

Inorganic Nitrogen & Nitrate Reduction in the Arabian Sea

S W A NAQVI & S Z QASIM*

National Institute of Oceanography, Dona Paula, Goa 403 004

Received 7 September 1982

Concentration of inorganic nitrogen compounds within the euphotic zone is very low and it increases sharply in the thermocline layer. A steady decrease in the $\text{NO}_3\text{-N}$ occurs from south to north at intermediate depths. This is associated with nitrate minima in the northern Arabian Sea. Two maxima in $\text{NO}_2\text{-N}$ are observed in the northern region. The shallow (primary) nitrite maximum with low nitrite occurs in the surface layer near the thermocline in conjunction with a relatively high dissolved oxygen. The intermediate (secondary) maximum is invariably associated with very low oxygen ($< 0.1 \text{ ml.l}^{-1}$). It is quite pronounced with nitrite reaching as high as $7 \mu\text{g-at.l}^{-1}$. The secondary maximum is not observed south of 12° N lat. Neither the nitrate minima nor the secondary nitrite maximum seem to be associated with the Persian Gulf water. It is suggested that these originate as a result of biological reduction of nitrate (denitrification) due to the prevailing reducing conditions associated with a pronounced depletion of dissolved oxygen below the thermocline. The nitrate deficits have been calculated using the relationships of the apparent oxygen utilization (AOU) with $\text{NO}_3\text{-N}$ and $\text{PO}_4\text{-P}$. The results indicate a steady northward increase in the nitrate deficits and in the depth range where denitrification occurs. Maximum values reaching up to $16.5 \mu\text{g-at.l}^{-1}$ are found around 20° N lat. Denitrification in the Arabian Sea may possibly extend up to 11 or 12° N lat.

The high rate of production of organic matter in the surface layers of the Arabian Sea leads to an increase in the oxygen utilization at intermediate depths. The supply of oxygen to the waters below the euphotic zone gets restricted by the existence of a strong density gradient. The horizontal advection is also poor due to semi-enclosed nature of the Arabian Sea. As a result of these features, the oxygen gets severely depleted below the thermocline, and at intermediate depths, reducing conditions prevail within a large volume of water. Due to extremely low concentrations of dissolved oxygen below the thermocline, nitrate is utilized by bacteria for the oxidation of organic matter. This reduction of nitrate to nitrite and presumably to gaseous nitrogen as the end product seems to occur widely in the region.

Estimates of the nitrogen budget in the oceans indicate that the annual input of the combined nitrogen to the sea from the atmosphere and rivers exceeds the burial of nitrogen in the sediments by 10^{13} to 10^{14} g (ref. 1-3). Therefore, to keep the nitrogen content of the atmosphere constant, there must be some mechanism by which free nitrogen is refluxed from the sea to the atmosphere. In view of this the phenomenon of marine denitrification assumes vital geochemical significance to which the Arabian Sea seems to make a significant contribution.

Attempts have been made earlier to calculate the amount of nitrate reduction in the Arabian Sea^{4,5}. However, these studies are rather inconclusive as the 2 sets of results obtained differed over a wide range. Naqvi *et al.*⁶ have evaluated the 2 procedures followed by the earlier workers for the calculation of nitrate

deficits and studied the denitrification process in the southeastern zone (lat. 11-15° N; long. 68-73° E). This paper, based on the observations from the eastern Arabian Sea, extends the work to the northern region (Fig. 1).

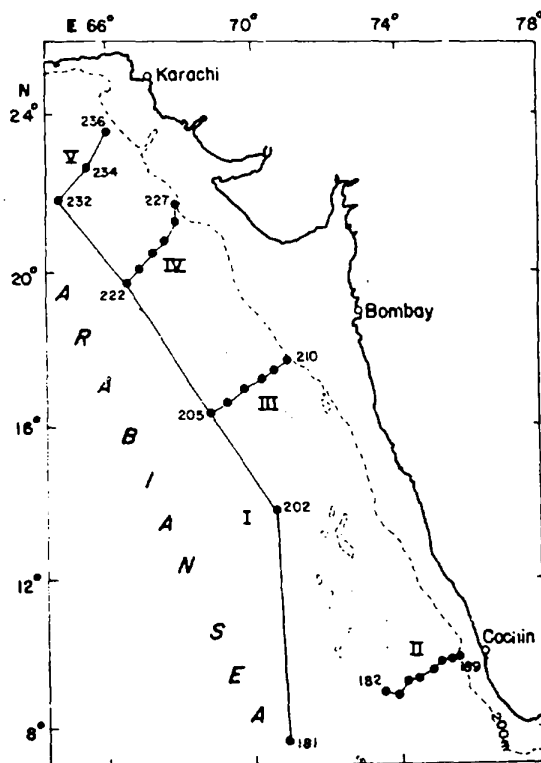


Fig. 1 Location of stations

*Present address: Department of Ocean Development, South Block, New Delhi 110011

Materials and Methods

The study is based on the data collected during the cruises of *R V Meteor* (Feb.-March 1965) as a part of the International Indian Ocean Expedition. Station locations are shown in Fig. 1. Sampling and analytical procedures are same as described by Dietrich *et al.*⁷.

Results and Discussion

Distribution of nitrate-nitrogen along a section parallel to the coast (I) and 3 sections perpendicular to the coast (II, III and IV) is shown in Fig. 2. The concentration of nitrate-nitrogen in the surface layer is very low. It increases sharply within the thermocline. Maximum concentrations are observed between 1000 and 2000 m. Thereafter, it decreases gradually with depth. A fall in the nitrate-nitrogen from south to north at all levels within the depth range 100-1200 m is quite striking. For instance, the $35 \mu\text{g-at.l}^{-1}$ contour lies at 700 m at st 181 as compared to 1100-1200 m in the northern region. Equally conspicuous is the occurrence of nitrate minima at intermediate depths in the northern region. The northward decrease in the

concentration of nitrate indicates that this nutrient is being progressively lost by some mechanism from south to north.

Distribution of nitrite along sections I, III, IV and V is presented in Fig. 3. Two nitrite maxima are seen in all the sections except in the section II where only the shallow maximum is observed. The concentration of nitrite at the shallow (primary) maximum is very low. The intermediate or the secondary nitrite maximum is quite pronounced with the nitrite reaching values as high as $7 \mu\text{g-at.l}^{-1}$.

Fig. 4 gives the distribution of dissolved oxygen along the section I. Oxygen values at the intermediate depths decrease steadily towards north and very low concentrations ($<0.1 \text{ ml.l}^{-1}$) occur in the northern region over a wide depth range. It should, however, be pointed out here that the oxygen determinations in the Arabian Sea have been carried out so far using the Winkler method. It has been found that at very low oxygen concentrations, reaching detection limit, the Winkler method gives consistently high values⁸. Therefore, the concentrations, as determined by this

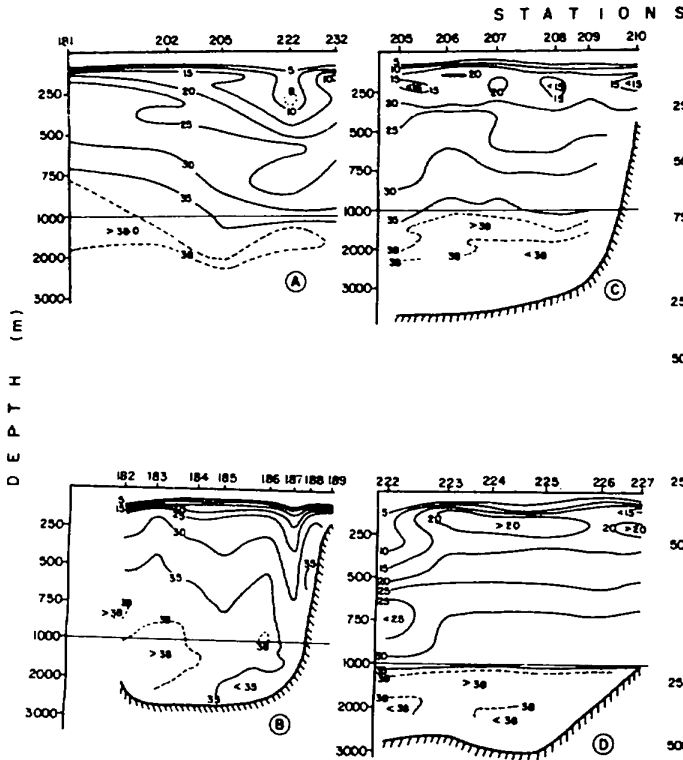


FIG. 2

Fig. 2--Distribution of nitrate-nitrogen ($\mu\text{g-at.l}^{-1}$) along (A) section I, (B) section II, (C) section III and (D) section IV

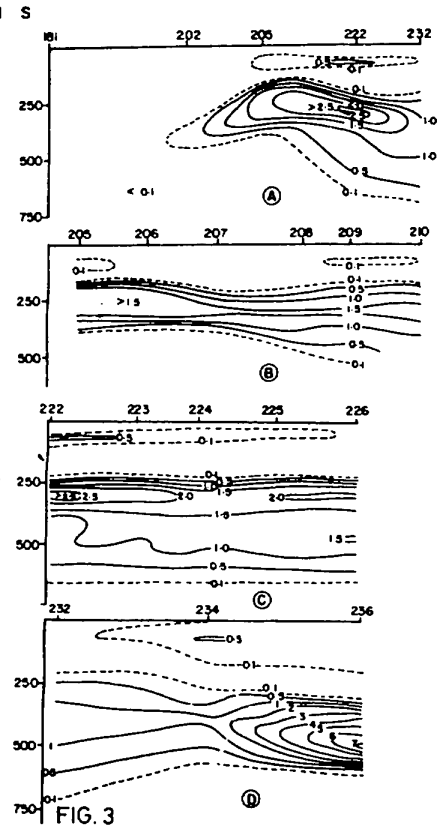
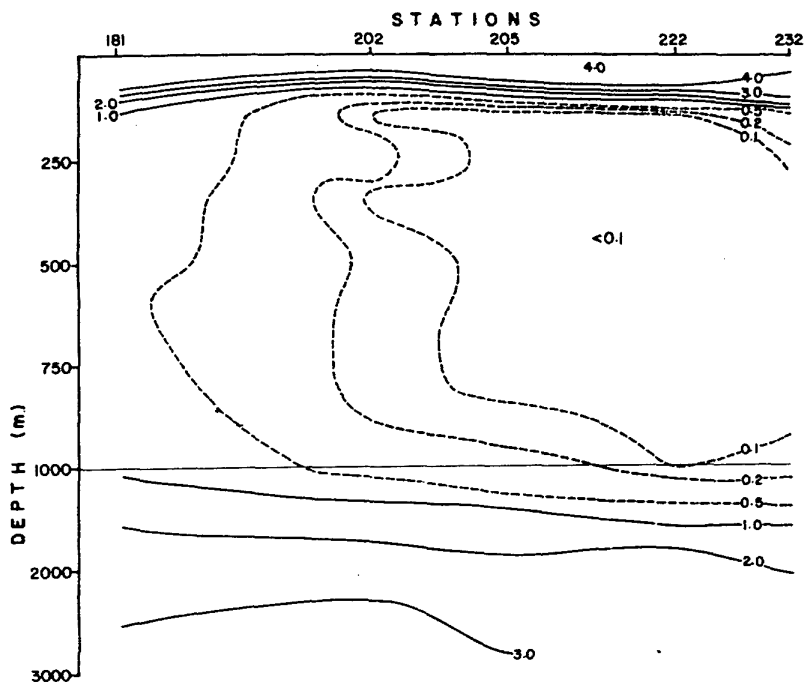


FIG. 3

Fig. 3--Distribution of nitrite-nitrogen ($\mu\text{g-at.l}^{-1}$) along (A) section I, (B) section III, (C) section IV and (D) section V


 Fig. 4—Distribution of dissolved oxygen (ml.l^{-1}) along section I

method, may be systematically high when the actual concentrations could be well near-zero.

The primary nitrite maximum is associated with relatively high oxygen concentrations. Encountered in the surface layers near the thermocline, this feature is attributed to the oxidation of organically derived ammonia or to the extra-cellular production of nitrite by phytoplankton during the assimilation of nitrate⁹. The secondary nitrite maximum is associated with very low oxygen concentrations ($<0.1 \text{ ml.l}^{-1}$; Fig. 4). It was first observed in the Arabian Sea by Gilson¹⁰ and has been studied in some detail by several others^{4-6,11}. A similar nitrite maximum at the intermediate depths has been observed in the eastern tropical Pacific^{12,13}. The origin of the secondary maximum is considered to be different from that of the primary maximum. Several workers believe it to arise from the biochemical oxidation of organic matter by nitrate (for a review see Deuser¹⁴). However, Carlucy and McNally¹⁵ suggested that it may also be caused by the oxidation of ammonia by nitrifying bacteria. These authors reported that nitrification may occur even at very low oxygen concentrations and, in some cases, the activity is faster when the dissolved oxygen concentration is low. In order to determine the cause of secondary nitrite maximum, profiles of nitrite at st 236, where concentration of nitrite was observed to be maximum, have been compared with ammonia-nitrogen and salinity (Fig. 5). Extremely high concentration of nitrite at 490 m depth ($7.08 \mu\text{g-at.l}^{-1}$, a value among

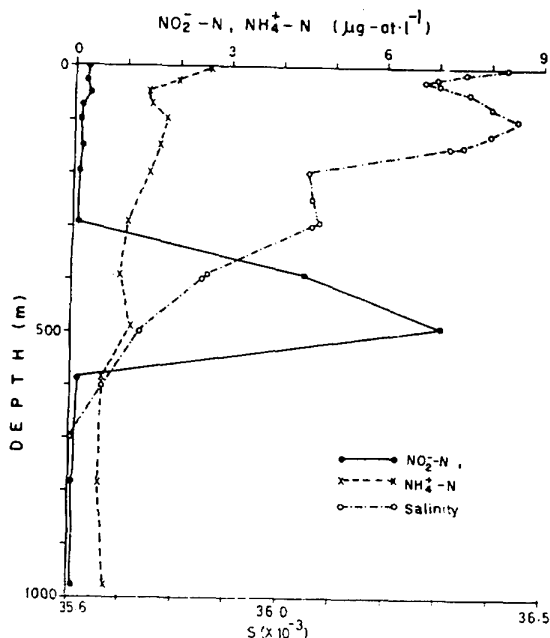


Fig. 5—Vertical profiles of nitrite-nitrogen, ammonia-nitrogen and salinity at st 236

the highest ever reported from the open sea), and the occurrence of ammonia at this depth, in levels not very different from the overlying and underlying waters, indicates that nitrite at this depth is not the result of nitrification. Its occurrence could only be due to

bacterial reduction of nitrate. The apparent deficits in nitrate in the northern region and the occurrence of nitrite at the intermediate depths, associated with very low oxygen concentrations, offer an evidence for the occurrence of denitrification in the Arabian Sea. Deuser *et al.*⁴ have reported the southern limit of the occurrence of secondary nitrite to be along 14°N lat. However, Naqvi *et al.*⁶ observed secondary nitrite maximum up to 12°N lat. The present results agree well with those reported by Lukashov¹¹ and Naqvi *et al.*⁶.

An association of the secondary nitrite maximum with the salinity maximum corresponding to the Persian Gulf water has been reported earlier⁴. This finding could not be confirmed in a recent study⁶. To examine the relative positions of these maxima in detail, the depths of the occurrence of maximum values of salinity, maximum values of secondary nitrite and minimum values of nitrate together with the depth of 26.6σ_t surface, representing the density level of the Persian Gulf water, are shown in Fig. 6, for the stations along sections I and IV, respectively. In some cases, the maxima in secondary nitrite and salinity are located close to each other, whereas in the others the 2 do not coincide. Furthermore, as seen from Figs 3 and 5, secondary nitrite maximum along the section V is much deeper than the depth where Persian Gulf water seems to be encountered (~300 m). From this, it can be deduced that the secondary nitrite maximum is not always associated with the Persian Gulf Water, and may occur over a wide depth and density ranges.

The nitrate minimum observed at intermediate depths of the northern Arabian Sea has been a subject of some discussion. Deuser *et al.*⁴ attributed it to the low original nitrate content of the Persian Gulf water, while others^{6,11} suggested that it may arise from a high rate of denitrification at these depths. As in the case of secondary nitrite maximum, the nitrate minimum and the Persian Gulf salinity maximum do not always coincide (Fig. 6). At some stations, 2 nitrate minima were observed. It should also be noted that the main flow of the Persian Gulf Water has been reported to occur east of 63°E long. and not along the west coast of India where it might appear in pockets¹⁶. Indeed, at st 222, no salinity maximum could be noticed corresponding to this water mass. Yet, the concentration of nitrate encountered at the minimum is the lowest and, as will be shown later, the denitrification is most intense at this station. Furthermore, as pointed out by Naqvi *et al.*⁶, the Arabian Sea high-salinity water which lies over the Persian Gulf Water, also has a shallow origin. Hence, the lower nitrate content of the Persian Gulf Water cannot be due to its shallow origin. These observations, therefore, suggest that a more likely

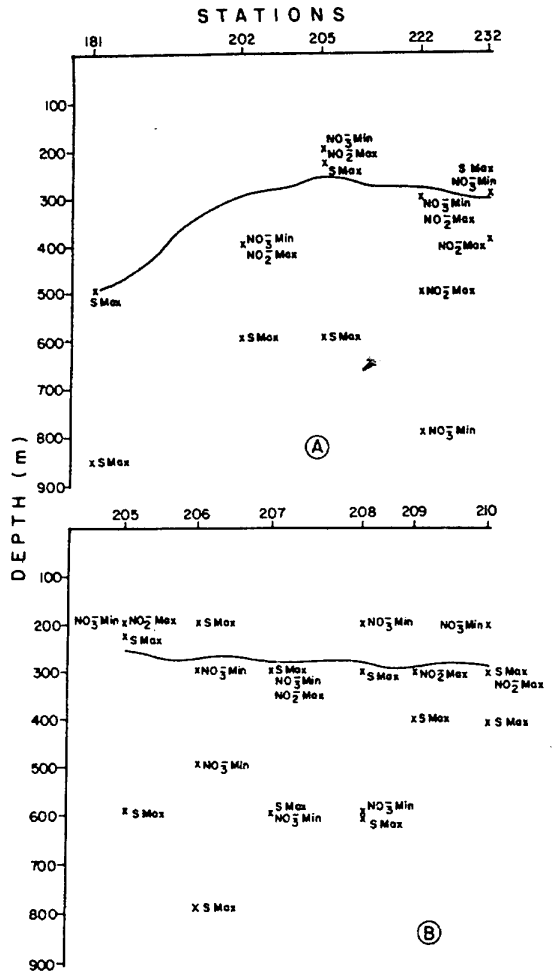


Fig. 6 - Depths of occurrence of maximum values of nitrite (NO₂⁻ Max), maximum values of salinity (S Max) and minimum values of nitrate (NO₃⁻ Min) along (A) section I and (B) section IV. (The contour represents the depth of 26.6σ_t surface)

origin of the nitrate minima appears to be a biochemical process rather than a physical phenomenon governing their origin⁴.

Computations of nitrate deficits require the estimation of original nitrate concentrations, i.e. the concentrations that would be expected if there were no denitrification. Two procedures have been followed in the Arabian Sea for such a computation. Deuser *et al.*⁴ calculated the original nitrate concentrations from the nitrate-salinity relationship for the Persian Gulf Water from the data obtained at 2 stations assumed to be outside the denitrification zone. This approach is based on the assumptions that denitrification is restricted to the Persian Gulf Water, and that this water mass has low original nitrate content because of

its shallow origin. These deductions are inconsistent with our results. Moreover, as pointed out by Naqvi *et al.*⁶, the 2 stations may be well within the denitrification zone. These factors to a large extent, might collectively affect the nitrate deficits as calculated by Deuser *et al.*⁴.

The procedure followed by Sen Gupta *et al.*⁵ involves the use of the relationships of apparent oxygen utilization (AOU) with nitrate and phosphate. They calculated the oxidative fraction of nitrate-nitrogen with the oxidative ratios and the 'reserved' fraction from the 'reserved' nitrate-'reserved' phosphate relationship derived for the region. Naqvi *et al.*⁶ modified this method by omitting the values corresponding to oxygen concentrations lower than 20 µg-at.l⁻¹ for the determination of apparent oxygen utilization (AOU)-NO₃ and (NO₃)_r-(PO₄)_r relationships. This was done to exclude the samples affected by denitrification, as it has been found that the denitrification may affect the slope of AOU-NO₃ regression line^{4,17}. The intercept of the (NO₃)_r-(PO₄)_r regression line so obtained was different from that obtained by Sen Gupta *et al.*⁵, while the slope value was almost the same. Naqvi *et al.*⁶ suggested that the high value of the intercept, presumably caused by the inclusion of values corresponding to very low oxygen concentrations, may result in slightly higher values of nitrate deficits. In the present study, the modified procedure has been followed for calculating the nitrate deficits.

AOU-NO₃-PO₄ relationships in the northern Indian Ocean are shown in Table 1. The value of ΔAOU/ΔPO₄ obtained by Naqvi *et al.*⁶ for the Arabian Sea is close to those reported for the Laccadive Sea, the Andaman Sea and the Bay of Bengal, but lower than the value for the northwestern Indian Ocean⁵ (Table 1). We have used this value for the calculations. The value for ΔAOU/ΔNO₃ used was 17.3 because of the reasons mentioned earlier. Using these oxidative ratios the nitrate anomaly (ΔN) has been calculated using the following equations:

$$\Delta N = (\text{NO}_3)_{\text{exp}} - (\text{NO}_3)_{\text{obs}} - (\text{NO}_2)_{\text{obs}} \quad \dots (1)$$

$$\text{where } (\text{NO}_3)_{\text{exp}} = (\text{NO}_3)_{\text{ox}} + (\text{NO}_3)_{\text{r}} \quad \dots (2)$$

$$(\text{NO}_3)_{\text{r}} = 13.7 (\text{PO}_4)_{\text{r}} - 8.9 \quad \dots (3)$$

$$(\text{NO}_3)_{\text{ox}} = \frac{\text{AOU}}{17.3} \quad \dots (4)$$

$$(\text{PO}_4)_{\text{r}} = (\text{PO}_4 - \text{P}) - (\text{PO}_4)_{\text{ox}} \quad \dots (5)$$

$$(\text{PO}_4)_{\text{ox}} = \frac{\text{AOU}}{248} \quad \dots (6)$$

Ammonia-nitrogen has not been included due to its low concentration.

The distribution of ΔN along the section I is given in Fig. 7. Positive values of ΔN are observed at all depths within the oxygen minimum layer (the depth range where oxygen concentration is lower than 0.1 ml.l⁻¹). The oxidative ratios, as calculated by Naqvi *et al.*⁶ and used in this study, are essentially applicable to the layer lying between the depths where there is a steep increase in AOU, and the depths where AOU is at its maximum. Also, these ratios and the (NO₃)_r-(PO₄)_r relationship used here may not be applicable to the region south of 11°N lat., the southern limit of observations of Naqvi *et al.*⁶. Negative values of ΔN were observed at all depths at st 181 (7°20'N; 70°40'E) indicating that the original or expected nitrate concentrations, as calculated from the Eq. (2), may be low for this area. Such a difference may arise from the errors in the calculations of (NO₃)_{ox} or (NO₃)_r, or from

Table 1—Relationships between Apparent Oxygen Utilization (AOU), Nitrate-Nitrogen and Phosphate-Phosphorus in the Northern Indian Ocean in the Layers between the Depths where a Steep Increase in AOU and AOU Maximum Occurs

[Numbers 1 to 5 refer to the sources from where ratios have been taken]

Relationship	Oxidative ratios (by atom ¹)				
	1	2	3	4	5
AOU-PO ₄	248	280	249	252	260
AOU-NO ₃	17.3*	17.5	19	18	21

* Values corresponding to oxygen concentration < 20 µg-at.l⁻¹ omitted.

1, The Arabian Sea north of 11°N lat.⁶; 2, the north-western Indian Ocean⁵; 3, the Laccadive Sea¹⁸; 4, the Andaman Sea²⁰, and 5, the western Bay of Bengal¹⁷.

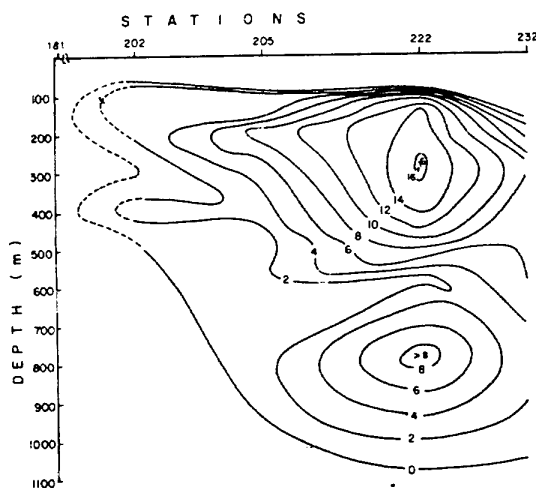


Fig. 7—Distribution of nitrate anomaly (ΔN, µg-at.l⁻¹) along section I

both. Variable oxidative ratios may introduce an error in the calculation of 'oxidative' nitrate and the 'reserved' nitrate concentrations in the southern region may be higher than those predicted by the Eq. (3). The latter effect is expected as the intermediate waters in the southern region will have a greater proportion of the water masses coming from higher latitudes and having an appreciably high 'performed' or 'reserved' nitrate than those formed at low and middle latitudes such as the Persian Gulf and the Red Sea waters.

Nitrate anomaly increases steadily towards north and large deficits in nitrate seem to occur in the northern Arabian Sea over a wide depth range (Fig. 7). Highest values of ΔN were observed at st 222, after which the values slightly decreased northward. Thus the denitrification appears to be most intense somewhere around 20°N lat., rather than in the northern most region. The minimum values of nitrate were associated with high values of ΔN , thus confirming the view that the nitrate minima originate directly due to the loss of nitrate by bacterial reduction. The depth range of nitrate reduction, as indicated in Fig. 7, decreases steadily southward, which is consistent with an increase in the oxygen concentration and a decrease in the thickness of the oxygen minimum layer (Fig. 4).

Sen Gupta *et al.*⁵ reported that denitrification in the Arabian Sea extends up to 4°N lat. whereas Deuser *et al.*⁴ suggested that the process may cease to occur at 14°N lat. Naqvi *et al.*⁶ have fixed the southern limit of denitrification at 11 or 12°N lat. This agrees very well with the deductions made in the present study. The possibility of small seasonal or yearly variations, caused by the differences in productivity and/or circulation, however, cannot be ruled out.

The highest value of ΔN noted in the present study was 16.5 $\mu\text{g-at.l}^{-1}$ at 294 m depth at st 222. For the same station Sen Gupta *et al.*⁵ calculated the maximum ΔN as 25 $\mu\text{g-at.l}^{-1}$. Naqvi *et al.*⁶ reported a maximum value of 9 $\mu\text{g-at.l}^{-1}$ along 15°N lat. using the same procedure. This value is comparable with the values determined in the present study. Against these reports, the results obtained by Deuser *et al.*⁴ appear to be too low. Judging from the values of ΔN , the denitrification in the Arabian Sea appears to be as intense as in the eastern tropical North Pacific^{1,18}. However, considerably higher values of nitrite in the

Arabian Sea than in the eastern tropical Pacific indicate that there are important differences in the intermediate stages of denitrification process in the 2 areas.

Naqvi *et al.*⁶ calculated the rate of denitrification in the Arabian Sea as 3.2×10^{12} g y⁻¹. This is based on an average value of the integrated nitrate anomaly as 3.114 g-at.m⁻² and an average residence time of 30 y for the layer in the Arabian Sea where denitrification occurs. This value represents about 5% of the annual global denitrification. The higher nitrate deficits observed in the northern Arabian Sea will tend to increase this value. However, despite the limitations and uncertainties inherent in such calculations, the estimate appears to be satisfactory.

References

- 1 Cline J D & Richards F A, *Limnol Oceanogr.* **17** (1972) 885.
- 2 Emery K O, Orr W L & Rittenberg S C, in *Essays in the natural sciences in honor of Captain Allan Hancock* (University of Southern California Press, Los Angeles) 1955, 299.
- 3 Holland H D, in *Proceedings of the Symposium on hydrogeochemistry and biogeochemistry*, Vol. 1 (the Clarke Company, Washington DC) 1973, 68.
- 4 Deuser W G, Ross E H & Mlodzinska Z J, *Deep-Sea Res.* **25** (1978) 431.
- 5 Sen Gupta R, Rajagopal M D & Qasim S Z, *Indian J mar Sci.* **5** (1976) 201.
- 6 Naqvi S W A, Noronha R J & Reddy C V G, *Deep-Sea Res.* **29** (1982) 459.
- 7 Dietrich G, Duing W, Grasshoff K & Koske P H, *Meteor Forschungsergebnisse*, 1966, Reihe A-No. 2.
- 8 Broenkow W W & Cline J D, *Limnol Oceanogr.* **14** (1969) 450.
- 9 Vaccaro R F & Ryther J H, *J Cons Int Explor Mer.* **25** (1960) 260.
- 10 Gilson H C, *Scientific Reports, John Murray Expedition 1933-1934*, **2** (1937) 21.
- 11 Lukashev Yu F, *Oceanology*, **20** (1980) 164.
- 12 Brandhorst W, *J Cons Int Explor Mer.* **25** (1959) 3.
- 13 Wooster W S, Chow T J & Barrett I, *J mar Res.* **23** (1965) 210.
- 14 Deuser W G, in *Chemical Oceanography*, Vol. 3, edited by J P Riley and G Skirrow (Academic Press, London) 1975, 1.
- 15 Carlucy A F & McNally P M, *Limnol Oceanogr.* **14** (1969) 736.
- 16 Varma K K, Kesava Das V & Gouveia A D, *Indian J mar Sci.* **9** (1980) 148.
- 17 Naqvi S W A, De Souza S N & Reddy C V G, *Indian J mar Sci.* **7** (1978) 15.
- 18 Codispoti L A & Richards F A, *Limnol Oceanogr.* **21** (1976) 379.
- 19 Sen Gupta R, Moraes C, Kureishy T W, Sankaranarayanan V N, Jana T K, Naqvi S W A & Rajagopal M D, *Indian J mar Sci.* **8** (1979) 215.
- 20 Sen Gupta R, Moraes C, George M D, Kureishy T W, Noronha R J & Fondecarr S P, *Indian J mar Sci.* **10** (1981) 228.