

## Chemical Oceanography of the Arabian Sea: Part VI—Relationship between Nutrients & Dissolved Oxygen in the Central Basin

S N DE SOUSA & S Y S SINGBAL

National Institute of Oceanography, Dona Paula, Goa 403 004

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Inorganic nitrate and phosphate relationships with apparent oxygen utilization (AOU) in the Central Arabian Sea were studied using data collected during 103 cruise of *R V Gveshani* (Feb. 1982). The consolidated ratio of  $\Delta\text{AOU}:\Delta\text{NO}_3:\Delta\text{PO}_4$  was 238:14.3:1. Using the ratio, a relationship between reserved phosphate and reserved nitrate was obtained. Vertical distribution of nutrients showed apart from the occurrence of primary and secondary nitrite maxima in the upper 500 m existence of tertiary nitrite maximum associated with lowering of oxygen concentrations in near-bottom waters. Relationships between reserved phosphate and reserved nitrate and  $\sigma_t$  were used to classify the water masses.

Chemical oceanographic studies<sup>1</sup> in the Arabian Sea concerned mostly with the distribution of different chemical constituents and not many attempts were made to study the quantitative relations between the nutrients and dissolved oxygen. In the present paper, relationships of phosphorus and nitrogen compounds with the dissolved oxygen in the water masses of Central Arabian Sea are presented.

### Materials and Methods

Fig. 1 shows position of stations occupied during the 103 cruise of *R V Gveshani* (Feb. 1982). Water samples from standard depths were collected using Niskin water samplers fixed on CTD rosette and alternatively water samples were also collected from hydrographic

casts using Nansen water samplers fitted with reversing thermometers. Subsamples were collected and analysed for salinity (using Autosol salinometer), dissolved oxygen<sup>2</sup>, phosphate<sup>3</sup>, nitrate<sup>4,5</sup> and nitrite<sup>6</sup>.

### Results and Discussion

Figs 2a and b show the isopycnals at 2 latitudinal sections respectively along 15° and 19°N while Fig. 3 shows the isopycnals along a NW-SE direction between sts. 2338 and 2381. The isopycnals in the depth range 200 to 1000 m run parallel to one another from E to W suggesting that the water masses which predominate in this depth range, namely, the Persian Gulf water and the Red Sea water have stabilized after reaching their respective density levels, the former with

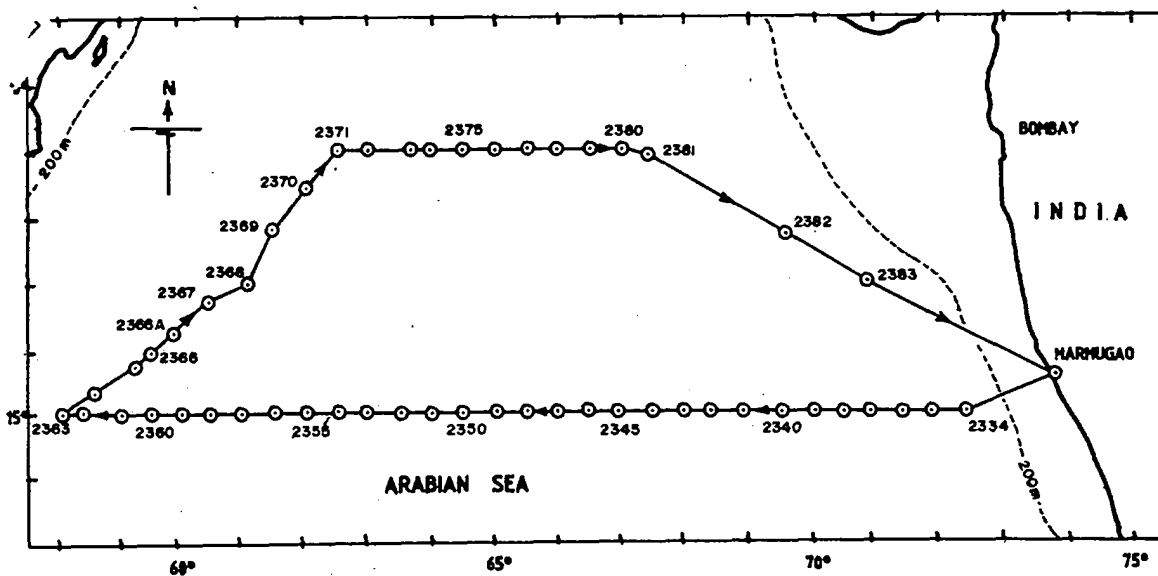


Fig. 1—Station locations

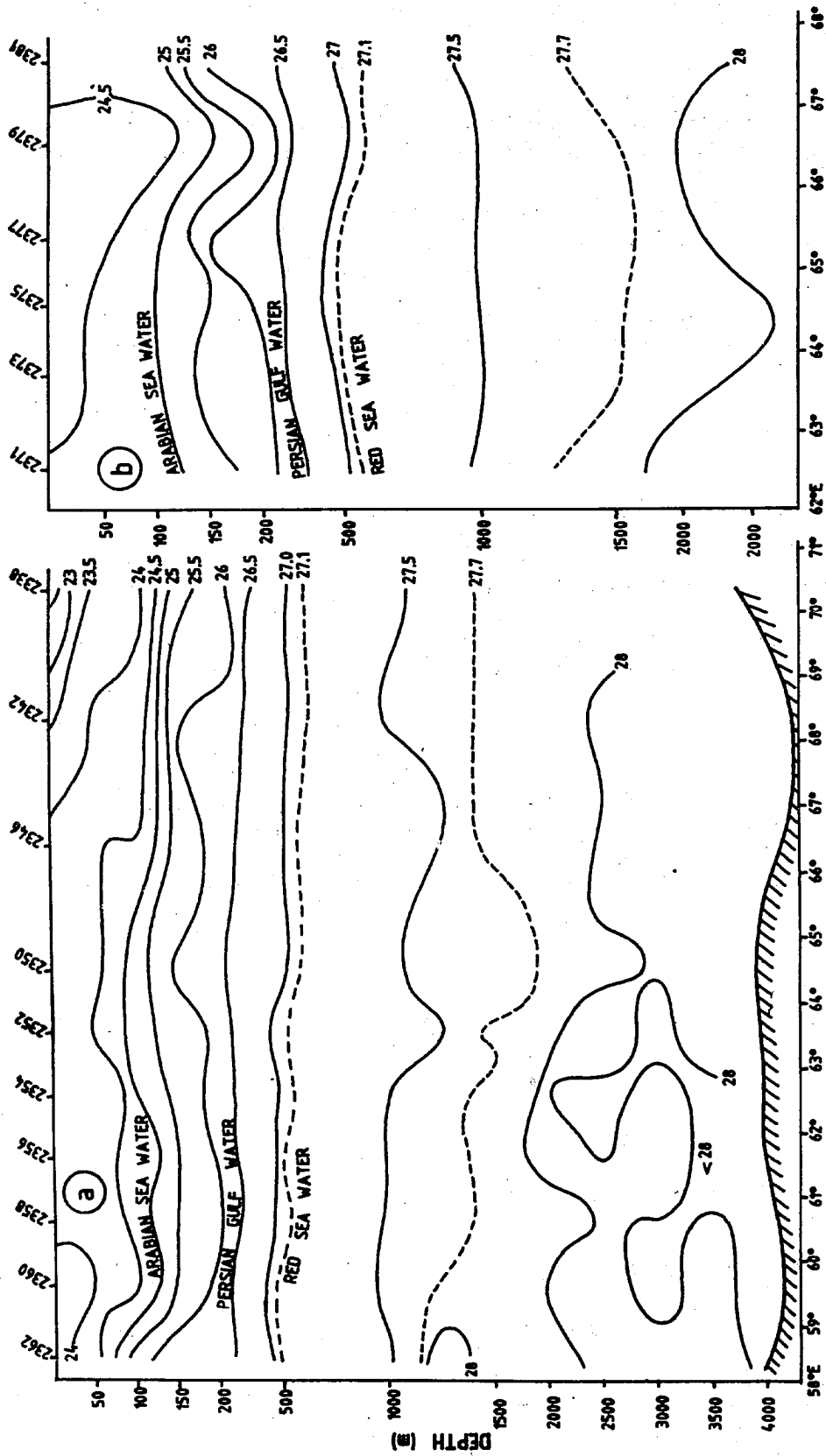


Fig. 2—Isopycnals at sections along 15°N (a) and 19°N (b)

$\sigma_t$  of 26.5 is observed at depths 200 to 300 m while the latter with  $\sigma_t$  of 27.1 occurs at the depths 500 to 600 m (Fig. 2). In the upper 200 m, however, the isopycnals slope towards deeper waters from N to S indicating downward movement of this water (Fig. 3). It is due to the sinking of the Arabian Sea high salinity water which is known to be forming<sup>1</sup> at the surface in the NE region and spreading in SW direction along 25  $\sigma_t$  density surface in the depth range 25 to 100 m.

Figs 4a and b show DO isopleths at the 2 latitudinal sections. In the upper 100 m or so the concentrations are high (4.5 to 5.5 ml. l<sup>-1</sup>). In this layer the isopleths slope downwards. This is due to the sinking of the high salinity surface water as it tries to reach its density level. Between 75 and 150 m DO concentration shows rapid decrease from 4.5 to 0.5 ml.l<sup>-1</sup>. A zone of very low DO concentrations (<0.5 ml.l<sup>-1</sup>) is observed between 150 and 1000 m. In the N this layer extends over the entire section (62°30' to 67°30'E) while in the S section it extends up to about 65°E. East of 65°E, DO concentrations at this depth range are somewhat higher (0.5 to 1 ml.l<sup>-1</sup>). A DO minimum layer showing extremely low concentration (<0.20 ml.l<sup>-1</sup>) is observed within the low oxygen zone. In the NE this layer is thick extending from 300 to about 1000 m, the thickness of the layer increasing from W to E (Fig. 4b). In the S, however, this DO minimum layer is thin extending from 200 to 400 m and from 61° to 62°20'E (Fig. 4a). Below 1500 m DO shows increasing concentrations towards the bottom.

Figs 5a and b show isopleths of phosphate along the 2 sections. It is observed that the vertical distribution of phosphate follows almost an opposite trend to that of DO especially in the upper 1000 m. In the upper 75 m phosphate concentrations are generally low (0.2 to 0.5  $\mu\text{g-at.l}^{-1}$ ) in the S section while in the N section it shows somewhat higher concentrations (0.85 to 1.7  $\mu\text{g-at.l}^{-1}$ ). However, at depths 75 to 150 m phosphate concentrations show rapid increase from 0.5 to 2  $\mu\text{g-at.l}^{-1}$  and from 1.7 to 2.9  $\mu\text{g-at.l}^{-1}$  respectively in S and N sections. Below these depths phosphate concentration increases slowly reaching a maximum of 3  $\mu\text{g-at.l}^{-1}$  and 3.9  $\mu\text{g-at.l}^{-1}$  respectively in these sections at about 1500 m.

Distribution of nitrate along S and N sections is shown by the isopleths in Figs 6a and b respectively. In the upper 50 m nitrate concentration is low varying from 0.38 to 4  $\mu\text{g-at.l}^{-1}$  in S section and increases slowly from the surface towards depth. The N section shows comparatively higher nitrate. From 50 to 150 m, nitrate shows steep concentration gradient increasing from 4 to 22  $\mu\text{g-at.l}^{-1}$  and thereafter it decreases slowly. A nitrate minimum zone with concentration decreasing from 22 to <16  $\mu\text{g-at.l}^{-1}$  is observed in Fig. 5a extending from 62°E to about 66°E in depths

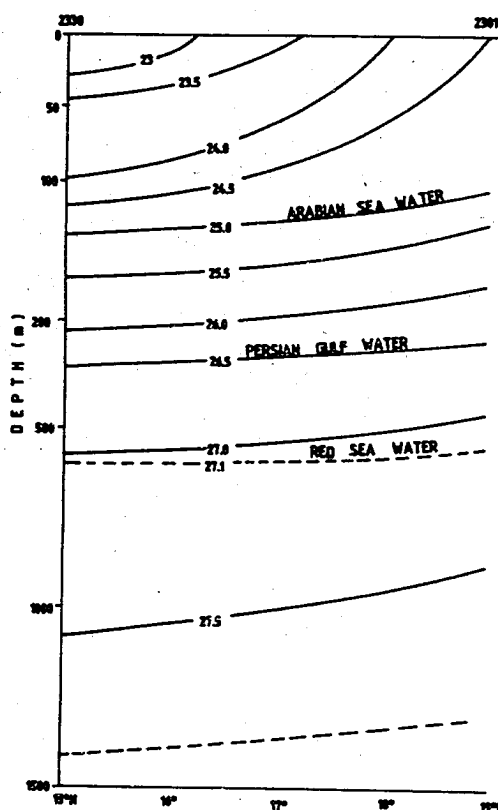


Fig. 3—Isopycnals at NW-SE section between sts 2338 and 2381

100 to 200 m. The N section, however, does not show any such minimum nitrate zone.

It is seen from Fig. 7 as reported earlier<sup>1</sup> that while dissolved oxygen concentration falls sharply in the depth range 75 to 100 m the concentrations of nitrate and phosphate show a rapid increase in the same depth range. Nitrite shows a primary maximum at 100 m at st 2354 (50 m at st 2377) and a secondary maximum of greater intensity at 200 m. The primary nitrite maximum is associated with the increasing concentration of nitrate and phosphate and a decreasing concentration of DO while the secondary nitrite maximum is associated with very low DO concentration and a decrease in nitrate concentration. Both nitrate and phosphate show maximum concentrations between 1500 and 2000 m. Another important feature observed from Fig. 7 is the presence of a 'tertiary nitrite maximum' at depths between 2000 and 3500 m. This tertiary nitrite maximum is also associated with a decreasing oxygen content.

It is reported that photosynthetic productivity in the Arabian Sea is higher than that in other oceanic areas<sup>7-10</sup>. High concentration of organic matter in the deeper layers, resulting from high photosynthetic activity at the surface depletes DO as a result of decay

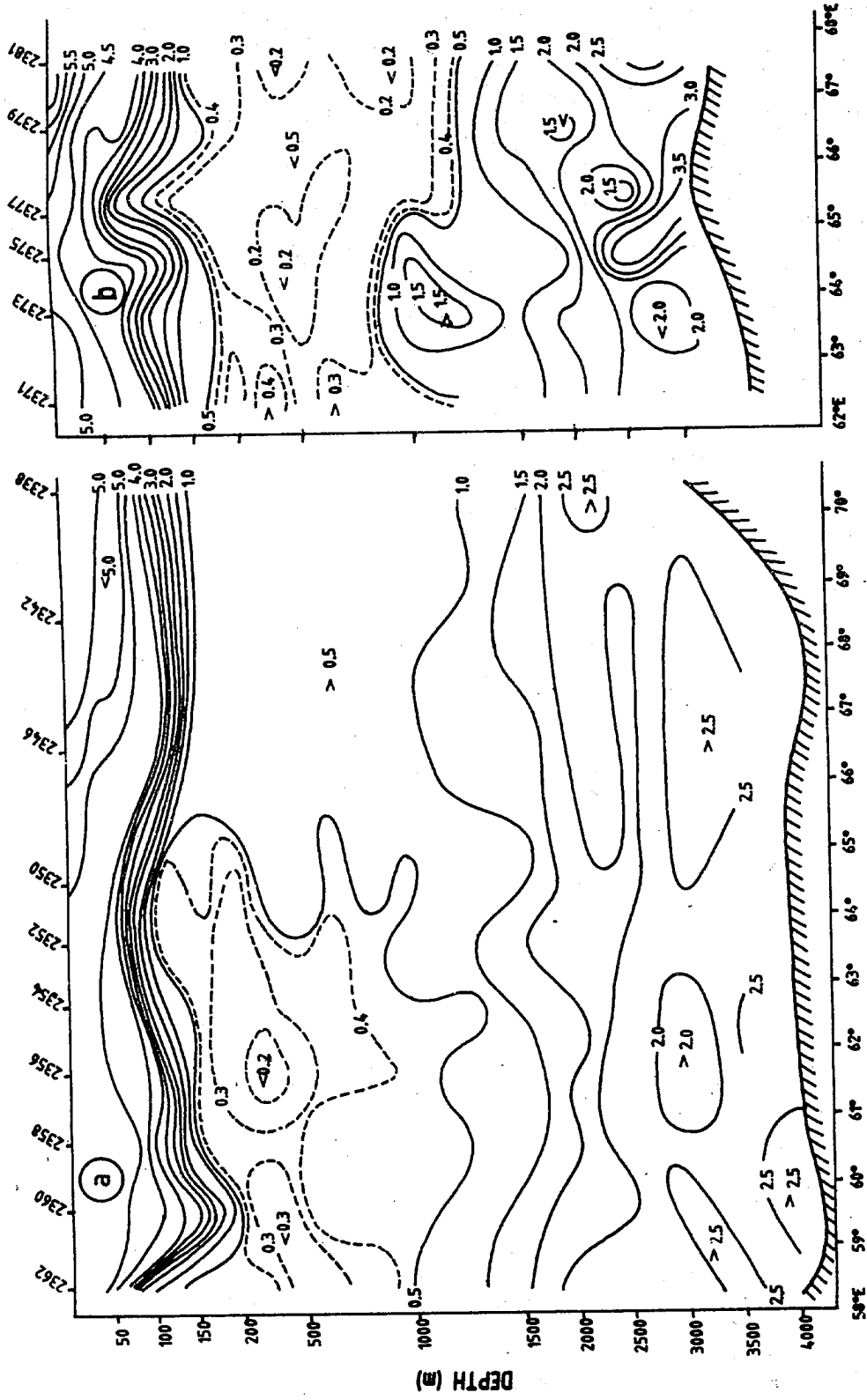


Fig. 4 - Isopleths of oxygen (ml. l<sup>-1</sup>) at 15°N (a) and 19°N (b) latitude sections

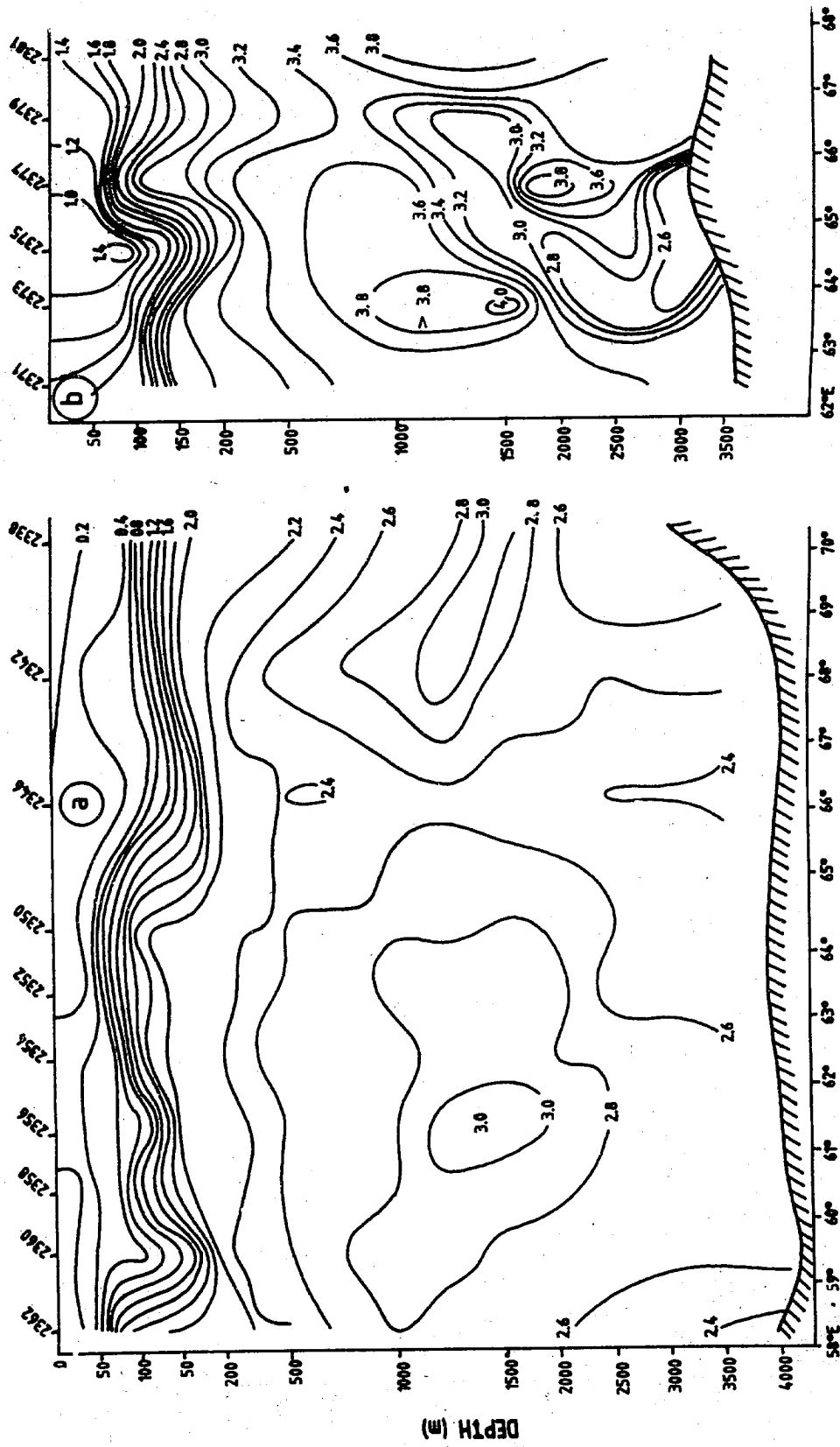


Fig. 5 - Isopleths of phosphate ( $\mu\text{g-at.l}^{-1}$ ) at  $15^{\circ}\text{N}$  (a) and  $19^{\circ}\text{N}$  (b) latitude sections

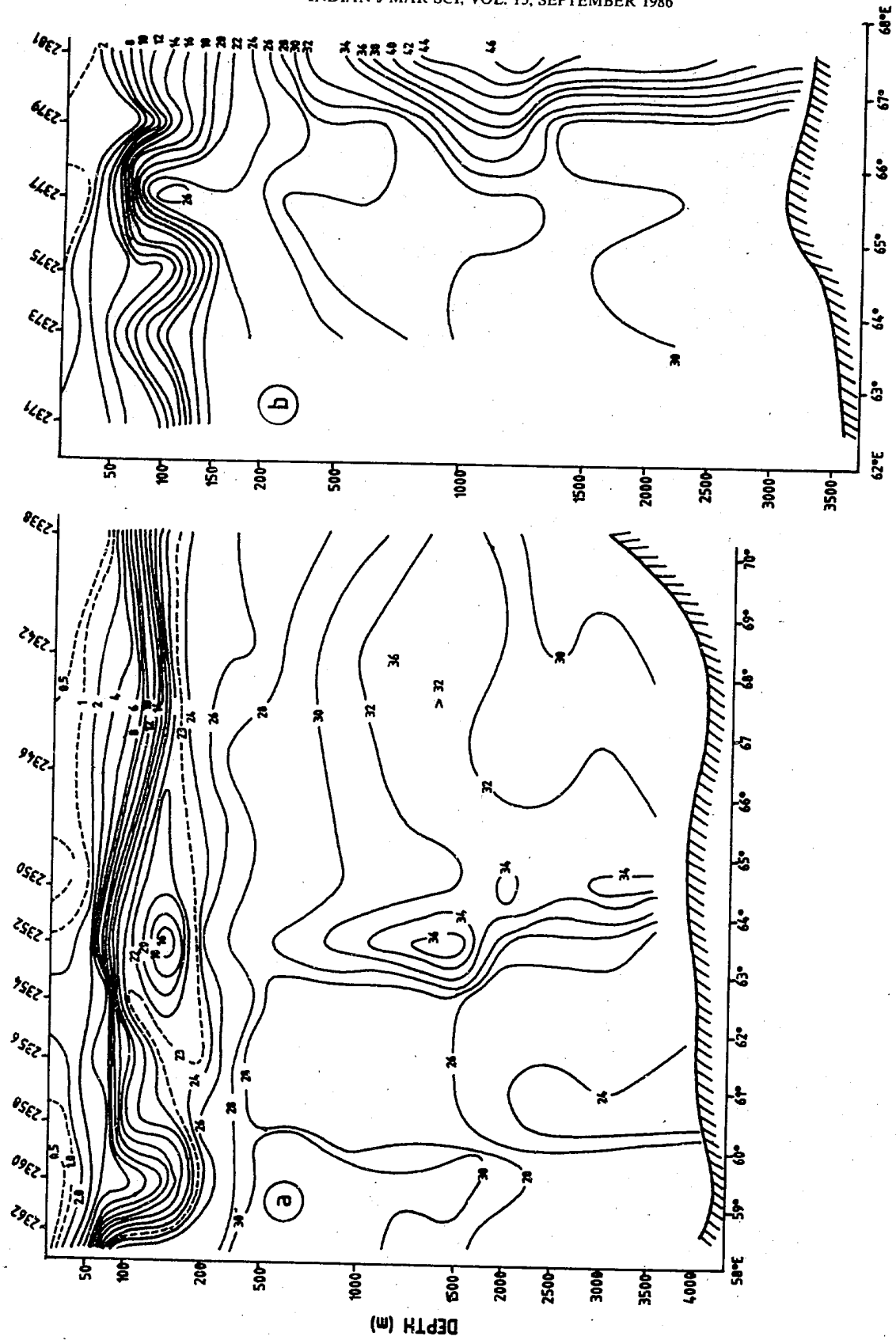


Fig. 6 - Isopleths of nitrate ( $\mu\text{g-at.l}^{-1}$ ) at  $15^\circ\text{N}$  (a) and  $19^\circ\text{N}$  (b) latitude sections

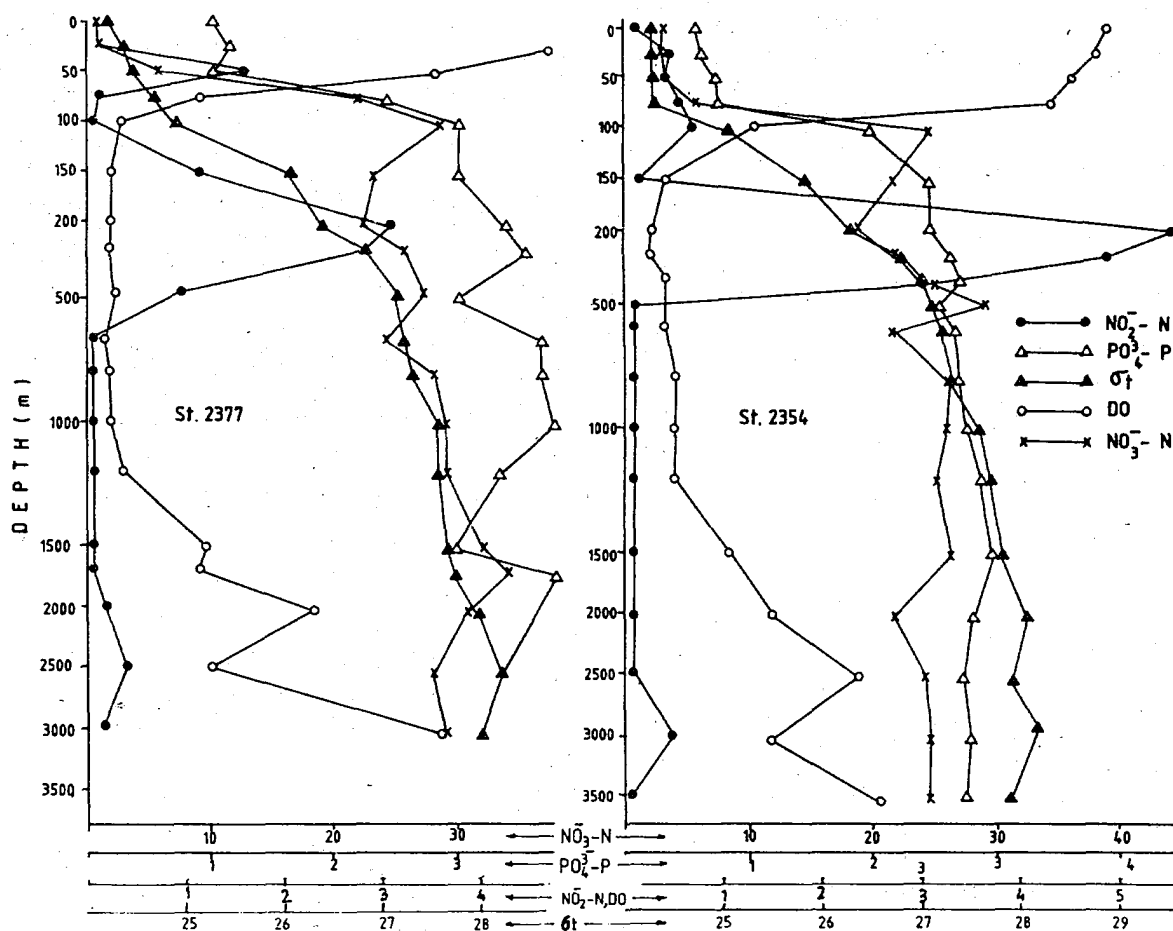


Fig. 7 - Vertical profiles of nitrate, nitrite, phosphate ( $\mu\text{g-at.l}^{-1}$ ) dissolved oxygen ( $\text{ml.l}^{-1}$ ) and  $\sigma_t$  at st 2354 and st 2377

and degradation. Simultaneously, with the mineralisation of organic matter, nitrate and phosphate are released to the water. The shallow nitrite maximum, thus, results from nitrification whereby ammonia released from the oxidation of organic matter is further oxidized. The secondary nitrite maximum, which is invariably associated with very low concentrations of DO and a decrease in nitrate concentration, is attributed to denitrification.

Sen Gupta *et al.*<sup>11</sup> have reported the presence of unoxidised or partially oxidised organic matter in deep waters up to 3000 m in the Bay of Bengal. Similar observations have been made<sup>12</sup> in the Arabian Sea during the 1st cruise of *R V Sagar Kanya* (monsoon of 1983). Fraga<sup>13</sup> has reported the presence of particulate and dissolved organic nitrogen at depths up to 4000 m in the western Arabian Sea. This is caused by the sinking of organic matter-organic detritus and faecal pellets to the deeper waters in undecomposed or partially decomposed state. In deeper waters in the

presence of higher concentration of dissolved oxygen the organic matter undergoes mineralization releasing inorganic nitrogen and phosphorus compounds. The mineralization of organic matter in near bottom waters is accompanied by the consumption of dissolved oxygen which shows a decrease in concentration at these depths (Fig. 7). The 'tertiary nitrite maximum' which is associated with the decrease in oxygen concentration probably appears as an intermediate product during the oxidation of organic matter in oxygen rich bottom waters which had earlier escaped mineralization in the upper layers due to insufficient amount of oxygen. Sen Gupta *et al.*<sup>11</sup> have estimated that in the Bay of Bengal the organic fractions of nitrogen and phosphorus constitute about 1/3 of their total concentrations between the depths 1000 and 3000 m.

*Relationship of phosphorus and nitrogen with apparent oxygen utilization*—Apparent oxygen utilization (AOU) =  $O_2' - O_2$ , where  $O_2$  is the observed

oxygen concentration and  $O_2$  is the solubility of oxygen in seawater of same salinity and at the same temperature, in equilibrium with atmosphere. In order to obtain a relationship between phosphate and AOU, all the observed phosphate values in the depth range 100 m to a depth of AOU maximum which varies between 1200 and 1500 m were plotted against the corresponding AOU values. The slope of the regression line gives the ratio of oxygen consumption to phosphate regeneration ( $\Delta AOU : \Delta PO_4$ ) as 238:1 by atoms with a correlation coefficient of ( $r$ ) 0.93. Similarly all the nitrate values in the same depth range were plotted against the corresponding AOU values, the slope of this regression line gives  $\Delta AOU : \Delta NO_3$  as 15.5:1 by atoms ( $r=0.84$ ), while a plot of nitrate against phosphate gives a slope  $\Delta NO_3 : \Delta PO_4$  as 14.3:1 ( $r=0.84$ ) by atoms. Combining these ratios the consolidated atomic ratio may be written as

$$\Delta AOU : \Delta NO_3 : \Delta PO_4 = 238 : 14.3 : 1 \quad \dots(1)$$

The theoretical value of the ratio  $\Delta AOU : \Delta PO_4$  given by Redfield *et al.*<sup>15</sup> is 276:1 by atoms. Sen Gupta *et al.*<sup>16</sup> reported a  $\Delta AOU : \Delta PO_4$  ratio of 270:1 for the northwestern Indian Ocean. However, the ratio obtained in the present case is close to the ratio 248:1 obtained by Naqvi *et al.*<sup>17</sup> for the eastern Arabian Sea. Cline and Richards<sup>18</sup> obtained low value 231:1 for the  $\Delta AOU : \Delta PO_4$  ratio in deep waters (>900 m) of eastern tropical North Pacific and suggested that the low ratio may indicate that phosphate has been released early in the decomposition of marine plankton. According to them it could also arise from low values of preformed phosphate. The ratio  $\Delta NO_3 : \Delta PO_4$  obtained in the present case (14.3:1) is lower than the ratio 16:1 reported by Sen Gupta *et al.*<sup>16</sup> for the northwestern Indian Ocean and the ratio 17.1:1 for the northern and eastern Arabian Sea<sup>19</sup>. However, it is close to 12.4:1 reported by Naqvi *et al.*<sup>17</sup> for eastern Arabian Sea.

Using the oxidative ratios  $\Delta AOU : \Delta PO_4$  and  $\Delta AOU : \Delta NO_3$ , it is possible to calculate that fraction of phosphate and nitrate which has resulted from the oxidation of organic matter. In the present study the oxidative phosphate and oxidative nitrate are given by:

$$PO_{4(ox)} = \frac{AOU}{238} \quad \dots(2)$$

and

$$NO_{3(ox)} = \frac{AOU}{15.5} \quad \dots(3)$$

while the reserved fractions of phosphate and nitrate, are given by:

$$PO_{4(r)} = PO_4 - \frac{AOU}{238} \quad \dots(4)$$

$$NO_{3(r)} = NO_3 - \frac{AOU}{15.5} \quad \dots(5)$$

When the reserved fractions of phosphate, obtained using Eq. 4, were plotted against the reserved nitrate values, calculated using relation (5), the following relationship is obtained:

$$(NO_3)_r = 13.71 (PO_4)_r + 0.016 \quad \dots(6)$$

The slope of the regression line in Eq. 6 (13.71) is similar to the value of 13.7 reported by Naqvi *et al.*<sup>17</sup> for the eastern Arabian Sea, and 12.2 obtained by Sen Gupta *et al.*<sup>16</sup>. Similar values are reported for the waters off Peru<sup>20</sup> and eastern tropical North Pacific<sup>18</sup>.

The ratio  $\frac{(\Delta NO_3)_r}{(\Delta PO_4)_r} = 13.71$  given by Eq. 6 is very close to the ratio  $\frac{\Delta NO_3}{\Delta PO_4} = 14.3$  in the present study. The

intercept 0.016 obtained presently is close to the intercept  $-1.7$  reported by Sen Gupta *et al.*<sup>16</sup>. However, it is much higher than  $-8.9$  reported by Naqvi *et al.*<sup>17</sup>. The relation between  $(PO_4)_r$  and  $(NO_3)_r$  given by Naqvi *et al.*<sup>17</sup>, i.e.

$$(NO_3)_r = 13.7 (PO_4)_r - 8.9$$

implies that for all values of  $(PO_4)_r < 0.65 \mu\text{g-at.l}^{-1}$  [most of the  $(PO_4)_r$  values lie in this range], the corresponding values of  $(NO_3)_r$  will be negative, and at  $(PO_4)_r = 0.65 \mu\text{g-at.l}^{-1}$  the  $(NO_3)_r$  will be zero, thus giving very low values of  $(NO_3)_r$  for relatively high values of  $(PO_4)_r$ . Moreover, the significance of negative  $(NO_3)_r$  values, which are unrealistic, is not understood. We feel that the intercept given by Naqvi *et al.*<sup>17</sup> is too low and might have affected their calculation of nitrate anomaly.

Eq. 6 can be used to calculate values of reserved nitrate  $(NO_3)_r$  corresponding to reserved phosphate  $(PO_4)_r$  values in areas where denitrification occurs and which in turn can be used to compute nitrate deficits ( $\Delta N$ ).

$$\Delta N = (NO_3)_{exp} - [(NO_3) + (NO_2)]_{obs} \quad \dots(7)$$

where  $(NO_3)_{exp}$  is the amount of nitrate expected to be present in the water sample before denitrification sets in while  $[(NO_3) + (NO_2)]_{obs}$  is the measured amount of nitrate + nitrite in the same sample. The expected nitrate  $(NO_3)_{exp}$  is given by

$$(NO_3)_{exp} = (NO_3)_{ox} + (NO_3)_r \quad \dots(8)$$

where  $(NO_3)_{ox}$  is the nitrate from oxidative origin given by Eq. 3 and  $(NO_3)_r$  is the reserved nitrate given by Eq. 6. Values of  $\Delta N$  were computed using Eq. 7 in conjunction with Eqs 3 and 6. Maximum nitrate



anomaly  $\Delta N$  of  $11.9 \mu\text{g-at.l}^{-1}$  is observed at st. 2352 where the nitrate showed a drop in concentration (Fig. 6a). It is, however, interesting to note that no secondary nitrite maximum was observed at this station suggesting that nitrite is a transient stage and that the reduction of nitrate proceeds beyond this stage. Cline and Richards<sup>18</sup> studying the denitrification in the eastern tropical North Pacific observed low concentrations of nitrite associated with very low concentrations of oxygen.

Comparison of Figs 4 a and 6a shows that high nitrate reduction occurs at relatively higher oxygen concentrations, which according to Cline and Richards<sup>18</sup> may have been caused by vertical mixing of oxygenated waters at the boundaries, or analytical uncertainties, or both.

*Relationship between density ( $\sigma_t$ ) and reserved fractions of nitrate and phosphate*—Water masses can be identified based on the relationships between nutrient and density<sup>21</sup>. In the present study, reserved fractions of nitrate and phosphate were plotted against  $\sigma_t$  assuming that these properties are characteristic of different water masses. Water in the depth range 100 to 175 m having  $\sigma_t$  between 24 and 25.75 has  $(\text{PO}_4)_r$  and  $(\text{NO}_3)_r$  varying widely from 0.3 to  $0.57 \mu\text{g-at.l}^{-1}$  and from 2.7 to about  $6 \mu\text{g-at.l}^{-1}$  respectively. This water largely includes Arabian Sea High Salinity Water, whereas the water in the depth range 176-300 m is characterized by a narrow range of  $\sigma_t$  varying from 26 to 26.85, and low reserved phosphate varying from 0.35 to  $0.5 \mu\text{g-at.l}^{-1}$ , while the reserved nitrate varies widely from 2 to  $6 \mu\text{g-at.l}^{-1}$ . This water mass consists mostly of Persian Gulf Water. Water in the depth range 301 to 450 m has a  $\sigma_t$  varying from 26.75 to 27 and reserved phosphate and reserved nitrate varying from 0.3 to 0.5 and from 3.5 to  $6.2 \mu\text{g-at.l}^{-1}$  respectively. Water in the depth range 451 to 600 m, which largely includes Red Sea water, is characterized by  $\sigma_t$  varying between 26.95 and 27.25 and relatively higher reserved phosphate ranging from 3 to  $7.5 \mu\text{g-at.l}^{-1}$  while the reserved nitrate fraction also is high varying between 4.5 and  $8.5 \mu\text{g-at.l}^{-1}$ . Water between 600 and 1000 m has  $\sigma_t$  varying between 27.25 and 27.6 with reserved phosphate and nitrate concentrations of

almost the same order as the water mass immediately above it. Water at depths greater than 1000 m with  $\sigma_t$  between 27.5 and 28 and having concentration of phosphate varying widely from 0.25 to  $0.95 \mu\text{g-at.l}^{-1}$  and steeply increasing concentration of reserved nitrate ranging between 4.5 and  $12.5 \mu\text{g-at.l}^{-1}$  has probably Antarctic origin and is termed North Indian Ocean deep water which is characterized by high dissolved oxygen  $(\text{PO}_4)_r$  and  $(\text{NO}_3)_r$  and low temperature.

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