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Some aspects of the oxygen-deficient conditions and denitrification in the Arabian Sea[1]

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ABSTRACT

Utilizing a fairly large amount of recently collected data, some outstanding questions concerning the Arabian Sea denitrification problem are addressed. The true levels of dissolved oxygen, determined colorimetrically, are about an order of magnitude lower than those reported previously from the oxygen minimum zone. Lateral advection of waters from south into the oxygen-deficient layer is suggested by the presence of an intermediate oxygen maximum discernible even at very low oxygen levels.

An unusual minimum in nitrate and a corresponding maximum in nitrite are observed occasionally within the depth range 700–1,200 m at several stations, generally located in the northeastern Arabian Sea. These features probably represent the development of a deeper denitrifying layer, in addition to the main denitrifying layer invariably found in the northern Arabian Sea at shallower depths. The deeper layer appears to be related to an increase in particulate organic carbon, probably resulting from seasonal changes in primary production, lateral advection of waters from the slope region off the Indian coast, or an *in-situ* production of organic matter.

Reoccupation of a number of stations reveals large short-term variability in denitrification intensity. Associated with the temporal variability, the southern boundary of denitrification appears to oscillate between Lats. 12 and 14N, except in the western Arabian Sea where it might shift to 18N during the southwest monsoon. Peak values of the integrated deficits do not occur within or near zones of high biological productivity; i.e., along the eastern and western boundaries. This is attributed to a more intense renewal of waters along these margins, through the northerly flow of waters, relatively rich in oxygen, to compensate for the vertical advection (upwelling) off Arabia, and through a hitherto undetected undercurrent off the west coast of India. Well-defined tongues of high and low integrated deficits, alternately extending northward and southward, respectively, possibly reflect net transports within the oxygen-deficient layer.

Rate of denitrification in the Arabian Sea is estimated from the exports of nitrate deficits out of the denitrification zone. The results indicate that the horizontal processes are responsible for the removal of the bulk (>85%) of the deficits. The deduced rate (29.5×10^{12} gN y^{-1}) is at least an order of magnitude higher than the previous estimates. Combining this value with the estimated "standing crop" of denitrified nitrogen, the renewal time of the oxygen-deficient layer is deduced as ~4 y. The short renewal time, supported by tritium data, is consistent with the observed short-term variability in denitrification intensity. The high rate of denitrification

1. Dedicated to the late Dr. H. N. Siddiquie, former Director of the National Institute of Oceanography.

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deduced in the present study appears to conform to global trends. It is suggested that currently accepted estimates of oceanic water column denitrification should be scaled-up by 40 to 100% in view of the present results.

1. Introduction

Several reports dealing with denitrification in the Arabian Sea have appeared in recent literature (Sen Gupta *et al.*, 1976; Deuser *et al.*, 1978; Naqvi *et al.*, 1982; Anderson *et al.*, 1982; Qasim, 1982; Naqvi and Qasim, 1983; Naqvi and Sen Gupta, 1985). Yet, the Arabian Sea continues to be the least known of all the major oceanic denitrification sites. Estimates of the extent of denitrification in this region are inconsistent. This is partly because the approaches followed by previous workers for computing nitrate losses were often incompatible with each other, and also due to different and rather arbitrary choices of the residence time employed to estimate denitrification rates. Moreover, all the studies carried out so far have been based on very limited samplings in terms of the geographical coverage of the area, and hence suffered from large extrapolations. Our work has led to the development of a simple, consistent procedure for estimating nitrate deficits (Naqvi and Sen Gupta, 1985). In this paper, I shall present an estimate of the denitrification rate in oxygen-depleted waters of the Arabian Sea, based on the exports of nitrate deficits computed with this method utilizing a fairly large data base. Also included here are the maiden reports on the colorimetrically-determined oxygen levels and an unusual occurrence of a deep denitrifying layer. Further, I shall present evidence for the temporal variability in denitrification, and discuss the implications of the results in the context of global marine nitrogen cycling and the development of oxygen-deficient conditions in the Arabian Sea.

2. Material and methods

a. Data used. The hydrographical and hydrochemical data on which this study is based were largely generated during some recent cruises of R. V. *Gaveshani* and R. V. *Sagar Kanya.* Although a good geographical coverage of the Arabian Sea was achieved during the International Indian Ocean Expedition (IIOE), the nutrient data obtained during the Expedition were inconsistent. For this reason, the use of IIOE data has rarely been resorted to. The more recent data collected by R. V. *Atlantis* II (Deuser *et al.*, 1978) are also re-examined. Table 1 lists the cruises, and the geographical positions of stations occupied are shown in Figure 1. The sparse coverage of the northern and western parts is the result of the recently-imposed restrictions on oceanographic observations within the exclusive economic zones of the respective countries. Some of the data included in this paper have been utilized in other works (e.g., Deuser *et al.*, 1978; Naqvi *et al.*, 1982; Naqvi and Qasim, 1983). Such data have been reprocessed following a new procedure (Naqvi and Sen Gupta, 1985).

Table 1. Sources of data.

Vessel and abbreviation	Cruise No.	Stations	Period	Symbol used in Fig. 1	Remarks
Atlantis II (AN)	8	57–79	9.8.63–23.8.63	⊠	
	93	2337–2356	15.1.77–31.1.77	⊡	Published*
Discovery (DI)	1	5007–5094	25.6.63–16.8.63		
Gaveshani (GA)	53	Mx 5-Mx 70	22.5.79–2.6.79	×	Published**
	118	2683–2706	17.4.83–28.4.83	⊙	Unpublished***
	159	3715–3723	24.11.85–1.12.85	◬	Unpublished
Meteor (ME)		181–236	6.2.65–12.3.65	☆	Published†
Sagar Kanya (SK)	13	1302–1344	16.2.85–12.3.85	●	Unpublished††
	14	1424–1457	8.4.85–25.4.85	◎	Unpublished††

*Deuser *et al.* (1978), reprocessed with the method of Naqvi and Sen Gupta (1985).
**Naqvi *et al.* (1982), reprocessed with the method of Naqvi and Sen Gupta (1985).
***Data from Stas. 2689–2695 published by Naqvi and Sen Gupta (1985).
†Sen Gupta *et al.* (1976); Naqvi and Qasim (1983), reprocessed with the method of Naqvi and Sen Gupta (1985).
††Courtesy Dr. M.D. Kumar and Mr. K. Somasundar.

b. Sampling and analytical procedures. Metallic Nansen bottles, TPN Hydrobios and PVC Niskin water samplers, and conductivity/salinity–temperature–depth (C/STD) rosettes, all fitted with reversing thermometers, were used for collecting water samples from standard depths to at least 2,000 m during the cruises of *Gaveshani* and *Sagar Kanya.* Nutrients, oxygen and salinity were determined shortly after collection on board ship. Analyses for nutrients were performed manually on board *Gaveshani,* but on board *Sagar Kanya,* a SKALAR 6-Channel Analyser 5100/1 was used.

Salinity was measured using the Autosal model 8400 salinometer. Inorganic phosphate was determined by the ascorbic acid–potassium antimonyl tartarate method of Murphy and Riley (1962). Nitrate was analyzed by the cadmium–mercury amalgam method of Morris and Riley (1963) as modified by Grasshoff (1964). Nitrite was determined following the method of Bendschneider and Robinson (1952). Dissolved oxygen was usually estimated with the Winkler method as modified by Carpenter (1965). However, during the 118th and 159th cruises of *Gaveshani,* oxygen estimations from the oxygen-minimum layer (~150–1,000 m) were carried out with the colorimetric method of Broenkow and Cline (1969), measuring the absorbance of triiodide ion at 352 mμ in a 1 cm quartz cell. Nitrite interference was checked with sodium azide. Some improvisation was made in the sampling gear. The petcock assembly, meant for conventional subsamplings from Niskin samplers, was replaced by a metallic adapter fitted with a replaceable rubber septum, through which water samples (25 cm^3) were drawn into air-tight syringes. The manganous sulphate and alkaline iodide solutions used in the colorimetric procedure were deoxygenated with

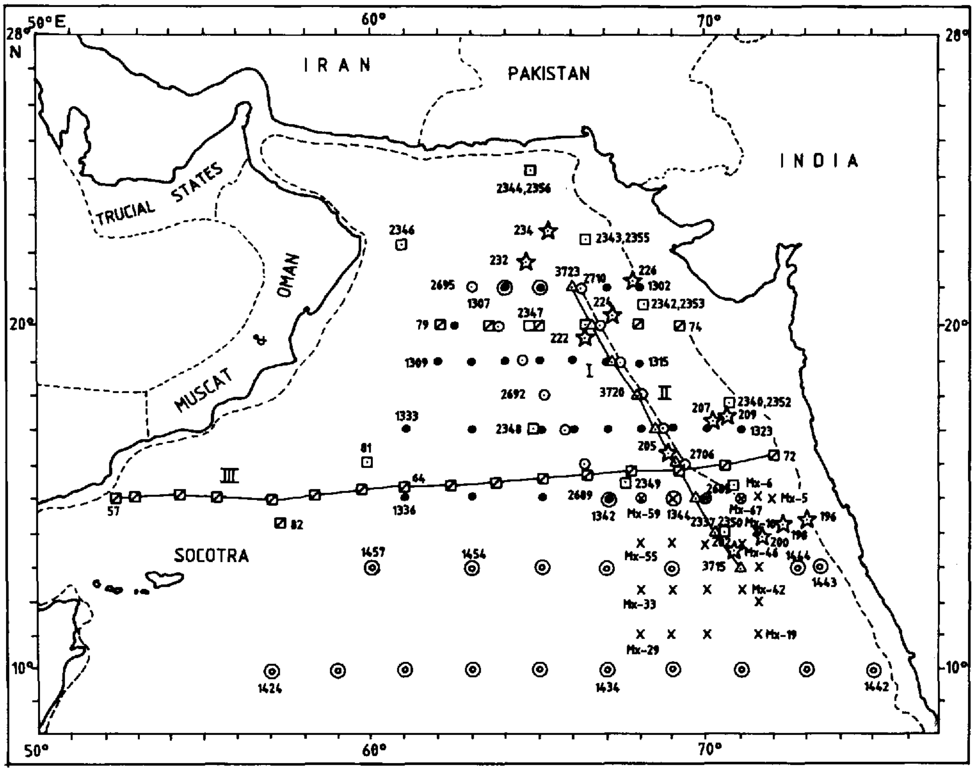

Figure 1. Location of stations (see Table 1 for the symbols).

nitrogen, but halfway through the 118th cruise a leakage in the valve emptied the N_2 cylinder and the degassing at Stas. 2693-2706 was performed by keeping the reagents under reduced pressure for half an hour before and during collection. This mode of deoxygenation might not have given the best results, but the oxygen concentrations determined were consistently low, generally below 3 μmol · dm^{-3}.

c. Computation of nitrate deficits. The expected nitrate concentrations were computed from the potential temperature and oxygen data, and were combined with the observed nitrate and nitrite concentrations to compute the nitrate deficits. The procedure has been described in detail by Naqvi and Sen Gupta (1985). The relevant equations are as follows:

$$\text{'NO'} = 429.81 - 12.4416\,\theta \quad 3 \leq \theta < 15 \tag{1}$$

$$\text{'NO'} = 290.66 - 2.9288\,\theta \quad 15 \leq \theta \leq 26 \tag{2}$$

$$\Delta N = (NO - O_2)/8.65 - NO_3 - NO_2 \tag{3}$$

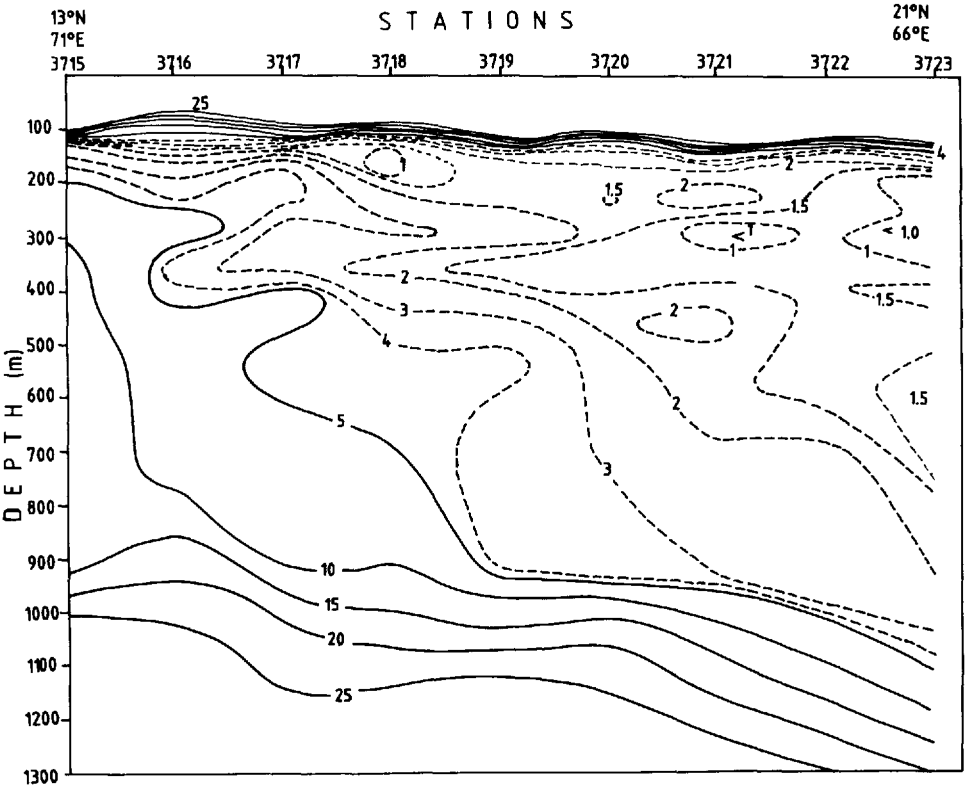

Figure 2. Colorimetric oxygen levels (μmol · dm^{-3}) in Section I.

Profiles of the nitrate deficit were numerically integrated at each station by computing the values at 1 m intervals using Lagrangian three-point interpolation between the observed data points. Eq. 3 often yielded slightly negative deficits for the oxygenated waters; such values were excluded from the integration. For a well-defined profile, the integration was done utilizing all positive values of ΔN. However, sometimes the boundaries of the layer with significant deficits, especially the lower one, were poorly defined. For example, at some stations, small positive values persisted to unreasonably great depths. In such cases, the integration began at 100 m and was terminated either at 1,000 m or at the depth where the deficit reached a plateau, whichever was smaller. However, if a deep ΔN maximum was present, the next data point lying below the maximum was taken as the lower limit for integration to accommodate this feature.

3. Results and discussion

a. Dissolved oxygen. A vertical section of dissolved oxygen determined colorimetrically during the 159th cruise of *Gaveshani* (Section I, Fig. 1) is presented in Figure 2.

The photometric oxygen levels are substantially lower (often by an order of magnitude) than those reported previously from the northern Arabian Sea based on analysis with the Winkler procedure (e.g., Sen Gupta *et al.*, 1976). The exceedingly low oxygen concentrations found within a large body of intermediate water (Fig. 2) compare very well with similar data from the oxygen-deficient environments in the eastern tropical Pacific (cf. Broenkow and Cline, 1969; Cline and Richards, 1972; Codispoti and Christensen, 1985).

A rapid northward increase in thickness of the oxygen minimum layer ($O_2 < 5$ $\mu mol \cdot dm^{-3}$) occurs between Lats. 13 and 17N (from ~100 to 800 m, Fig. 2). This is accompanied by steady northward decreases in oxygen concentrations. Even at very low oxygen levels, two minima could be observed, especially pronounced in the southern part of the section (Fig. 2). The shallow minimum was invariably observed at all the stations within the upper thermocline. This is at variance with Wyrtki's (1971) observation that most oxygen minima in the northern Arabian Sea belong to the deep category. A majority of the deeper minima were found at 300–400 m depth (Fig. 2), lying considerably shallower compared to most previous reports. While Wyrtki (1971, 1973) reported the deep minimum in the Arabian Sea to be located at ~600 m, Sen Gupta *et al.* (1976) observed this feature between 800 and 1,100 m. This discrepancy might arise from analytical errors associated with the Winkler procedure. The two minima are separated by an oxygen maximum (Fig. 2), which in most cases was found to occur at $\sigma_\theta = 26.8$ surface, the density level of the subantarctic mode water (Sen Gupta and Naqvi, 1984). Its occurrence within the oxygen-poor waters provides evidence for horizontal advection from the south. Such advection perhaps plays an important role in preventing the Arabian Sea from turning completely anoxic at mid-depth.

b. Temporal variability in denitrification and occurrence of a deep denitrifying layer. Several stations were occupied more than once to assess the magnitude of changes in reducing conditions with time. A comparison of results from a thrice-sampled location (19N; 66°26′–67°15′E) is made in Figure 3. The vertical profile of dissolved oxygen at Sta. SK1314 exhibits a consistent offset to higher concentrations within the depth range *ca.* 150–1,000 m, ostensibly due to titrimetric estimation. Oxygen concentrations measured colorimetrically on the other two occasions are comparable, although the April 1983 values (GA 2703) are slightly higher, and more variable, presumably due to the differences in modes of deoxygenation of the reagents. Nitrate profiles show considerable variability with the 1983 observations yielding substantially lower concentrations consistently. Significantly, highest concentrations of nitrite and nitrate deficits also occurred during the same period, indicating more intense overall reduction.

An unusual minimum in nitrate with corresponding maxima in nitrite and nitrate deficit formed a striking feature of the observations made in April 1983. Indeed this

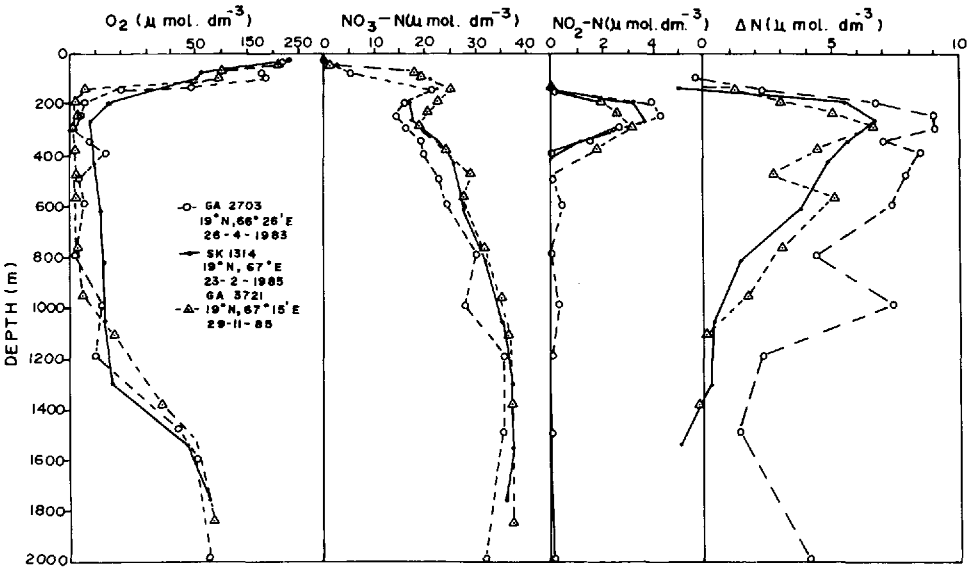

Figure 3. Comparison of oxygen, nitrate, nitrite and nitrate deficit profiles at a thrice-sampled location.

unusual feature was not confined to Sta. GA 2703 alone; it occurred at several stations between 900 and 1,200 m in the northeastern Arabian Sea (Section II, Fig. 4). However, a similarly oriented section located about 250 km west of Section II, worked during the same period, did not show this feature (Naqvi and Sen Gupta, 1985). Intrigued by these anomalous observations, we reoccupied most of the stations exhibiting the deep nitrate minimum and nitrite maximum during the 159th cruise of *Gaveshani* in November 1985 (Section I); the results are illustrated in Figure 5. The deep nitrate minimum was observed again, albeit at only two stations and at slightly shallower depths; it was also relatively weakly developed. The corresponding nitrite maximum, more intensely developed, was confined to only one station (Sta. GA 3719; 739 m). Analysis for the particulate organic carbon (POC) carried out at 5 stations during the same cruise indicated an unusual increase in POC between 750 and 1,000 m (Bhosle and Dhople, 1987). Although the observed POC concentrations were somewhat higher (39–1,037 $\mu g\ dm^{-3}$) than those reported previously from the Indian Ocean (46.5–157 $\mu g\ dm^{-3}$—Romankevich, 1984), it is unlikely that the consistent increases observed between 750 and 1,000 m resulted merely from errors in sampling or analysis. The results suggest that denitrification at these depths could be limited by the availability of organic carbon, and that an injection of organic matter through some mechanism might lead to the development of a deeper denitrifying layer in addition to the one represented by the main secondary nitrite maximum. What produces these features is not clearly understood. In an area such as the Arabian Sea, where the

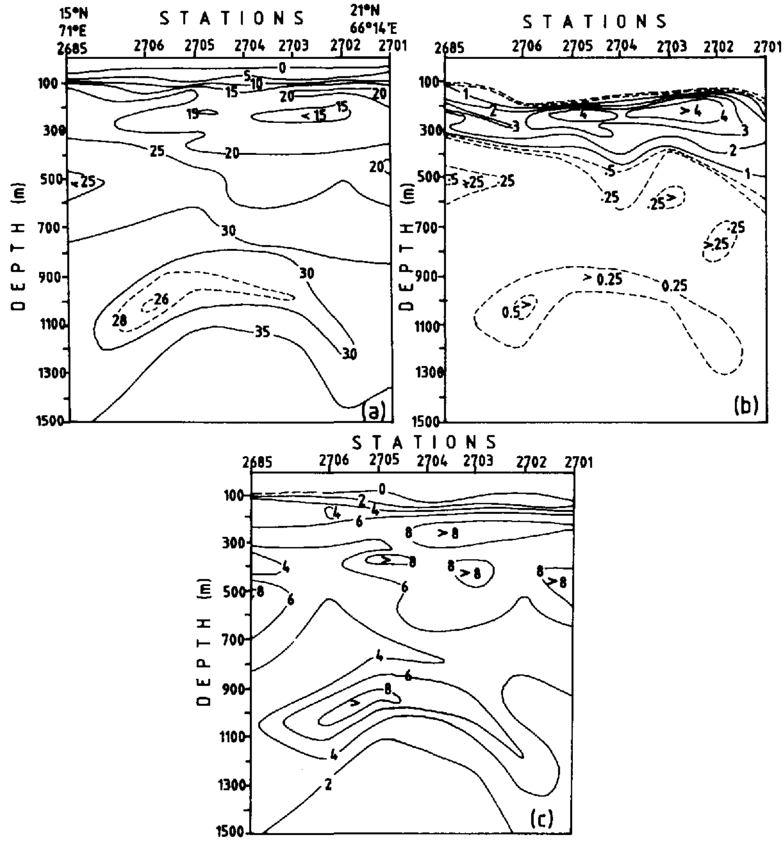

Figure 4. Distribution of properties in Section II: (a) nitrate; (b) nitrite; and (c) nitrate deficit, units—μmol dm^{-3}.

surface productivity exhibits exceptionally high variability both in space and time (for example, it may vary seasonally by a factor of 8—Qasim, 1982), it could result either from a variable flux of organic matter with time, or from lateral advection of waters from a more productive area. However, considering that denitrification is probably fueled by macro-organic particles (Liu and Kaplan, 1984) which have high sinking rates (Karl and Knauer, 1984), these are unlikely events. A more appealing mechanism could be related to the observations of Karl and Knauer (1984) in the Pacific. Based on sediment trap experiments at a station off Point Sur, California, these authors observed increases in the fluxes of POC, particulate organic nitrogen, and the rate of nucleic acid synthesis at comparable depths (between 700 and 900 m—the oxygen minimum zone). This together with microbiological and chemical analyses of the material intercepted at these depths led them to suggest the possibility of "chemolithotrophic-based carbon production system supported by the presence of

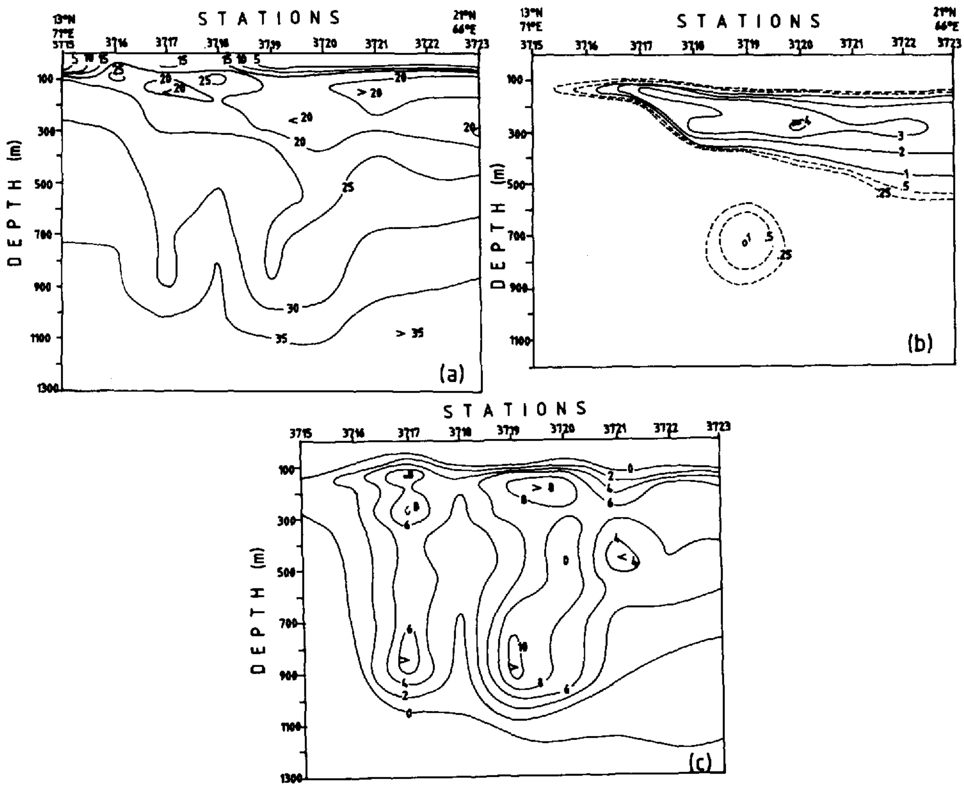

Figure 5. Distribution of properties in Section I: (a) nitrate; (b) nitrite; and (c) nitrate deficit, units—μmol dm^{-3}.

reduced inorganic compounds (e.g., NH_4^+, HS^-) found in association with the sinking particles." These deductions have, however, been contested by others (e.g., Betzer *et al.*, 1984). In any case, the deeper denitrifying layer appears to be an unstable feature. It was not observed during the cruises of *Sagar Kanya* during February–April, 1985, and of *Atlantis* II in January 1977 (Deuser *et al.*, 1978). However, it is evident in some historical data (e.g., at Sta. ME 222).

Figure 6a depicts the distribution of integrated nitrate deficit based on the *Sagar Kanya* observations (February–April, 1985), while similar results based on a recalculation of *Atlantis* II data are projected in Figure 6b. The two figures appear to be radically different. Although due to a more intensive geographical coverage of the area achieved during the cruises of *Sagar Kanya,* some of the finer trends seen in Figure 6a could be missing in Figure 6b, the large quantitative differences in the integrated deficits provide additional evidence for the temporal variability.

Thus the results presented above show significant changes in concentrations of combined nitrogen species with time. Stations SK 1314 and GA 3721 were occupied in

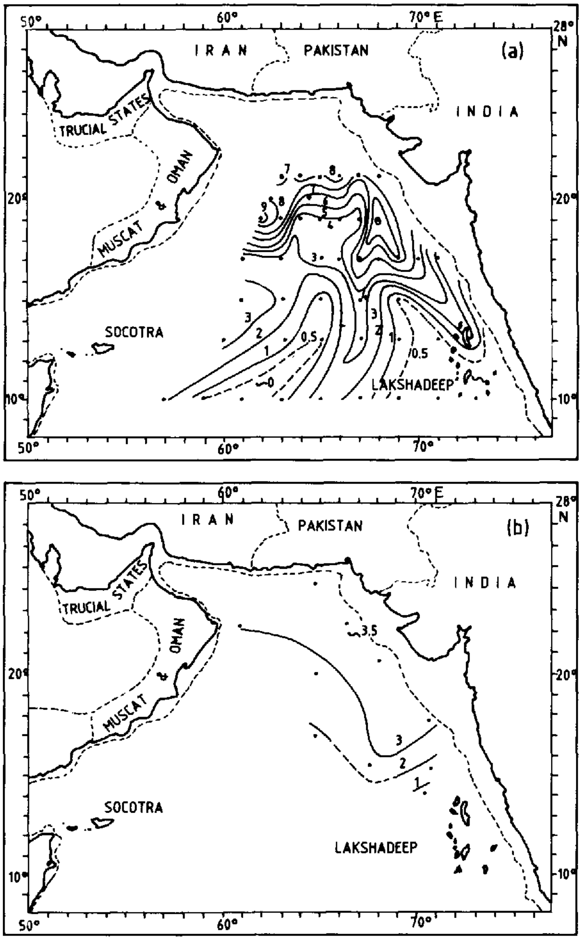

Figure 6. Distribution of the integrated nitrate deficit (g-at. m^{-2}) between approx. 100 and 1,000 m in the Arabian Sea: (a) *Sagar Kanya* observations in Feb.–April, 1985; and (b) *Atlantis* II observations in January, 1977.

the same year, during pre- and post-southwest monsoon seasons respectively, and so the differences in NO_3, NO_2, and ΔN profiles (Fig. 3) give a measure of seasonal variations. Differences between Figures 4 and 5 would be both inter- and intra-annual, while the large temporal variability evident in Figure 6 should be largely interannual since both the *Sagar Kanya* and *Atlantis* II observations were made in more or less the same season. It may, however, be pointed out that, on a short time scale, it is difficult to resolve the seasonal changes from interannual variations, because the latter will largely result from the variability of a seasonal phenomenon—the monsoons. How the reducing environment reacts to the monsoons is difficult to ascertain, since both the surface productivity and mid-depth circulation respond to the seasonal rhythm. The important point is that the resultant changes are clearly discernible on a short time scale of a few years, possibly months.

Associated with this variability, horizontal extent of the denitrification zone also changes with time. In the eastern Arabian Sea, where sufficient data are available to assess such variations, the southern boundary could extend to Lat. 12N, as indicated by the *Gaveshani* observations in May 1979. Other data (*Atlantis* II, Jan. 1977; *Gaveshani*, Nov. 1985) suggest a shift to the north by 2 degrees during periods when seemingly milder reducing conditions prevail. Some variability with longitude is indicated by the *Sagar Kanya* data, but the southern limit of denitrification inferred from these data generally falls between the two extremes. On the other hand, the southern boundary appears to shift northward in the western Arabian Sea during the SW monsoon, probably as a result of the northerly flow of oxygenated waters that make up for the vertical advection (upwelling) off the Arabian coast. An examination of the *Discovery* data taken in July–August 1963 (Royal Society, 1963) reveals low deficits associated with very low nitrite concentrations at all depths as far north as Lat. 18N. Probably atypical and representing conditions prevailing only during the peak monsoon, this represents an anomalous feature of denitrification in the Arabian Sea: the zones of most intense denitrification are not those which are biologically most productive, since the primary production is highest in the northwestern Arabian Sea (Ryther *et al.*, 1966). Even in the eastern Arabian Sea, the integrated deficits exhibit a decrease toward the Indian coast (Fig. 6a) in sharp contrast with similar eastern boundary environments in the Pacific Ocean, where the amount of denitrification decreases offshore (Cline and Richards, 1972; Codispoti and Packard, 1980). The principal locus of denitrification appears to lie in the northeastern Arabian Sea (Fig. 6a), considerably away from the productive shelf in an area of low to moderate productivity as inferred from Qasim's (1982) data. Incidentally, it is in this region that the deep nitrate minimum is generally observed. The occurrence of lower deficits closer to the coast than away from it, which is against the trend expected from primary productivity, reflects on the importance of circulation. A narrow northerly flow at intermediate depths close to the continental margin may explain the observed discrepancy. Such a flow is expected from the theoretical considerations (McCreary, 1981), but has not been substantiated from field observations in the eastern Arabian Sea so far, presumably due to a lack of closely-spaced sampling (Dr. Satish Shetye, personal communication, 1986).

A distinct feature of Figure 6a is the presence of several tongues of high and low integrated deficits, alternately extending southward and northward, respectively. The main high-deficit tongue is oriented almost meridionally around Long. 67E, while the main low-deficit tongue, somewhat broader, is located to its west. These features appear to extend continuously over several hundred kilometers, and it seems unlikely that these are produced by geographical variations in the downward flux of organic matter, considering the patchiness of primary production in the Arabian Sea. Instead, they may represent a net flow within the intermediate layer. If this is true, then considerable amounts of the products of denitrification would be exported out of the denitrification zone through horizontal advection. This will be discussed in some detail in the following section.

c. Rate of denitrification. Two estimates of the rate of denitrification in the Arabian Sea are available in the literature (10^{11}–10^{12} gN y^{-1}—Deuser *et al.*, 1978, and 3.2×10^{12} gN y^{-1}—Naqvi *et al.*, 1982). In both cases, the standing crop of denitrified nitrogen estimated from nitrate deficits was divided by an estimated residence time of the denitrifying layer to arrive at the denitrification rate. However, estimates of the residence time differ widely (from 3–30 y by Deuser *et al.*, 1978 to 77 y by Qasim, 1982), which has been largely responsible for the disagreement in the computed rates. An attempt is made here to estimate the rate of denitrification in the Arabian Sea from the exports of nitrate deficits out of the denitrification zone. A schematic representation of the procedure together with the constants used is made in Figure 7. Similar methods applied to the ETNP and the eastern tropical South Pacific (ETSP) have yielded rates comparable to those estimated from the activity of the electron transport system (ETS) (Codispoti and Richards, 1976; Codispoti and Packard, 1980). The advantage of this approach lies in its insensitivity to the choice of the thickness of the denitrifying layer, which, in some other procedures, may lead to large overestimations of denitrification rates (Anderson *et al.*, 1982).

It is not entirely clear whether the deficits calculated with Eq. 3 quantitatively represent terminal production of molecular nitrogen, or a correction factor should be applied to convert the estimated deficits into the amounts of molecular nitrogen liberated. This is partly because the fate of ammonia released during biochemical oxidation of organic matter in marine denitrifying environments is not entirely known. The yield of molecular nitrogen could exceed nitrate losses by 16% if ammonia is oxidized by nitrate, as postulated by Richards (1965), and by 20% if a nitrification-denitrification couple involving $NH_4^+ \rightarrow N_2O \rightarrow N_2$ is responsible for the observed lack of ammonia accumulation in oceanic oxygen minimum zones, as suggested by Codispoti and Christensen (1985). Omission of N_2O from the mass balance would lead to a further underestimation of the amount of molecular nitrogen production, albeit to a smaller extent (there has been no report so far on the levels of N_2O in the Arabian Sea, but the expected concentrations should not be very different from those observed in the Pacific (Naqvi and Sen Gupta, 1985)). Against these factors, there is also a possibility that the nitrogen production could be overestimated due to the recycling of combined nitrogen compounds through the nitrifying and denitrifying layers, as visualized in the steady state one-dimensional (vertical) reaction-diffusion model presented by Anderson *et al.* (1982). Utilizing the data of Deuser *et al.* (1978), Anderson *et al.* (1982) estimated the depth-averaged 'denitrification efficiency' (the

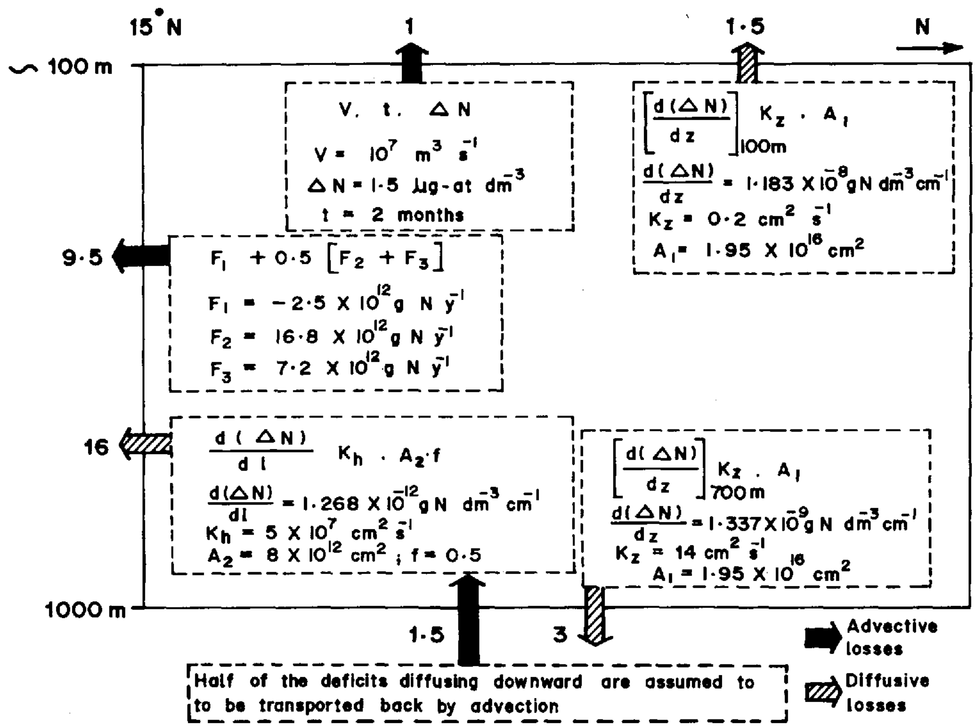

Figure 7. Schematic representation of the procedure followed for estimating the rate of denitrification. V = volume of water upwelling at 100 m level within the Arabian upwelling zone; t = duration of the upwelling; ΔN = average nitrate deficit in upwelling water; F_1 = advective transport across Section III, west of Long. 61E; F_2 = advective transport across Section III, east of Long. 61E; F_3 = average of all the observations along Lat. 15N, east of Long. 61E; $d(\Delta N)/dz$ = 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. 17N between 100 and 1000 m; f = fraction of the section affected by southerly flow.

ratio of the nitrogen production to nitrate reduction) in the Arabian Sea as 0.57. The following points should, however, be taken into consideration:

(1) Although Anderson *et al.* (1982) confined their model to the center of denitrification zone where horizontal advection will be at minimum, the application of one-dimensional models is perhaps still not justifiable in an area such as the Arabian Sea where strong horizontal gradients exist in temperature and salinity, resulting in vigorous lateral mixing (Bennett, 1970).

(2) As pointed out by Codispoti and Christensen (1985), since N_2O could be a major product of nitrification at very low oxygen levels, nitrite diffusion from the denitrifying layer should not greatly affect the extent of denitrification. In other words, the 'efficiencies' computed by Anderson *et al.* (1982) could be low.

(3) Nitrite concentrations in the Arabian Sea are generally $<4\ \mu mol \cdot dm^{-3}$ (Naqvi, 1986), considerably lower than those frequently found in the ETSP. Since the nitrite maximum is generally located within or just below the strong upper thermocline, where vertical diffusivity is rather small, the diffusion of nitrite through the upper boundary will not be very large. Perhaps, the same is true for diffusion through the lower boundary as well. Here, although the vertical diffusivity would be larger, the nitrite gradients are much smaller.

It is difficult to evaluate the relative importance of the above mentioned factors. Nevertheless, it is likely that possible underestimations due to the production of some molecular nitrogen without corresponding decreases in nitrate content may be approximately balanced by an overestimation associated with the nitrite loss. If so, the nitrate deficits computed from Eq. 3 may be fair approximations of the extent of molecular nitrogen production.

(i) Advective losses

Horizontal advection. The *Atlantis* II data collected during the IIOE (August 1963) along a trans-Arabian Sea section (Section III, Fig. 1) were utilized to estimate the horizontal, advective transports of nitrate deficits to the south. The nitrate deficits (Fig. 8a) were combined with dynamic computations (Fig. 8b) for estimating net export of deficits associated with the horizontal advection between ~100 and 1,000 m across this roughly zonal section. The procedure followed was analogous to that of Codispoti and Richards (1976). The dynamic computations were made as described by Pond and Pickard (1978) with 1,000-db surface as the reference level. However, to include Sta. AN 72, where the water depth was 949 m, the reference level was changed to 800-db for the station pair AN 71 and 72. Although there are no direct current meter data available to justify the selection of 1,000-db surface as the reference level, this level has widely been used by previous workers for dynamic calculations in the Arabian Sea (e.g., Düing, 1970; Bennett, 1970; Wyrtki, 1971, 1973). The net southerly transport of nitrate deficits between 100 and 1,000 m was estimated to be 1.4×10^{13} gN y^{-1}.

However, it will be appropriate to make some reservations here:

(1) Apart from the uncertainty associated with the choice of the reference level, it is not quite certain in an area such as the Arabian Sea, where the surface circulation shows exceptionally high variability both in the magnitude and direction, as to the depth to which the seasonal effects penetrate. Based on the bimonthly distributions of the Red Sea salinity maximum, Bennett (1970) demonstrated that the seasonal changes do occur even at ~700 m depth. His results also indicated considerable isentropic flow at any time with speeds up to 10 cm s^{-1}. On the other hand, the annually averaged data showed sluggish mean geostrophic flow; this was attributed to the horizontal velocity fluctuations. In view of these seasonal fluctuations in geostrophic flow, it is not clear if the transport estimate across Section III is a reasonable

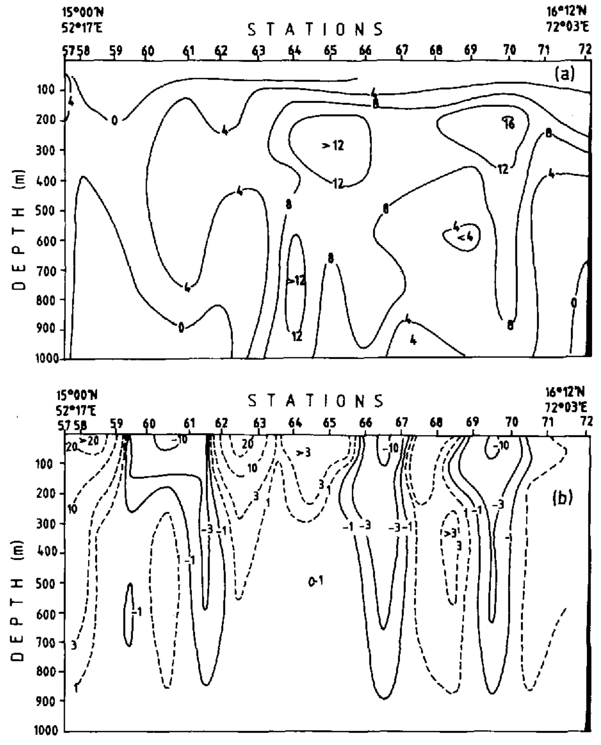

Figure 8. (a) Distribution of nitrate deficits (μg-at. dm^{-3}) in Section III (*Atlantis* II IIOE data); and (b) Relative barocline currents (cm s^{-1}) in Section III computed with 1,000-db surface as the reference level: solid lines—southerly flow; broken lines—northerly flow.

annual figure. Yet, notwithstanding the annually averaged weak geostrophic currents, it is certain that significant amounts of nitrate deficits would be lost through lateral advection.

(2) The nitrate deficits computed with the IIOE *Atlantis* II data (Fig. 8a) appear to be rather high compared to most values based on recent observations (cf. Naqvi *et al.*, 1982; Naqvi and Sen Gupta, 1985; Naqvi, 1986). Whether this is due to unusually intense reducing conditions that could have existed during the period of observations, or merely the result of a systematic error in measurements, is difficult to ascertain. The pre-1964 nitrate data are perhaps not of the same quality as the present day data. Also, vertical spacing of the samples achieved during the concerned cruises was relatively large.

The *Atlantis* II data were used as a last resort. This was because a trans-Arabian Sea section could not be worked in the present study for reasons mentioned earlier. The transport estimate was, however, moderated with the ample observations made on board *Gaveshani* and *Sagar Kanya* along Lat. 15N, east of Long. 61E (Fig. 1) in the following manner (see Fig. 7). First, the transports computed for the common parts of the sections located along Lat. 15N were averaged and summed up, and then the mean of this value and the transport estimated across Section III, east of Long. 61E was added to the transport estimated for the same section west of 61E. The net southerly transport computed in this manner within the depth range ~100 and 1,000 m came to 9.5×10^{12} gN y^{-1}.

Although the averaging procedure is rather crude, the errors introduced are not expected to be large since the bulk of the net southerly transport appears to be restricted to the region east of Sta. AN 64. On splitting the transport across Section III, it was found that a net southerly export (16.8×10^{12} gN y^{-1}) occurred east of Long. 61E, while west of this longitude the net transport (2.5×10^{12} gN y^{-1}) was actually directed northward.

Vertical advection. The principal loci of intense seasonal upwelling in the Arabian Sea lie along the Somali and Arabian coasts (Currie *et al.*, 1973; Swallow, 1984), although weak upwelling also occurs off the Indian coast during the SW monsoon (Wyrtki, 1973) and off the Pakistani and Iranian coasts during the NE monsoon (Brewer and Dyrssen, 1985). The upwelling region off Somalia is located outside the denitrification zone, and hence it will not be considered here. On the other hand, intense upwelling occurring off the southeast Arabian coast could remove significant amounts of nitrate deficits from the denitrifying layer.

As indicated earlier, the *Discovery* data collected during July–August 1963 from the upwelling region off the Arabian coast yielded very low deficits up to Lat. 18N. The corresponding nitrite concentrations were also very low, seldom exceeding 1 μmol · dm^{-3}, in sharp contrast with observations in the eastern Arabian Sea at comparable latitudes. Although the possibility that the *Discovery* nitrate data might be systematically high cannot be ruled out since rather large negative values of ΔN were computed consistently at most stations, it is quite possible that most of the deficits would already have been removed from the denitrifying layer by upwelling in the period preceding the observations. The low deficits indicate that the upward movement of water could be compensated for largely by the lateral flow of waters from outside the denitrification zone; i.e., from the south. Relatively strong northerly flow extending to considerable depths observed between Stas. AN 57 and 59 (Fig. 8b) is consistent with this interpretation. Such seasonal northerly flow appears to play an important role in the renewal of intermediate waters in the western Arabian Sea.

The upward transport of water at the 100 m level in the upwelling region off the Arabian coast has been estimated to be around 10^7 m^3 s^{-1} (Bottero, 1969). Assuming that the water upwelling at this level is characterized by nitrate deficits of 1–2 μg-at dm^{-3}, and that such removal occurs for a period of 2 months, the export of nitrate deficits associated with the vertical advection would be $7\text{–}14 \times 10^{11}$ gN y^{-1} (Fig. 7). Similar losses in regions of weak upwelling/offshore divergence will probably be much smaller and could be ignored. Although the estimate is rough, it does indicate that the magnitude of vertical advective transports is much smaller than the horizontal advective losses.

(ii) Diffusive losses

Horizontal diffusion. To determine the quantum of nitrate deficit losses from horizontal diffusion, the nitrate deficits, interpolated at 5 depths (150, 300, 500, 700 and 900 m) at Stas. SK 1302–1344, were averaged for each of the three zonal sections along 15, 17 and 19N latitudes. The mean horizontal gradient between Lats. 15 and 19N was estimated as 1.268×10^{-12} gN dm^{-3} cm^{-1}. A value of 5×10^7 cm^2 s^{-1} for the horizontal diffusion constant was selected from the literature (Defant, 1956). This value, which is close to Bennett's (1970) estimate based on the bimonthly distribution of salinity at $\sigma_\theta = 27.2$ surface, was considered to be reasonable by Wyrtki (personal communication, 1986). It was assumed that the upstream and cross-stream diffusive losses were negligible (cf. Codispoti and Richards, 1976). From Figure 8b the fraction of the section affected by the southerly flow was estimated as ~0.5. These values, together with an estimated cross section of 8×10^{12} cm^2 give the horizontal diffusive flux of nitrate deficits as 16.0×10^{12} gN y^{-1} (Fig. 7). This value is of the same order as the horizontal advective transport. However, it is about two orders of magnitude higher than the corresponding value from the ETNP (Codispoti and Richards, 1976). Obviously, the difference is due to a higher value of the horizontal exchange coefficient selected here than the one utilized for the ETNP (10^6 cm^2 s^{-1}). Higher horizontal diffusivity in the Arabian Sea reflects intense lateral mixing, presumably resulting from strong meridional gradients in both temperature and salinity, and evident from the remarkably linear potential temperature-salinity relationships at constant depth (Bennett, 1970).

Diffusion through the upper boundary. The data from Stas. GA 3715–3723 and SK 1302–1344 were utilized for determining the magnitude of vertical diffusive flux of nitrate deficits through the upper boundary. Nitrate deficits computed at 4 successive depths, one above the 100 m level and three below it, were fitted into a second degree least-squares polynomial, and the resulting curve was differentiated to estimate the vertical gradient at 100 m depth. The mean vertical gradient deduced was 1.183×10^{-8} gN dm^{-3} cm^{-1}. The choice of the vertical exchange coefficient, as in the case of horizontal diffusive losses, introduces some uncertainty. Although a value of 1 cm^2 s^{-1} has been reported by Wafar *et al.* (1986) from the Laccadive Sea, other measurements (e.g., Osborn, 1980) have shown that vertical diffusivity within the thermocline is rather small. Values between 0.1 and 0.3 cm^2 s^{-1} for the 100 m level in the middle appear to be more realistic (Prof. K. Wyrtki, personal communication, 1986). With these values ($K_z = 0.2$ cm^2 s^{-1}, $A = 1.95 \times 10^{16}$ cm^2), the losses of nitrate deficits associated with vertical diffusion through the upper boundary come to 1.5×10^{12} gN y^{-1} (Fig. 7), roughly equal to the vertical advective losses.

Diffusion through the lower boundary. Estimates of nitrate deficit losses through the lower boundary are ambiguous owing to some hitherto poorly-understood physical processes which govern the property distributions in the intermediate and deep waters of the northern Indian Ocean. A brief review of the existing information, relevant to the problem at hand, may be useful here.

Bennett (1970) identified three depth zones in the northern Indian Ocean from a consideration of the conservation of heat and salt: a layer of uniform vertical advection, deeper than 1,700 m; a layer of constant vertical diffusive flux, lying between 400 and 1,200 m; and an intermediate transition layer. In the deeper layer (depth > 1,700 m), the ascending motion, fed by the northerly flow of deep waters, appears to balance the downward diffusion. The layer between 400 and 1,200 m, on the other hand, was shown to be characterized by a uniform vertical diffusive flux, with the vertical exchange coefficient increasing with depth. The ascending motion may be slow, even negligible, within the upper zone. Since the deeper layer is characterized by uniform upwelling, the rate of which may be much higher in the Indian Ocean than in the Pacific or the Atlantic (Warren, 1981; Swallow, 1984), a southerly flow should be expected within the transition zone (1,200–1,700 m). However, according to Bennett (1970), the return flow occurs not within the transition zone, but close to the deep oxygen minimum, a view shared by Wyrtki (1973). This implies that considerable upward movement could extend to the layer of uniform vertical diffusion. However, the southerly flow close to the oxygen minimum has not been substantiated. On the other hand, the occurrence of a deep silicate maximum coinciding with a salinity maximum provides evidence for the return flow at ~3 km (Edmond *et al.*, 1979; Warren, 1981; Naqvi and Kureishy, 1986).

If the return flow occurs at depths <1,000 m, it would probably be included in the horizontal advective transport estimated earlier. However, if this flow is located at depths >1,000 m, some of the deficits diffusing below 1,000 m may be lost to the south with the return flow, and hence should be accounted for. Considering the second possibility, the upward movement of water was assumed to be negligible, and the downward diffusive flux of nitrate deficits was estimated at 700 m (mid point between 400 and 1,000 m). The mean vertical gradient of nitrate deficit at this depth was deduced to be 1.337×10^{-9} gN dm^{-3} cm^{-1}, utilizing data from Stas. GA 3716–3723 and SK 1302–1344, and assuming a linear decrease between two observed data points, one lying above and the other below 700 m depth. Using Bennett's (1970) estimate for the vertical exchange coefficient at 700 m (14 cm^2 s^{-1}), the downward diffusive flux could be computed as ~3×10^{12} gN y^{-1} (Fig. 7). However, since it is possible that vertical diffusion at the lower boundary may be balanced by the ascending motion (in which case the net losses will be zero), only ½ of the value computed above has been taken to represent the losses through the lower boundary so that it would fall between the two extremes.

Table 2. Denitrification rate in the Arabian Sea based on advective and diffusive losses of the nitrate deficits from the denitrifying layer.

Nature of losses	Rate (10^{12} gN y^{-1})
Horizontal advection	9.5
Vertical advection	1
Diffusion through the southern boundary	16
Diffusion through the upper boundary	1.5
Diffusion through the lower boundary	1.5
Total (Rate of denitrification)	29.5

(iii) Denitrification rate and renewal time of oxygen-deficient waters

From the nitrate deficit losses computed above and summarized in Figure 7 and Table 2, the rate of denitrification in the Arabian Sea comes to 29.5×10^{12} gN y^{-1}. Since the data utilized were collected during different seasons and years, the estimate represents some sort of a time-averaged figure. This is about 9 times the rate estimated by Naqvi *et al.* (1982) and 30–300 times the value arrived at by Deuser *et al.* (1978).

In order to estimate the 'standing crop' of denitrified nitrogen, the weighted mean of the integrated deficits, computed utilizing data from all the stations shown in Figure 1, was multiplied by the area of the denitrification zone (1.95×10^6 km^2; i.e., north of Lat. 13N, east of Long. 52E, and outside the continental shelf, roughly equal to the corresponding area in the ETNP). The value so obtained (1.15×10^{14} g) is close to the estimate of Naqvi *et al.* (1982) (9.5×10^{13} g), but much higher than that of Deuser *et al.* (1978) (4×10^{12} g). Dividing the estimated 'standing crop' with the rate of denitrification, the average renewal time of the oxygen-deficient layer (~100–1,000 m) comes to approximately 4 y.

An order-of-magnitude check on the above estimates could be made by applying some constraints in the light of available information from other denitrification sites. Liu and Kaplan (1984) found a direct correspondence between the fluxes of carbon consumed during nitrate reduction, normalized to surface productivity, ϕ_c/P, and the fraction of surface organic production available within the denitrifying layer as macroparticles, $\Delta f/P$, computed from the model of Suess (1980). While the data from all the sites considered (ETNP, ETSP, Darwin Bay and Cariaco Trench for the water column denitrification) showed a distinct relationship, the data point representing the Arabian Sea (based on the estimate of Deuser *et al.*, 1978) deviated widely from the global trend. Liu and Kaplan (1984) attributed it to a possible underestimation of the extent of denitrification in this region. Utilizing data from several stations within the denitrification zone, Somasundar and Naqvi (1987) computed the average amount of carbon consumed during nitrate reduction as 3.86 ± 0.32 g-at m^{-2}. Combining this value with the above estimate of renewal time, and normalizing the annual flux to

Qasim's (1982) average of surface productivity (835 mgC m^{-2} d^{-1}), the amount of carbon used up for nitrate reduction could be computed as ~4%, as against 0.4% deduced by Liu and Kaplan (1984). This is roughly equal to the corresponding value from the ETNP (6%), a region very similar to the Arabian Sea in several respects (Naqvi, 1986). For the same stations, the fraction of surface primary production available as macroparticles within the denitrifying layer was 17.6 ± 4.3%. Plotted in the ϕ_c/P vs $\Delta f/P$ diagram of Liu and Kaplan (1984), these values conform well to the global trend.

The estimate of the rate of denitrification made here would suffer from the same uncertainties that are inherent in such computations. Moreover, in view of the evidence for large short-term temporal variability presented earlier, considerable variations in the rate of denitrification should be expected. Nonetheless, since it conforms to the global pattern, the rate deduced should be a good first approximation.

d. Implications of the results. Development of the oxygen-deficient conditions. The short renewal time of the oxygen-deficient layer (*ca.* 100–1,000 m) deduced here, consistent with the observed large short-term variability in denitrification intensity, qualitatively supports Swallow's (1984) view that the oxygen-depleted intermediate waters in the Arabian Sea are not stagnated. This is also evident from Figure 9, which gives a vertical north-south section of tritium based on GEOSECS data (Ostlund *et al.*, 1980). If the intermediate layers were to remain stagnated for long periods due to the presence of Asian landmass in the north, as has been believed so far (e.g., Dietrich, 1973; Wyrtki, 1973; Qasim, 1982), one would expect an upward tilt in tritium isolines from south to north in the Arabian Sea. Such is not the case. Indeed one observes a slight increase in tritium penetration from south to north (Fig. 9). The development of reducing conditions in the Arabian Sea, therefore, can not be a consequence of stagnation of waters. Instead, the acute deficiency of dissolved oxygen probably results from low oxygen content of waters responsible for the renewal plus a high oxygen demand owing to high rate of organic production, as suggested by Swallow (1984).

Marine combined nitrogen budgets. As indicated earlier, the rate of denitrification deduced in the present study is one to two orders of magnitude higher than the previous estimates. It is of the same order as the contributions from the ETNP and ETSP (Codispoti and Richards, 1976; Codispoti and Packard, 1980). This would necessitate scaling-up of present estimates of oceanic water column denitrification by about 40 to 100% (Liu and Kaplan, 1984; Codispoti and Christensen, 1985). Revision of Codispoti and Christensen's (1985) estimate, for example, would lead to a total water column denitrification rate of ~85 × 10^{12} gN y^{-1}. This would in turn increase the magnitude of the anomaly in marine combined nitrogen budget, i.e., apparent excess of net losses over net inputs to 93 × 10^{12} gN y^{-1}. It has been suggested that the oceanic nitrogen system is not in a steady state, with the sea acting alternately as a net sink or a net

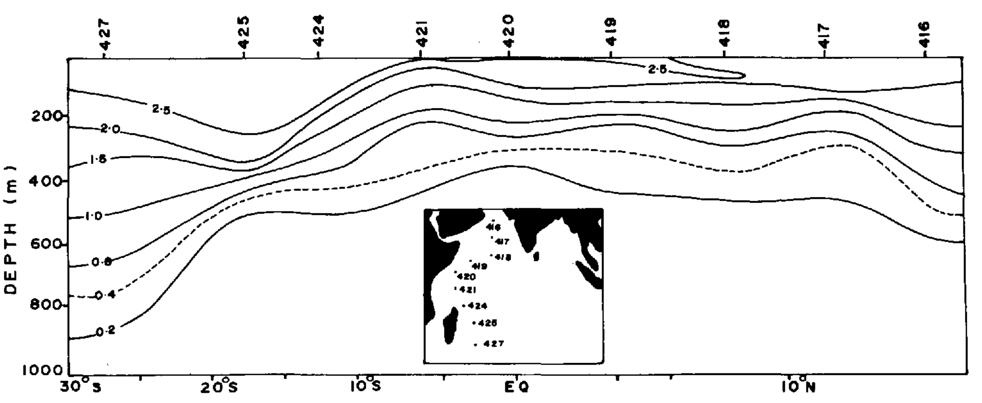

Figure 9. Vertical section of (TU) tritium through the northwestern Indian Ocean (modified from Ostlund *et al.*, 1980).

source of fixed nitrogen (McElroy, 1983; Codispoti and Christensen, 1985). Large increases in the denitrification rate observed recently in the ETSP lend support to this view (Codispoti *et al.*, 1986). The results from the Arabian Sea (occasional development of a deep denitrifying layer and geographical changes in the extent of denitrification) seem to reinforce this assertion. However, the question as to whether the size of the anomaly is really so large, or it results, at least in part, from inaccurate estimates of some components of the budget (e.g., sedimentary denitrification and nitrogen fixation—Naqvi *et al.*, 1986) remains to be satisfactorily answered.

4. Conclusions

The central conclusion of this work is that the contribution of the Arabian Sea to global denitrification is much larger than previously believed. The high rate of denitrification deduced here is consistent with the relationship between the rate of denitrification and organic carbon supply observed elsewhere in the oceans. It would appear that the three major oceanic denitrification sites (ETNP, ETSP and Arabian Sea) contribute almost equally to the global denitrification pool. Also, in view of the elevated estimate for denitrification in the Arabian Sea, a re-evaluation of other components of marine fixed nitrogen budget is required.

Denitrification in the Arabian Sea shows considerable short-term variability, as in the ETSP, although to a smaller extent. This has two implications. First, the variable rate of denitrification, best manifested by the occasional development of a deep denitrifying layer, supports the hypothesis of fluctuations in the fluxes of combined nitrogen to and from the sea (McElroy, 1983, Codispoti *et al.*, 1986). Secondly, it would imply quick renewal of the oxygen-depleted waters, against the long-prevalent notion about stagnation of intermediate layers in the Arabian Sea; this is supported by the tritium data.

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