse gas (CODISPOTI and CHRISTENSEN, 1985; NAQVI and NORONHA, 1991).

That oxygen-deficient conditions develop widely at mid-depth in the Arabian Sea, has been known since the John Murray Expedition (GILSON, 1937). However, it is only in the last 15 years that their effects on the nitrogen cycle were quantitatively investigated. The intent of the present paper is to make a synthesis of some recent data on the nitrogen cycle in the Arabian Sea and to present a reasonable combined-nitrogen budget for this region.

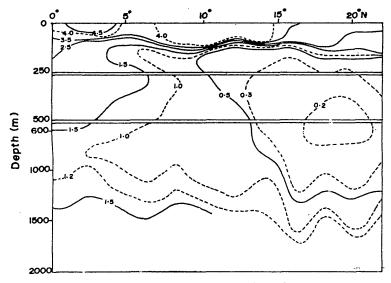


Fig. 1. Vertical section showing distribution of oxygen (cm<sup>3</sup> dm<sup>-3</sup>) in the upper 2 kilometers along 65°E longitude (from SEN GUPTA et al., 1976).

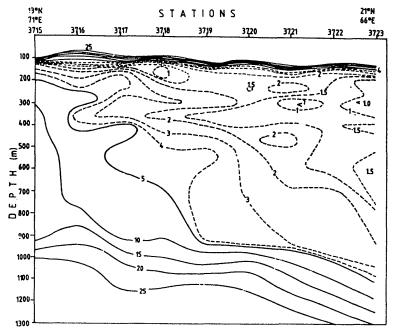


Fig. 2. Colorometrically - determined oxygen levels (μM) within the oxygen minimum along a transect parallel to the Indian coast (from NAQVI, 1987).

## Dissolved oxygen

Below the mixed layer in the Indian Ocean, the dissolved oxygen in the upper kilometer or so decreases rapidly north of the equatorial belt (Fig. 1). Thus, the oxygen minimum is most intense in the northernmost parts of this ocean unlike the Pacific and Atlantic Oceans, where the lowest oxygen concentrations are found along the eastern boundaries. This anomaly reflects in part the absence of eastern-boundary upwelling sites in the eastern Indian Ocean; instead, the most intense upwelling centres are located in the northwestern sector - off Somalia and Arabia. Moreover, the most-ly-zonal flow in the equatorial Indian Ocean seems to prevent the trans-equatorial

movement of waters in the upper kilometer (SHARMA, 1976); such exchange appears to be confined to the western boundary and it probably undergoes large seasonal changes (SWALLOW, 1984). According to SWALLOW (1984) the equatorial Indian Ocean acts like a holding tank where the intermediate water masses, originally well-oxygenated, lose their oxygen content. Consequently, while the renewal of the intermediate waters in the Arabian Sea itself is perhaps rapid, the re-oxygenation is not proportionately large.

Almost all the data on dissolved oxygen in the Arabian Sea have been generated following the titrimetric (Winkler) procedure, which is known to be unsuitable at very low oxygen levels. A vertical section of oxygen in the northeastern Arabian Sea based on the more reliable colorometric measurements is shown in Fig. 2. As expected, the oxygen concentrations within a thick layer are extremely low as is the case with the two other major oceanic oxygen-deficient zones located in the eastern tropical Pacific (BROENKOW and CLINE, 1969; CLINE and RICHARDS, 1972; CODISPOTI and CHRISTENSEN, 1985).

## Evidence for denitrification

The Arabian Sea has been recognized as a major oceanic denitrification site (RICHARDS, 1965). The principal evidence for the occurrence of water column denitrification is the widespread presence of a secondary nitrite maximum (SNM) within the core of the oxygen minimum (Fig. 3), first observed during the John Murray Expedition (GILSON, 1937). It has been demonstrated by several workers that considerable deficiency in inorganic combined nitrogen exists within this layer (SEN GUPTA et al., 1976; DEUSER et al., 1978; NAQVI et al., 1982). This is evident in Fig. 4 which gives a plot of the nitrate tracer "NO" [defined as O<sub>2</sub> + 9.1 (NO<sub>3</sub> + NO<sub>2</sub>)] vs potential temperature in the northeastern Arabian Sea. A pronounced minimum in "NO" between approximately 14 and 18°C (coinciding with the SNM) strongly suggests loss of nitrate beyond nitrite presumably due to biochemical reduction. A plot of nitrite vs O<sub>2</sub> (determined colorometrically) within the SNM (Fig. 5) indicates that the SNM occurs when the oxygen concentrations fall below approximately 3 µM. In fact, most of the points with  $NO_2 > 0.2 \mu M$  correspond to  $O_2 < 2\mu M$ . The corresponding oxygen concentrations observed in the eastern tropical Pacific are 1  $\mu$ M north of the equator (CLINE and RICHARDS, 1972) and 2.2 µM off Peru (CODISPOTI and CHRISTENSEN, 1985). These compare very well with the experimentally determined critical oxygen concentrations (below which denitrification should occur) for bacteria isolated from the oxygen-depleted environments of the eastern tropical North Pacific (ETNP) and Saanich Inlet (1.2-3.85 µM - DEVOL, 1978).

Table 1. Heterotrophic bacterial populations at selected stations (from NAQVI, 1986).

Location	Depth	(m) Most	proba	ble numbe	r of ba cm <sup>-3</sup> )	cteria <sup>*</sup>	O <sub>2</sub> (μΜ)	NO <sub>2</sub> (μΜ)
		1	2	3	4	5	·	·
15°N,	10	1100	450	0	9	3		0 -
73°E	50	450	35	0	25	0		0
	150	1400	1400	6	95	0		0
15°N,	95	4500	1500	300	60	0		0.06
68°E	200	450	450	450	0	60	2.2	3.98
21°N,	10	2500	250	0	40	95	209	0
64°E	25	1500	1500	0	30	0	204	0
	200	14000	11000	0	70	475	2.3	0
	500	11000	11000	0	30	30	2.2	1.26
21°N,	10	11000	11000	0	200	0	189	0
66°14′E	80	4500	2500	0	40	0	170	0.10
	200	14000	14000	0	110	0	1.2	0.31
	500	400	400	0	140	0	4.5	1.36

<sup>\* 1 -</sup> Total heterotrophs; 2 - Nitrate reducing bacteria; 3 - Nitrite reducing bacteria; 4 - Ammonifiers; 5 - Nitrate non-reducers.

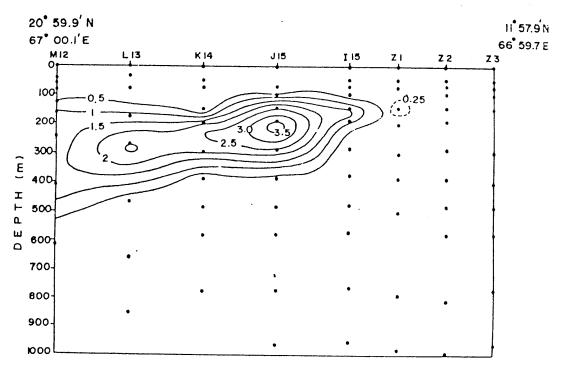


Fig. 3. Vertical section showing distribution of nitrite ( $\mu$ M) along 67°E longitude (from NAQVI and NORONHA, 1991).

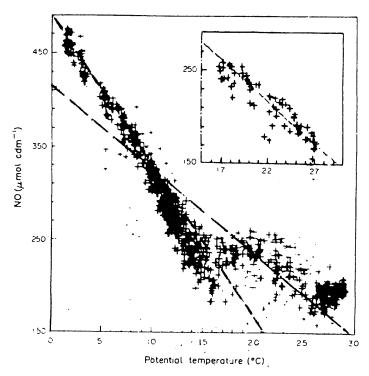


Fig. 4. Plot of "NO" vs potential temperature for the eastern Arabian Sea (between 12° and 17°N latitude, east of 67°E longitude). The straight lines give the least squares fits to the data corresponding to  $\theta \le 9$ °C and  $17 \le \theta \le 27$ °C; for the latter range (inset), samples from only outside the denitrification zone were considered (from NAQVI et al., 1990).

Microbiological evidence for denitrification within the oxygen minimum of the north-eastern Arabian Sea is presented in Table 1 which gives the most probable numbers of bacteria at selected locations. Denitrifiers appear to be quite abundant within the SNM. It is interesting to note that the nitrifiers are also found in sizeable numbers at very low oxygen concentrations. This is in conformity with some previous reports suggesting that significant nitrification may take place even within the oxygen-deficient layer (e.g., WARD et al., 1989).

It is clear from the results summarized above that the minimum oxygen concentrations in the Arabian Sea are low enough to trigger denitrification, and the available chemical and microbiological evidence suggests that dissimilatory nitrate reduction could be the dominant respiratory process at mid-depth.

Spatial changes in denitrification and primary productivity

Utilizing all the available data on nitrite, NAQVI (1991b) has recently delineated the geographical boundaries of the denitrification zone in the Arabian Sea (Fig. 6). The most interesting and anomalous feature of the Arabian Sea denitrification is that it does not correlate spatially with primary productivity of the overlying surface waters (Fig. 7). Thus the three main upwelling centres (off Somalia, southeast Arabia and southwest India) appear to be located outside the denitrification zone. Indeed, a comparison of Figs. 6 and 7 reveals that, if the nitrite distribution at the secondary maximum generally reflects the intensity of denitrification as assumed by NAQVI (1991b), the zone of the most vigorous denitrification seems to be characterized by some of the lowest primary productivity rates in the region.

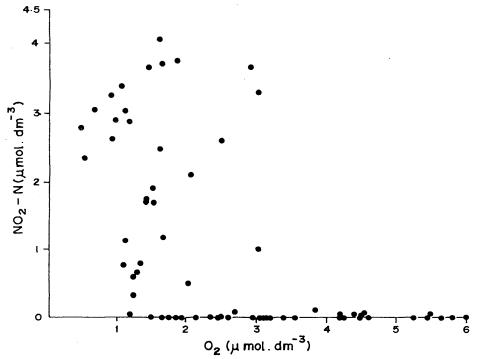


Fig. 5. Plot of nitrite vs dissolved oxygen (determined colorometrically) within the SNM.

It had been assumed by earlier workers that denitrification occurred everywhere in the northern Arabian Sea. Fig. 6 shows that such is not the case since very low nitrite concentrations, very often below the detection limit, are observed in the north-

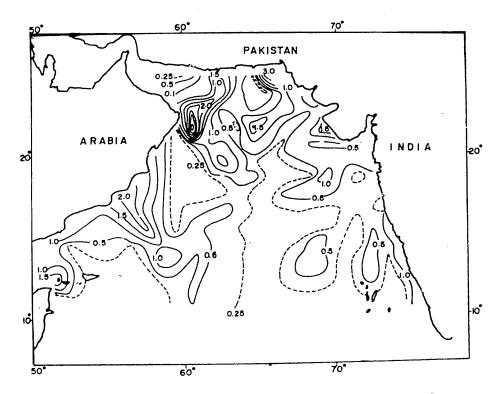


Fig. 6. Distribution of nitrite ( $\mu$ M) at the secondary maximum averaged for each 1-degree square using all the available data (maximum values at each station). The hatched areas represent zones of upwelling off Arabia (A), Somalia (B) and southwest India (C). Extensions of zones B and C south of Lat.  $10^{\circ}$ N are not shown due to the absence of SNM. The 200-m depth contour is also shown (from NAQVI 1991b).

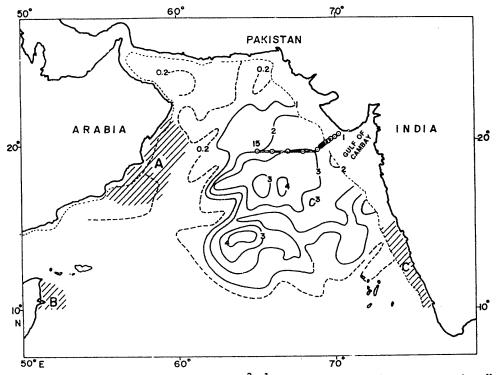


Fig. 7. Distribution of primary production (g C m<sup>-2</sup> d<sup>-1</sup>) averaged for each 1-degree square using all the available data north of Lat. 12°N (from NAQVI, 1991b). Note that the low productivity cell seen off Arabia is probably an artifact produced by uneven temporal and spatial coverage.

ernmost and western parts. Operationally bounding the denitrification zone by the 0.2  $\mu$ M NO<sub>2</sub> contour, the area of the Arabian Sea affected by denitrification could be computed as 1.37 x  $10^6$  km<sup>2</sup>, about 30% smaller than the previous estimate (1.95 x  $10^6$  km<sup>2</sup> - NAQVI, 1987).

NAQVI (1991b) suggested that the exchange of oxygen between the surface and subsurface layers through vertical mixing might play a key role in determining the extent of denitrification in the Arabian Sea. This may be mainly controlled by the thermohaline stratification related to surface circulation. During the northeast (winter) monsoon, the prevailing general counter- clockwise circulation maintains low (< 25°C - WYRTKI, 1971) surface temperatures in the northern and western Arabian Sea favouring vertical mixing. On the other hand, the advection of warm, low salinity waters from the equatorial region leads to strong stratification in the eastern and central Arabian Sea, inhibiting vertical mixing. Maintenance of reducing conditions in the Arabian Sea could thus be linked to this feature.

#### Nitrate losses

As stated earlier, there exist large deficiencies in inorganic combined nitrogen within the SNM. In order to compute the nitrate deficit ( $\Delta$  N, the difference between the expected nitrate concentration and the sum of observed nitrate and nitrite concentrations) three approaches have been followed. SEN GUPTA et al. (1976) and NAQVI et al. (1982) estimated the expected nitrate from a stoichiometric model (RED-FIELD et al., 1963) as the sum of the "oxidative" and "preformed" fractions, a method similar to that followed by CLINE and RICHARDS (1972) in the ETNP. DEUSER et al. (1978), on the other hand, utilized a nitrate-salinity relationship to compute the expected nitrate. NAQVI and SEN GUPTA (1985) proposed the use of "NO" to compute nitrate deficits. This approach is based on the premise that "NO" behaves conservatively outside the denitrification zone and should therefore exhibit linear relationship with temperature within the layer where the salinity-temperature relationship is linear. Also, it involves the assumption that for a given potential temperature, the "preformed" nitrate concentration should be approximately the same. The observed linear relationships between "NO" and potential temperature (NAQVI and SEN GUPTA, 1985; SOMASUNDAR et al., 1987; NAQVI et al., 1990; Fig 4) and the general agreement between the deficits calculated with the NO-potential temperature regressions and those obtained from a two end-member isopycnal mixing model (NAQVI et al., 1990) appear to justify these assumptions. Based on the data presented in Fig. 4, NAQVI et al. (1990) proposed the following set of equations to compute the nitrate deficits:

"NO" = 
$$415.934 - 8.974 \theta \ (\pm 11.81) \ 10.39 \le \theta \le 27^{\circ} C$$
 (1)

"NO" = 
$$490.254 - 16.126 \theta \ (\pm 6.94) \ \theta < 10.39^{\circ}C$$
 (2)

$$\Delta N = ("NO" - O_2)/9.1 - NO_3 - NO_2$$
(3)

The numbers in parentheses for equations (1) and (2) denote 1 s.d. of the least square fit. The discontinuity at ~10°C probably corresponds to the transition from the North Indian High-salinity Intermediate Water, characterized by low preformed nutrients, to the North Indian Deep Water with high preformed nutrient contents.

A typical example of the vertical distribution of nitrate deficit computed with this method is shown in Fig. 8 along a meridional transect at 67°E. A comparison of Figs. 3 and 8 reveals close similarity in the distribution of nitrite and nitrate deficit, although, as expected, the nitrate deficit is more widely distributed due to horizontal and vertical mixing. In addition to the main denitrifying layer seen in Figs. 3 and 8, a deeper denitrifying layer has also been observed occasionally at depths ranging from 700 to 1,200 m (NAQVI, 1987). The analysis of the particulate organic carbon (POC)

carried out on one such occasion indicated an increase in POC at these depths (BHOSLE and WAGH, 1989). Given that the oxygen concentrations are low enough at these depths for denitrification to occur (Fig. 2), it has been suggested that denitrification could be limited by the availability of organic carbon, and that an injection of organic carbon through some mechanism [such as *in-situ* production (KARL and KNAUER, 1984) and/or lateral input] could lead to the development of a deeper denitrifying layer. This feature was, however, not observed during several surveys conducted during 1987-1988 (NAQVI et al., 1990; NORONHA, 1990; NAQVI and NORONHA, 1991).

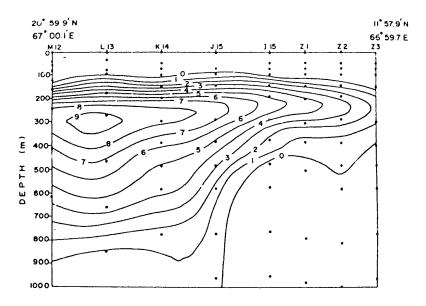


Fig. 8. Vertical section showing the distribution of nitrate deficit ( $\mu$ M) along 67°E longitude (from NAQVI and NORONHA, 1991).

#### Rate of denitrification

Computation of denitrification rate from nitrate deficits estimated by the procedure outlined above suffers from some uncertainties. Louis Codispoti, who reviewed this paper, drew our attention to what he refers to as the "one pass" problem. He argues that as the water re-circulates in and out of the denitrification zone, it may be exposed to more than one denitrification cycle. Therefore, the estimated deficits might be produced over more than one cycle leading to an overestimation of the denitrification rate when the rate is computed from the total inventory of nitrate deficits (see below). The second complicating factor involves the conversion of the estimated deficits to the amount of molecular nitrogen produced. It has been suggested that the extent of molecular nitrogen production may exceed nitrate deficit, the inequality depending upon the fate of ammonia regenerated from organic matter in the denitrifying environments (CODISPOTI and RICHARDS, 1976; CODISPOTI and CHRISTENSEN, 1985; NAQVI, 1987). Finally, there is a possibility that the nitrogen production could be overestimated due to the recycling of combined nitrogen compounds through the nitrifying and denitrifying layers as proposed by ANDERSON et al. (1982). Utilizing a one-dimensional (vertical) reaction-diffusion model, these authors estimated the depth-averaged "denitrification efficiency" (the ratio of nitrogen production

to nitrate reduction) in the Arabian Sea as 0.57. However, this figure has been considered to be low by NAQVI (1987). It is difficult to quantitatively evaluate the relative importance of the above factors. However, as they have opposing effects, these may more or less cancel each other.

DEUSER et al. (1978), NAQVI et al. (1982) and MANTOURA et al. (1992) computed the denitrification rate in the Arabian Sea by estimating the "standing crop" (total inventory) of denitrified nitrogen (uncorrected nitrate deficit). However, these estimates rested heavily on the rather subjective choice of the ventilation time (3-30 y) of the denitrifying layer, and varied from 0.1 Tg N y<sup>-1</sup> by DEUSER et al. (1978) to 11.9 Tg N y<sup>-1</sup> by MANTOURA et al. (1992). It may be mentioned here that most recent estimates of the total inventory of nitrate deficits in the Arabian Sea are in reasonably good agreement with each other (95 Tg N by NAQVI et al., 1982; 115 Tg N by NAQVI, 1987; and 118 Tg N by MANTOURA et al., 1992), and the disagreement over the rates deduced from the inventories, which as stated earlier may be affected by the "one pass" problem, owes to various choices of the renewal time.

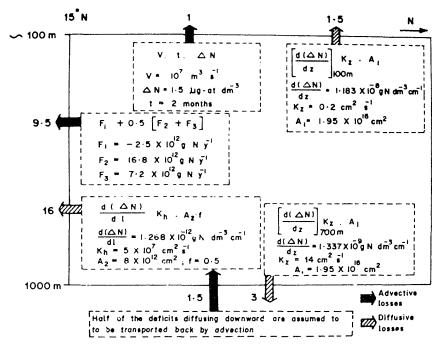


Fig. 9. Estimated losses of nitrate deficits through advection and diffusion from the denitrification zone. V = volume of water upwelling at 100 m level within the Arabian upwelling zone; t = duration of upwelling;  $\Delta N$  = average nitrate deficit in upwelling water;  $F_1,F_2$  = advective transports across ~15°N latitude, west and east of 61° longitude during August 1963;  $F_3$  = average of all the observations along 15°N latitude, east of 61°E longitude; d( $\Delta N$ )/dz = average vertical gradient of nitrate deficit;  $K_z$  = vertical diffusion constant;  $A_1$  = area of the denitrification zone; d( $\Delta N$ )/dl = average horizontal (north-south) gradient of nitrate deficit;  $K_h$  = horizontal diffusion constant;  $A_2$  = area of cross section at Lat. 17°N between 100 and 1000 m; f = fraction of the section affected by the southward flow.

NAQVI (1986, 1987) utilized all the reliable data then available and combined the estimated deficits with dynamic computations and diffusion constants to estimate the exports of nitrate deficits from the denitrification zone through advection and diffusion (Fig. 9). This procedure led to a rate of denitrification of ~30 Tg N y<sup>-1</sup>. It is comparable to the estimates from the ETNP (CODISPOTI and RICHARDS, 1976) and the eastern tropical South Pacific (ETSP) (CODISPOTI and PACKARD, 1980). NAQVI (1987)

proposed that in view of the high rate of denitrification in the Arabian Sea, estimates of the global water-column denitrification should be scaled up by at least 40%.

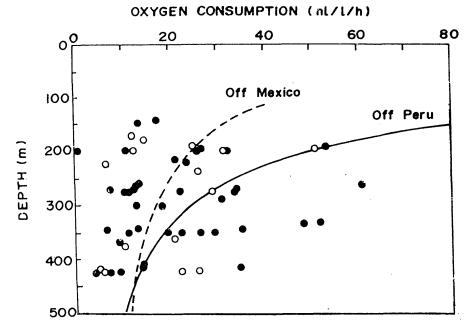


Fig. 10. Variation of the ETS activity (expressed as the oxygen consumption rate using a dimensionless R:ETS = 0.086) with depth for all the stations shown in Fig. 12. The solid and open circles represent samples taken from within and outside the secondary nitrite maximum, respectively. For comparison, depth profiles of oxygen consumption rates from the eastern tropical Pacific (GARFIELD et al., 1983) are also shown. The profile off Peru has been adjusted for the differences in sensitivity of assays and efficiency of filters (from NAQVI and SHAILAJA, 1992).

NAQVI and SHAILAJA (1992) have recently measured the activity of the respiratory electron transport system (ETS) within the oxygen minimum layer of the Arabian Sea. Their results are summarized and compared with similar data from the two Pacific denitrifying sites in Fig. 10. It may be pointed out, however, that the profile off Peru represents observations at a single station that was located fairly far offshore and that the denitrification zone off Peru can extend to very shallow depths (<100 m - see, for example, CODISPOTI et al., 1986). Notwithstanding these differences. Fig. 10 reveals that the ETS activities within the oxygen minimum layer of the Arabian Sea are of the same order as in the eastern tropical Pacific Ocean. There is one very important difference, however: the measured activities and consequently the denitrification rates [computed using a conversion factor, RNO<sub>3</sub> (gN m<sup>-3</sup> y<sup>-1</sup>):ETS (µeq. I<sup>-1</sup> h<sup>-1</sup>), of 3.68] within the SNM (Figs. 11 and 12) do not decrease systematically with distance from the shore. This trend is inconsistent with the spatial distribution of primary production (Fig. 7). On the other hand, the ETS activity corresponds very well to the data on the nitrogen system (for example, NO2 - Fig. 12). The highest activities were measured at Sta. L13 (Figs. 11 and 12), where the highest nitrate deficits were also computed (Fig. 8). Interestingly, however, this site seems to be characterized by relatively low primary production rates (Fig. 7). Thus, the ETS measurements appear to confirm that the subsurface denitrification is uncoupled with the primary productivity in the overlying surface waters, as suggested by the data on the nitrogen system. This anomaly, essentially reflecting the asymmetry of the system where highest primary production occurs off the Arabian Peninsula while lowest oxygen occurs off India, is addressed in detail in a following section.

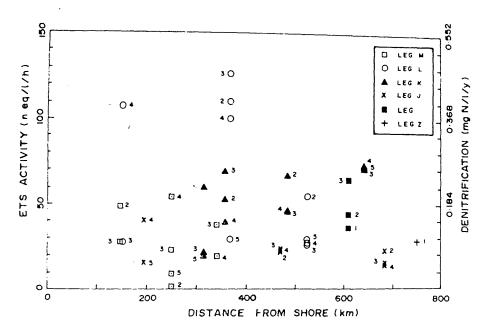


Fig. 11. ETS activities and denitrification rates within the secondary nitrite maximum (NO2 >  $0.2\,\mu$ M) as a function of nearest distance from the shore. A dimensionless R:ETS of 0.15 is used. Complete reduction of NO3 to 1/2 N2 (5 electrons flow) is assumed. The numbers 1 to 5 represent samples coming from the depth ranges 145-150, 193-220, 260-303, 334-368 and 411-425 metres, respectively (from NAQVI and SHAILAJA, 1992).

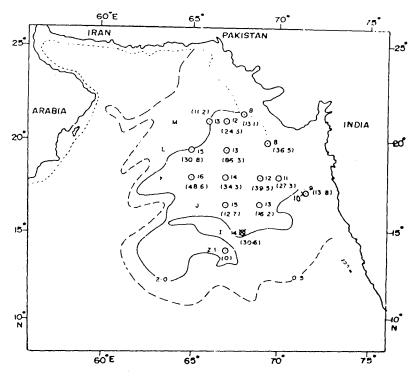


Fig. 12. The ETS-based denitrification rates (figures within parentheses, gN m<sup>-2</sup> y<sup>-1</sup>) integrated over the water column with NO<sub>2</sub>  $\geq$  0.5  $\mu$ M. The crosses and circles represent stations (identified by the legs M,L,etc. and numbers outside parentheses) worked during January-February and December 1988, respectively. The contours represent the distribution of nitrite ( $\mu$ M) at the secondary maximum (see Fig. 6). Note that denitrification rate = 0 at Sta. Z1 reflects <0.5  $\mu$ M nitrite at the time of observation (modified from NAQVI and SHAILAJA, 1992).

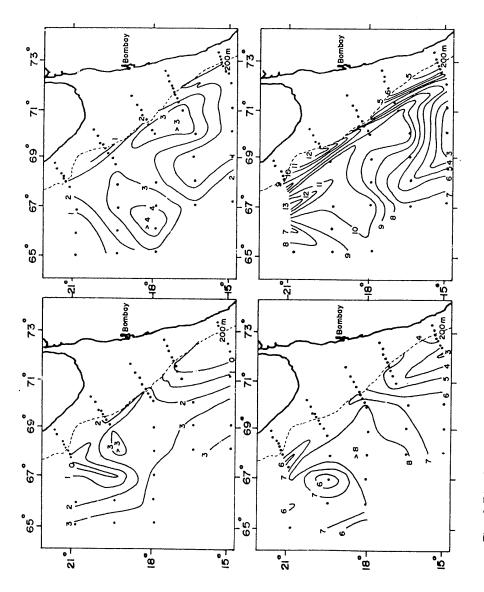


Fig. 13. Distributions of nitrite (upper panels) and nitrate deficit (lower panels) during the southwest (left panels) and northeast (right panels) monsoon seasons (modified from NAQVI et al., 1990).

The ETS-based denitrification rates integrated at each station over the depth range with NO<sub>2</sub>  $\geq$ 0.5  $\mu$ M (Fig. 12) suggest a mean rate of 28.35 gN m<sup>-2</sup>y<sup>-1</sup>. Integrating this value over the area of the Arabian Sea with nitrite concentrations at its secondary maximum greater than 0.5  $\mu$ M (1.15 x 10<sup>12</sup> m<sup>2</sup>), the overall rate of denitrification in the Arabian Sea comes to 32.6 Tg N y<sup>-1</sup> (the 0.5  $\mu$ M NO<sub>2</sub> concentration has been taken for integration considering the conclusions of ANDERSON *et al.*, 1982; in any case, denitrification within the layer with NO<sub>2</sub> <0.5  $\mu$ M will probably be quantitatively unimportant). Thus, the estimates based on the box model calculations involving the exports of nitrate deficits from the denitrifying layer and on the ETS activity are in remarkably good agreement, and it can be concluded that the Arabian Sea contributes almost as much to the oceanic water column denitrification as each of the two major denitrifying sites in the eastern tropical Pacific Ocean.

# Temporal changes in denitrification

The unique seasonal reversal of the surface circulation is translated into a large seasonality in biological productivity (QASIM, 1982; BANSE, 1987). Consequently, the particle fluxes to the deep North Indian Ocean also exhibit a large seasonal signal associated with the monsoons (NAIR *et al.*, 1989; ITTEKKOT *et al.*, 1990). How these fluctuations affect the oxygen minimum would depend upon how the subsurface circulation responds to the monsoons or what is the time scale of the renewal processes. If, for example, the oxygen-deficient waters were stagnant, as believed earlier (WYRTKI, 1973; QASIM, 1982; SEN GUPTA and NAQVI, 1984), one would expect little short-term changes in the intensity of the oxygen minimum. However, as summarized below, the available evidence points to the contrary.

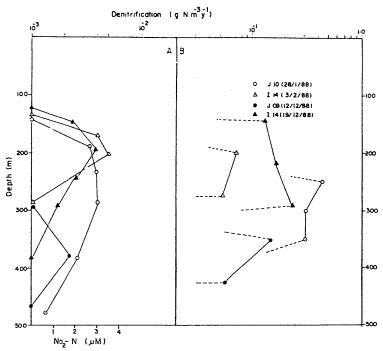


Fig. 14. Temporal changes in the ETS-based denitrification rate (B) and nitrite (A) at two sites.

The first clear evidence for the short-term changes in reducing conditions was provided by NAQVI (1987). However, his data were not adequate to differentiate between the inter- and intra-annual changes. Observations in the northeastern Arabian Sea during two consecutive southwest and northeast monsoon seasons have since

revealed significant seasonal changes in the chemical composition of the oxygen-deficient waters (NAQVI et al., 1990). These authors studied the distributions of nitrite and nitrate deficit at four isopycnal surfaces and found large variability in the two tracers which was thought to reflect changes in the subsurface circulation. These results clearly demonstrate that the water circulation at the depths of the oxygen minimum responds surprisingly rapidly to the changing winds, especially in the eastern Arabian Sea. During the southwest monsoon, when the eastern Arabian Sea seems to behave like a typical eastern boundary environment (SHETYE et al., 1990), a poleward undercurrent appears to carry low-nitrite, low-nitrate deficit (and more oxygenated) waters northward off the Indian continental margin, suppressing denitrification; this feature appears to reverse during the northeast monsoon (Fig. 13). This remarkable response of the intermediate-depth water circulation to the monsoonal rhythm is expected to bring about intense lateral mixing, contributing to the high horizontal diffusivity of the Ar bian Sea.

Evidence for the large intra-annual changes in denitrification in the Arabian Sea is also provided by the ETS data presented in Fig. 14. Repeat measurements at two sites within a period of approximately 10 months revealed factor of 2 changes in the ETS activity, although in different directions. At the near-shore stations (J9 and J10), the rates observed were higher during January 1988 as compared to December 1988, whereas an opposite trend was seen at the offshore site (I14). The data on the nitrogen system reflected these variations as exemplified by the nitrite profiles included in Fig. 14. Ostensibly, these resulted from differential changes in the subsurface circulation and organic carbon supply. These observations suggest a very fragile balance between consumption and renewal processes.

The available data thus strongly suggest a link between the monsoons and the intensity of the oxygen minimum, with the latter being more intense (higher nitrate deficits) during the northeast monsoon (Fig. 13). In part, this may be due to the fact that the renewal processes (lateral advection of more oxygenated waters from the south) may be more vigorous during the southwest monsoon; this may make up for the higher respiration rates expected from the higher particle flux. It will be proposed in a following section that the transport of labile organic material by quasi-horizontal processes may be important in fuelling denitrification. However, how it could contribute to the observed temporal variability is not known. The higher deficits observed during the northeast monsoon might also result from a stronger vertical stratification caused by the northward flow of the warm, fresher equatorial surface water. It may, however, be noted that this trend may not be valid for the northern and western parts of the Arabian Sea where, as discussed earlier, denitrification may be limited by the reoxygenation associated with the winter cooling of the surface waters (NAQVI, 1991b). Unfortunately, there are not enough data available to investigate the seasonal changes in denitrification in these areas.

# Renewal time of denitrifying waters

As suggested earlier, the observed short-term temporal variability in the oxygen-deficient conditions requires a rapid renewal of the intermediate waters. Computations of the residence time involving data on the primary productivity, nitrogen system, and ETS activity are consistent with these observations. Combining NAQVI's (1987) weighted mean of the "standing crop" of denitrified nitrogen (59 g m<sup>-2</sup>), assumed to apply over an area of  $1.15 \times 10^{12}$  m<sup>2</sup>, with an overall rate of denitrification of 30 Tg N y<sup>-1</sup>, the renewal time of waters affected by denitrification could be estimated as 2.26 y. This may be regarded as an upper limit since the depth range over which the deficits were integrated by NAQVI (1987) considerably exceeded the denitrifying water column. A more direct estimate could be obtained by dividing the mean value of the

nitrate deficit integrated over the denitrifying zone (23.94 gN m<sup>-2</sup>) with the mean ETS-based denitrification rate (28.35 gN m<sup>-2</sup> y<sup>-1</sup>). This yields a value of 0.84 y. These estimates are somewhat lower than those (1.6-3.4 y) of SOMASUNDAR and NAQVI (1988) based on the model of LIU and KAPLAN (1984). The latter approach, however, involves the assumption that denitrification in the Arabian Sea is fuelled entirely by the sinking organic matter, which may not be valid, as will be shown in the following section.

Role of dissolved and/or suspended organic matter

As discussed earlier, the lack of correspondence between the subsurface denitrification and the biological production in the overlying surface waters, evident from data on the nitrogen system as well as the ETS activity, represents a striking feature of the Arabian Sea denitrification. This distinguishes the Arabian Sea from the denitrification sites of the Pacific Ocean. This anomaly could arise from a more effective re-oxygenation of intermediate waters beneath the productive zones and/or a different, possibly additional, mode of input of the biodegradable organic matter to the subsurface layers of the Arabian Sea.

As suggested by NAQVI (1991b), the mixed layer induced reoxygenation could indeed be the key factor limiting denitrification in the northernmost and western parts. However, advective processes originating within the region or in the adjoining Gulf of Oman may also be important (BANSE, 1984; 1990). Along the Indian coast, the lower nitrate deficits could be sustained by the seasonal reoxygenation associated with the poleward undercurrent during the southwest monsoon (NAQVI *et al.*, 1990) and a possible advection of denser (although somewhat fresher) water from the inner shelf during the northeast monsoon (NAQVI, 1991b).

A more vigorous renewal of the subsurface waters alone may not account for the obvious decoupling between denitrification and primary production, however. It may be noted that a rapid renewal should not affect the overall respiratory potential as reflected by the ETS activity. Therefore, it is likely that some mechanism(s) in addition to the vertical supply with the sinking particles is responsible for transporting labile organic carbon to the subsurface layers. The most likely mode of such inputs are (1) quasi-horizontal transport of suspended particulate matter (SPM) from the bottom nepheloid layers over the continental margin; and (2) supply of dissolved organic matter (DOM) through advection and diffusion from the surface waters.

A well-defined particle maximum has been known to occur at the cores of the oxygen minimum, nitrite maximum and nitrate minimum within the denitrifying zone off Peru (PAK et al., 1980). Although the particle maximum in part reflects a high bacterial biomass (SPINRAD et al., 1989), it has been suggested that it may originate principally from lateral transport of particles from the bottom nepheloid layers over the shelf/upper slope (PAK et al., 1980). A similar particle maximum has not been looked for in the Arabian Sea, but it could exist in this region as well, particularly in view of the high horizontal diffusivity caused by the seasonal reversal of subsurface coastal circulation (NAQVI et al., 1990). It has been proposed that the DOM could account for the bulk of oxygen utilization within subsurface waters (SUGIMURA) and SUZUKI, 1988). A recent study (KUMAR et al., 1990) has revealed active recycling of dissolved organic carbon within the oxygen minimum in the Arabian Sea with the minimal values ( $\sim 60 \mu M$ ) associated with the secondary nitrite maximum (Fig. 15). The role of DOM in controlling the subsurface water chemistry may be more important in the Arabian Sea than in other oceanic areas because in addition to the processes mentioned above (winter convection, formation of the subsurface water over the shelf, and a seasonal poleward undercurrent), the Arabian Sea also receives recently-formed

waters from the two marginal seas - the Red Sea and Persian Gulf. These processes may facilitate introduction of substantial quantities of labile DOM to the oxygen-minimum layer. The extent of these inputs could be evaluated as follows:

Going on the premise that a maximum of 50% of the organic carbon available within the denitrifying layer as macro-particles could be used up for denitrification (LIU and KAPLAN (1984), we place an upper limit on the carbon supply associated with the sinking particles that may be used up for denitrification at 24 g C m<sup>-2</sup> y<sup>-1</sup>. The mean ETS-based denitrification rate (28.35 g N m<sup>-2</sup> y<sup>-1</sup>) corresponds to a carbon flux of approximately 36 g m<sup>-2</sup> y<sup>-1</sup> assuming the atomic ratio between carbon oxidized to nitrogen reduced, maintained during denitrification, to be 140:109 (NAQVI et al., 1990). The estimate of the carbon available for denitrification is probably generous because the primary production rates in the surface waters overlying the denitrifying zone are substantially lower than the mean value (278 gC m<sup>-2</sup> y<sup>-1</sup>) used here (Fig. 5). Also our choice of the mean thickness of the denitrifying layer (150-450 m) may be high. The inequality between the ETS-based rates and those which can be sustained by the vertical particle fluxes is much bigger if data from the stations located around the horizontal centre of denitrification zone are considered. At L13, for example, the total available carbon within the denitrifying layer was computed to be ~29 g m<sup>2</sup> y<sup>1</sup>, while the carbon flux required for denitrification was 111 g m<sup>-2</sup>y<sup>-1</sup>. It is, therefore, obvious that the vertical particle- associated fluxes alone can not sustain the observed denitrification rates, and at least 1/3 of the carbon supply should be through lateral processes and/or vertical mixing, presumably as DOM and/or SPM. This would require an input of approximately  $0.4 \times 10^6 \text{ m}^3 \text{ s}^{-1}$  of water with a degradable carbon of 150 μM [the difference between the surface water concentration and the lowest value observed within the core of the oxygen-deficient layer (KUMAR et al., 1990)] into a 300-m thick layer throughout the northern Arabian Sea (area ~2 x 10° km²). This compares favourably with the quantum of outflows from the Red Sea and the Persian Gulf (SWALLOW, 1984). These calculations clearly show, at least at a first approximation, that the excess carbon required to sustain the high respiration rates could be supplied by the physical processes. Invoking of a major role for DOM/SPM in fuelling the subsurface respiration can explain not only the high respiration rates, but also provide a possible explanation for the rather uniform respiration rates, as the high horizontal diffusivity of the Arabian Sea is expected to lead to a rapid dispersal of the DOM/SPM along isopycnal surfaces.

# Nitrous oxide cycling

Nitrous oxide (N<sub>2</sub>O), an intermediate in the redox chemistry of the nitrogen cycle, is an important greenhouse gas. It also contributes to the stratospheric ozone depletion. Numerous investigations have been conducted to evaluate the oceanic contribution to the overall N<sub>2</sub>O cycling (e.g. CLINE *et al.*, 1987; BUTLER *et al.*, 1989; OUDOT *et al.*, 1990). Owing to its rapid turnover within the low-oxygen waters, particular attention has been paid to determine the fate and fluxes of N<sub>2</sub>O in the eastern tropical Pacific (COHEN and GORDON, 1978; ELKINS *et al.*, 1978; PIEROTTI and RASMUSSEN, 1980; CODISPOTI and CHRISTENSEN, 1985). Similar information was lacking so far from the North Indian Ocean, barring some measurements of the surface saturations by WEISS (1978). Two recent studies (LAW and OWENS, 1990; NAQVI and NORONHA, 1991) have provided the much-needed data on the N<sub>2</sub>O cycling in the northwestern Indian Ocean.

Working in the western Arabian Sea, which experiences strong upwelling during the southwest monsoon, and along a transect extending to the equator from the Gulf of Oman, LAW and OWENS (1990) found a high degree of surface saturation (167±46%)

throughout the northwestern Indian Ocean in the period following the SW monsoon (September-October, 1986). The N<sub>2</sub>O fluxes across the air-sea interface estimated by these authors were consequently high (15.51 $\pm$ 7.66 µmol m<sup>-2</sup> d<sup>-1</sup> based on a stagnant-film model and 8.64 $\pm$ 4.32 µmol m<sup>-2</sup> d<sup>-1</sup> calculated from the CO<sub>2</sub> transfer velocities assuming an annual average wind speed of 5 m s<sup>-1</sup>). The total atmospheric flux for the region bounded by latitudes 15 and 25°N and longitudes 50 and 7° E was estimated as 0.22-0.39 Tg N<sub>2</sub>O. LAW and OWENS (1990) considered it to be 5- 18% of the total marine source from merely 0.43% of the total oceanic area. To arrive at this figure, however, they took one of the lowest estimates for the total N<sub>2</sub>O flux from the oceans (1.4- 2.8 Tg N y<sup>-1</sup>) by BUTLER *et al.* (1989) based on the observations made during an El Nino year in areas which did not include the major upwelling environments. The contribution of the Arabian Sea would be 3-5% if the total marine source is taken as 5 Tg N y<sup>-1</sup> (see CODISPOTI *et al.*, this volume).

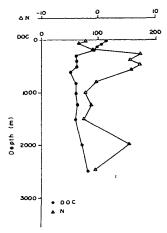


Fig. 15. Vertical profiles of nitrate deficit (μM) and dissolved organic carbon (μM) at a station (Lat. 20°54′N; Long. 63°07′E) in the Arabian Sea (from KUMAR et al., 1990).

In contrast with the observations of LAW and OWENS (1990), which were made mostly outside the denitrification zone, NAQVI and NORONHA (1991) concentrated largely on the reducing zone in the northeastern Arabian Sea during December 1988. The surface saturations observed in the two studies were remarkably similar [186±37% by NAQVI and NORONHA (1991) as compared to 186±40% by LAW and OWENS (1990) north of 15°N latitude]. However, the atmospheric fluxes estimated by NAQVI and NORONHA (1991) (4.46±2.60 µmol m<sup>-2</sup> d<sup>-1</sup> - Table 2) are lower because these are based on lower wind speeds. Indeed, their estimate for the entire Arabian Sea (0.44 Tg N<sub>2</sub>O) is comparable with the total flux north of 15°N computed by LAW and OWENS (1990). These results demonstrate clearly that the northwestern Indian Ocean serves as a large source of atmospheric N<sub>2</sub>O.

The occurrence of high N<sub>2</sub>O saturations throughout the Arabian Sea away from the upwelling centres represents yet another anomalous feature of the oceanography of this region. Assuming that the high atmospheric fluxes are sustained by eddy diffusion from beneath the mixed layer, NAQVI and NORONHA (1991) estimated the vertical exchange coefficients required to maintain the observed fluxes; these are included in Table 2. They concluded that the high supersaturations result from the large vertical gradients just below the mixed layer. A similar explanation (occurrence of very high nutrient concentrations close to the euphotic zone) has been given by RYTHER et al. (1966) for the high productivity. This is also reflected in the rather uniform particle fluxes obtained through the sediment traps (NAIR et al., 1989), although it may be

Surface N2O saturations, atmospheric fluxes and vertical diffusivity at the top of the thermocline (from NAQVI and NORONHA, 1991). Table 2.

							1				
Station	Station Latitude Lon Number (N)	Longitude (E)	Temp (°C)	Salinity (x10 <sup>-3</sup> )	N <sub>2</sub> O (obs)	N2O (eq) (nM)	Sat (%)	Flux (umol m <sup>-2</sup> d <sup>-1</sup> )	Depth of =24.3 (m)	d (N2O) /dz (umol m <sup>-4</sup> )	Vertical diffusivity $(m^2 d^{-1})$
T14	15000.0	67°59.9'	27.8	36.402	12.92	5.70	226.6	8.88	77.1	3.706	2,39
115	15000.7	66,29,8	27.7	36,810	12.18	5.70	213.5	9.26	61.2	1.915	4.83
J15	1629.6	67,00.8	27.6	36.691	5.18	5.73	90.4	1	1	,	1
K05	18°23.8'	70°40.8'	27.0	36.087	11.72	5.84	200.6	3.59	ı	1	ı
K07	18019.81	70°32.8'	27.9	35.298	7.81	5.71	136.8	1.48	64.9	1.097	1.34
808	18016.01	70°25.01	27.5	35.418	10.60	5.78	183.4	3.36	86.4	0.747	4.49
212	18,000.21	69,00.00	27.2	36,435	8.99	5.79	155.2	2.49	52.3	1.587	1.58
K13	17059.81	67°59.3'	26.9	36,674	10.62	5.83	182.0	4.83	52.8	0.670	7.19
K14	18000.11	67,00,11	27.2	36.860	12.23	5.78	211.7	7.75	59.0	0.830	9.35
X18	17°59.9'	65,00.4	27.0	36.863	8.17	5.82	140.5	2.85	51.6	0.499	5.71
1.13	19030.1	67,00.3	26.6	36,778	7.52	5.88	127.9	1.19	52.1	0.580	2.05
Z Z	20059.91	67,00.00	27.1	36,789	11.68	5.80	201.3	2.35	83.9	0.318	7.38
2.01	14000.1	67,00.00	27.1	36.595	10.57	5.81	182.0	4.95	65.6	0.562	8.81
202	13000.1	67,00.00	28.1	36.729	14.51	5.64	257.5	5.59	72.6	1.141	4.90
203	11°57.9'	66°59.7	27.9	36.709	10.77	5.68	189.6	3.87	78.7	1.704	2.27
Mean+S.D.	٠					186	5.3±36.	186.3±36.7 4.46±2.60	1	.18±0.91	4.79±2.77

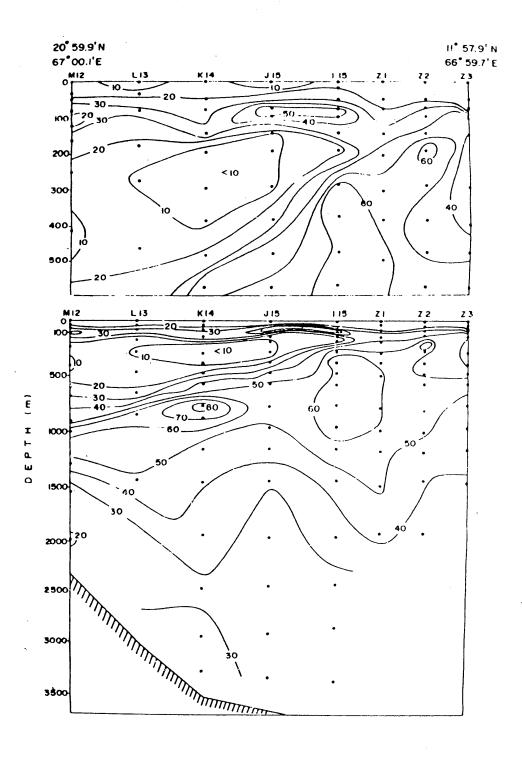


Fig. 16. Vertical section showing distribution of nitrous oxide (nM) along  $67^{\circ}$ E longitude (from NAQVI and NORONHA, 1991).

pointed out that the sites where the sediment traps were deployed were outside the upwelling zones.

The vertical distribution of N<sub>2</sub>O in the Arabian Sea (Fig. 16) is very similar to that observed in the other oxygen-depleted environments. As expected, minimal values (< 10 nM) occur in association with the SNM (compare Fig. 16 with Fig. 3), presumably due to the consumption of N<sub>2</sub>O during denitrification. The maxima in the N<sub>2</sub>O profile (> 50 nM) are located at the peripheries of the SNM. Outside the denitrifying zone, only one broad maximum in N<sub>2</sub>O is observed (Fig. 16; also see LAW and OWENS, 1990). The increased production of N<sub>2</sub>O at low (not near- zero) oxygen concentrations has been well known, but has been interpreted differently by different authors to support its production through nitrification or denitrification [see NAQVI and NORONHA (1991) and CODISPOTI et al. (this volume) for discussions]. Re-interpreting the data on the isotopic composition of dissolved N<sub>2</sub>O from the Pacific Ocean (YOSHIDA et al., 1989; KIM and CRAIG, 1990), NAQVI (1991a) and NAQVI and NORONHA (1991) have proposed that a nitrification-denitrification couple represented by the pathway NH<sub>4</sub><sup>+</sup>-> NH<sub>2</sub>OH->NO->N<sub>2</sub>O could be dominantly responsible for N<sub>2</sub>O accumulation at low oxygen levels.

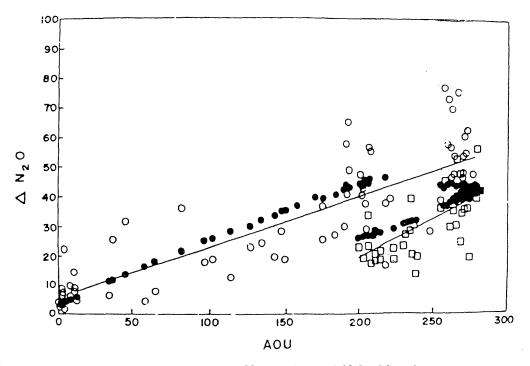


Fig. 17. Relationship between the apparent  $N_2O$  production ( $\Delta N_2O$ , nM) and apparent oxygen utilization (AOU,  $\mu$ M) excluding the samples with  $O_2 < 0.25$  cm<sup>3</sup> dm<sup>-3</sup>. Open circles and squares represent observations at depths  $\leq 1000$  m and > 1000 m, respectively. Solid circles are based on calculations involving Eq. (4). Straight lines give the linear least squares regressions for the two depth ranges.

The probable loss of N<sub>2</sub>O through denitrification may be a quantitatively significant term in the nitrogen budget. This should be more so if its production is dominantly through nitrification or a nitrification-denitrification couple. The large horizontal and vertical gradients in N<sub>2</sub>O concentrations at the boundaries of the reducing zones are expected to result in the transport and subsequent reduction of N<sub>2</sub>O within the oxygendeticient zones. NAQVI and NORONHA (1991) estimated that ~1.4 Tg N<sub>2</sub>O-N could be

lost within the water column in this manner. An interesting feature of the N<sub>2</sub>O distribution in the Arabian Sea is that it is characterized by large east-west gradients (decrease toward the continental margin) off the coasts of both India (NAQVI and NORONHA, 1991 - Fig. 3B) and Oman (LAW and OWEN, 1990 - Fig. 1). These observations suggest that the marginal sediments in contact with the low-oxygen (not denitrifying) waters in the Arabian Sea could also serve as a significant sink of N<sub>2</sub>O. From the observed gradients, NAQVI and NORONHA (1991) estimated a minimal loss of N<sub>2</sub>O to the eastern margin (2000 km x 1 km) as  $0.8 \, \text{Tg N y}^{-1}$ . Thus, excluding the intrinsic production and consumption of N<sub>2</sub>O within the denitrifying layer (CODISPOTI and CHRISTENSEN, 1985), its advective transports into the reducing zones, and its losses to the sediments along the northern and western margins, the annual losses of N<sub>2</sub>O to the reducing zones in the Arabian Sea work out to be ~2.2  $\, \text{Tg N}$ .

However, CODISPOTI (personal communication, 1991) considers the above estimate for sedimentary losses to be too high. He suggested that a more vigorous renewal of waters near the margins could also produce the observed gradients. He has provided an estimate for the N<sub>2</sub>O destruction rate within sediments underlying the SNM off Peru which is only 1% of the destruction rate estimated by CODISPOTI and CHRISTENSEN (1985) for the SNM. To arrive at this figure, he assumed a diffusive sublayer (diffusion through which was regarded as the limiting step) thickness of 0.06 cm based on DEVOL's (1987) "bell jar" experiment in the Tres Marias Depression in the ETNP. He pointed out that such experiments provided gentle stirring. During periods of vigorous stirring, the sedimentary effect on N<sub>2</sub>O loss could be larger, although it will be concentrated in the water above the sediments. Although it is possible that the horizontal gradients observed off India as well as Oman result to some extent from advective processes, we feel that the losses within sediments and in overlying waters could be quite significant.

Table 3. Local sources and sinks of inorganic combined nitrogen in the Arabian Sea

SOURCE/SINK	STRENGTH	(Tg N y <sup>-1</sup> )	REFERENCE
SOURCES			
River runoff	0.1	SOMASUNDAR	et al. (1990)
Red Sea	0.8	NAQVI et a	1. (1986); BETHOUX (1988)
Persian Gulf	0.3	This study	,*
Nitrogen fixation	1.5		et al. (1990)
Atmospheric inputs	0.7	This study	, ,
TOTAL	3.4		
SINKS			
Water column deni-		NAQVI (198	7); NAQVI and SHAILAJA
trification	30.0	(1992)	
Sedimentary deni-		This study	, , ,
trification	1.0		
Nitrous oxide loss		LAW and OW	NENS (1990); NAQVI and
to the atmosphere	0.3	NORONHA (1	991)
Nitrous oxide loss w	i-	NAQVI and	NORONHA (1991)
thin reducing zones	2.2		
Burial	0.2	SOMASUNDAR	t et al. (1990)
TOTAL	33.7 .		

 $<sup>^{\</sup>star}$ Assuming similar "excess" nitrogen concentrations in the Red Sea and Persian Gulf.

 $<sup>^{**}</sup>$ Utilizing global estimate (CODISPOTI and CHRISTENSEN, 1985) and the area of the Arabian Sea.

<sup>\*\*\*</sup> Using the estimate of CHRISTENSEN et al. (1987) for the shelf sediments of Washington (0.57 pmol cm $^{-2}$  s $^{-1}$ ).

The relationship between the apparent N2O production [  $\Delta$ N2O = (N2O)obs -(N2O)eq] and the apparent oxygen utilization (AOU) in the Arabian Sea appears to be linear, albeit within two ranges (Fig. 17) as in other oceanic areas (YOSHINARI, 1976; ELKINS et al., 1978; CLINE et al., 1987; OUDOT et al., 1990). The different behaviour in the upper (depth ≤ 1000 m) and lower (depth > 1000 m) parts of the water column could arise in part from a hydrochemical discontinuity in the vertical structure at about  $10^{\circ}$ C (NAQVI *et al.,* 1990) in addition to the known dependence of N<sub>2</sub>O production on temperature (YOSHIDA and ALEXANDER, 1970). The slope of the N2O-AOU regression line for the shallower layer is similar to those reported from some other areas (e.g., ELKINS et al., 1978; COHEN and GORDON, 1978; OUDOT et al., 1990). The value for the deep waters  $(0.26 \times 10^{-3})$  is, however, higher than those observed elsewhere, implying a higher- than-the-average rate of N2O production in the deep Arabian Sea. The results of LAW and OWENS (1990) are in general agreement with these findings. These authors found a  $\Delta N_2O/\Delta AOU$  ratio of 0.31 x 10<sup>-3</sup> in the higher AOU range (> 197  $\mu$ M). The  $\Delta$ N<sub>2</sub>O-AOU relationships in the lower AOU range, however, appear to be somewhat different. This could result at least in part from the differential treatment of the data [such as the omission of all values corresponding to O<sub>2</sub> < 0.25 cm<sup>3</sup>dm<sup>-3</sup>, in order to eliminate the samples affected by denitrification by NAQVI and NORONHA (1991)]. When the data from the Arabian Sea are fitted to a regression function similar to that of ELKINS et al. (1978), the following relationship is obtained:

$$\Delta N_2O(nM) = 3.20 + (0.1066 + 0.00455t)AOU,$$
 (4)

where t is the temperature in  $^{\circ}$ C and AOU has the unit of  $\mu$ M. Eq. (4) shows an independent variation of  $\Delta$  N<sub>2</sub>O with AOU which is intermediate of that observed by ELKINS *et al.* (1978) and that seen by BUTLER *et al.* (1989). The temperature dependence is, however, much weaker, in conformity with the results of LAW and OWENS (1990). The positive intercept on the  $\Delta$  N<sub>2</sub>O axis reflects the high degree of surface saturation in the Arabian Sea.

Table 4. Advective transports of nitrate into (+) and out (-) of the Arabian Sea below 400 m

LAYER	WATER TRANSPORT*	MEAN NO3 CONC.** (μM)	NO <sub>3</sub> FLUX
$400 \text{ m} - \sigma_{\theta} = 27.1$ $\sigma_{\theta} = 27.1 - 27.4$ $\sigma_{\theta} = 27.4 - 27.65$ $\sigma_{\theta} = 27.65 - 4 \text{ kr}$ 4  km - Bottom TOTAL (400 m - B	-0.9 5 +0.6 n -0.3 +8.0	27.9 31.4 37.8 37.6 35.5	-3.7 -12.5 +10.0 -5.0 +125.3 +114.1

METZL et al. (1990)

#### Nitrogen budget

Estimated strengths of various local sources and sinks of the inorganic combined nitrogen in the Arabian Sea are presented in Table 3. This budget differs from that proposed recently by SOMASUNDAR *et al.* (1990) in several respects. First, it takes into account inputs from the atmosphere, and losses through sedimentary denitrification and as N<sub>2</sub>O (to the atmosphere and within the reducing zones), not considered by SOMASUNDAR *et al.* (1990). Second, we do not consider any change due to biological production; the organic matter exported out of the euphotic zone is assumed to undergo decomposition within the Arabian Sea itself. Third, and more importantly, the loss

<sup>&</sup>quot;Estimated from the available data for the respective boxes.

due to denitrification (flux to the atmosphere =  $2.05 \,\mathrm{Tg} \,\mathrm{N} \,\mathrm{y}^{-1}$ ) considered by SOMASUNDAR *et al.* (1990) was much lower than the value (denitrification rate =  $30 \,\mathrm{Tg} \,\mathrm{N} \,\mathrm{y}^{-1}$ ) chosen by us. Consequently, unlike the budget of SOMASUNDAR *et al.* (1990) which implies that the Arabian Sea acts as a net source of inorganic combined nitrogen, our calculations suggest it to be a net sink of substantial magnitude ( $\cdot$  30 Tg N y<sup>-1</sup>). This, of course, is to be expected since the Arabian Sea houses one of the few oceanic reducing sites. We note here that one of the terms in Table 3 subject to greatest uncertainty is sedimentary denitrification. In order to estimate this term, we have used the mean sedimentary denitrification rate determined off the Washington coast (CHRISTENSEN *et al.*, 1987) which may be too low for the Arabian Sea shelf sediments. Also, we have ignored contributions from the deep seafloor. Therefore, we believe that our estimate of sedimentary denitrification may be conservative. The overall strength of the Arabian Sea sink may thus be higher than estimated here.

The nitrogen required for the mass balance should be supplied through advection and diffusion from the south. Using the recent estimates of METZL et al. (1990) of the advective flows into and out of the Arabian Sea, for 5 layers deeper than 400 m, together with estimated average nitrate concentrations (Table 4), we computed a net advective transport of nitrate below 400 m as ~114 Tg N y<sup>-1</sup>. Most of it seems to occur through the flow of the bottom water. Even allowing room for the uncertainties inherent in the calculations involved, it is obvious that the large nitrogen deficiency in the upper layers is largely made up by the inputs from the bottom layer (depth > 4,000 m). As the net exchange between 400 and 4,000 m is much smaller than the transport below 4,000 m, most of the inputs into the bottom layer should be transferred to the upper layers. This is probably facilitated by a high rate of upwelling of deep water in the North Indian Ocean (WARREN, 1981; SWALLOW, 1984; SOMASUNDAR and NAQVI, 1988). We believe that this may be the principal mechanism causing the Arabian Sea to act as a nutrient trap and leading to the elevated biological production in the region. If so, then one would expect the primary productivity and denitrification in the Arabian Sea to undergo large fluctuations associated with the climatic cycles.

We propose that the primary production in the Arabian Sea and the intensity of the mid-lepth oxygen minimum could be intimately linked with the thermohaline circulation in the deep Indian Ocean. The high rate of deep water upwelling in the North Indian Ocean, as observed today, could be driven by a combination of regional and global processes. It may be controlled regionally by the monsoonal wind-driven coastal upwelling off Arabia and Somalia. This may be augmented by the production of the North Atlantic Deep Water (NADW) since the upwelling of deep waters in the Pacific and Indian Oceans is necessary to drive the NADW production as a part of the overall global "conveyor" system (see, for example, BROECKER and DENTON, 1990). During the last glacial maximum (LGM), however, when the coastal upwelling in the Arabian Sea was probably much weaker (DUPLESSY, 1982), and there was little or no formation of the NADW (STREETER and SHACKLETON, 1979; DUPLESSY et al., 1988), the upward movement of the deep water in the Indian Ocean is expected to have been much slower. This would cause a decrease in the overall fertility of the Arabian Sea [which is supported by a lower carbonate content of the glacial sediments often attributed to terrigenous dilution (see, for example, PRELL and CURRY, 1981)], and a better oxygen balance [which is supported by the carbon isotopic data on benthic foraminifera (KALLEL et al., 1988)]. The available evidence suggests that there probably existed a deep front separating the upper (depth < 2km) and lower water columns during the LGM indicating that the deep circulation pattern was indeed different. It is very likely that as the rate of deep water upwelling decreased, the deep cell contributing to the return or outflow water (BROECKER et al., 1985) intensified. In view of a weaker

North Atlantic source, the Indian Outflow Water could have formed a more important source for production of the glacial Antarctic Bottom Water. This would in effect result in the transfer of nutrients from the upper/intermediate layers to the deep sea as suggested by the data on carbon isotopes (KALLEL *et al.*, 1988) as well as cadmium (E.A. Boyle, personal communication, 1990), which has implications on the glacial-interglacial atmospheric CO<sub>2</sub> changes (BOYLE, 1988). The very low ( $-1^{\circ}$ /oo vs PDB)  $\delta^{13}$ C in benthic foraminifera during the LGM indicates that nearly-anoxic conditions might have developed in parts of the deep North Indian Ocean. However, denitrification at mid-depth, as seen today, was perhaps much less intense during the LGM.

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