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*Nitrite Distribution in Peru Current Waters*¹

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ABSTRACT

Studies of the nitrite-nitrogen distribution off the western coast of South America have shown significant concentrations in surface waters (up to $0.5 \mu\text{g-at/l}$) and a widespread primary maximum near the top of the thermocline. Below the surface layer, where the oxygen minimum contains less than 0.2 ml/l of dissolved oxygen, a secondary maximum was present south of 10°S , within 1000 km of the coast. Concentrations greater than $3 \mu\text{g-at/l}$ were observed at nine stations. The secondary maximum was associated with rather narrow limits of specific volume, but the vertical samples were too far apart to permit an adequate description of this maximum. The highest concentrations tended to occur off southern Peru and northern Chile and were closely related to the salinity maximum of the Peru-Chile Undercurrent.

Introduction. In the remineralization of organic nitrogen compounds in the sea, nitrite has been recognized as an intermediate between ammonia and nitrate. A convenient method for determining nitrite has been available for many years, and numerous measurements have been made. In most regions of the open ocean, little or no nitrite can be detected at the surface or in deep water, but significant concentrations are commonly observed near the bottom of the surface layer. This "primary" maximum has been attributed to ammonia oxidation in decomposing organic matter; however, it may also be due to the extracellular release of nitrite accompanying the assimilation of nitrate-nitrogen by marine phytoplankton (Vaccaro and Ryther 1959).

The presence of a deeper "secondary" nitrite maximum was first observed by Gilson (1937) at several stations in the Arabian Sea; these observations were made during the JOHN MURRAY Expedition in 1933-1934. Gilson did not attempt to explain the presence of this maximum (with concentrations up to $7.4 \mu\text{g-at NO}_2\text{-N/l}$), nor did he emphasize its relation to the low concentration of dissolved oxygen at the same depths.

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Brandhorst (1959), in a study of nitrite distribution in the eastern tropical Pacific, found the primary maximum to be present throughout the area in close association with the layer of highest vertical stability. Nitrite concentrations as high as $1.45 \mu\text{g-at NO}_2\text{-N/l}$ were observed. Within part of this region, the water below the thermocline contains an extremely low concentration of dissolved oxygen (less than 0.1 ml/l , or less than 2% of saturation); here was found a secondary nitrite maximum with concentrations up to $2.52 \mu\text{g-at NO}_2\text{-N/l}$. Brandhorst attributed this maximum to nitrate reduction in the prevailing quasianaerobic conditions.

In view of the association of the secondary nitrite maximum with the near absence of dissolved oxygen in the region west of Central America, where Brandhorst's observations were made, it seemed desirable to examine the region south of the equator, where a similar pool of low-oxygen water has been reported off the coast of Peru (Wooster and Cromwell 1958). This paper reports the results of observations made in October 1960 during the STEP-I Expedition of the University of California's Scripps Institution of Oceanography.

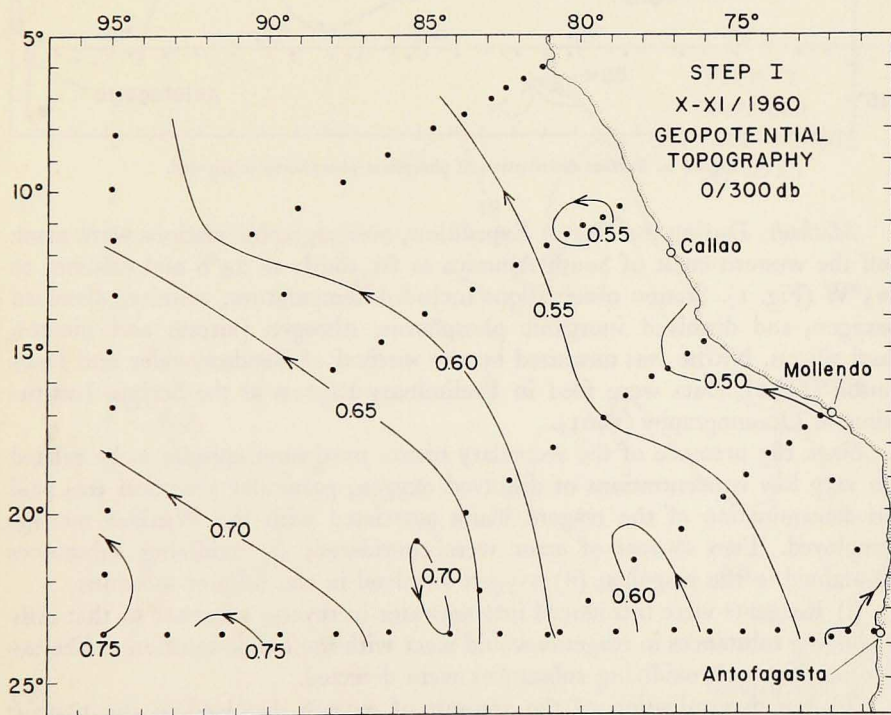


Figure 1. Geopotential topography, 0/300 db, in dynamic meters. Thermosteric anomaly used rather than specific-volume anomaly. Dots show positions of oceanographic stations.

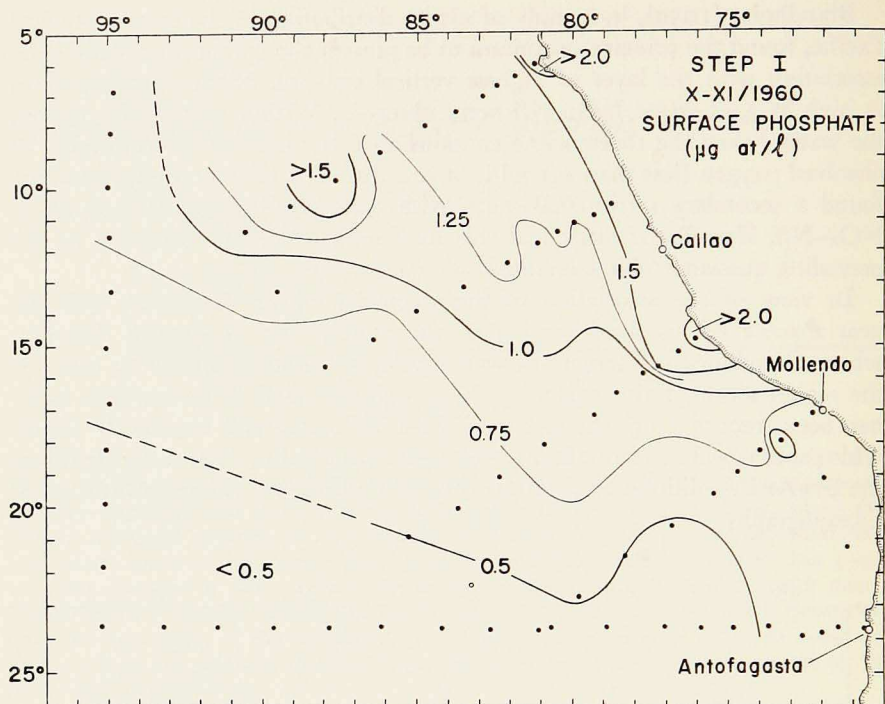


Figure 2. Surface distribution of phosphate-phosphorus in $\mu\text{g-at/l}$.

Methods. During the STEP-I Expedition, oceanographic stations were made off the western coast of South America as far south as 24°S and offshore to 95°W (Fig. 1). Station observations included temperature, salinity, dissolved oxygen, and dissolved inorganic phosphorus, nitrogen (nitrate and nitrite), and silicon. Nitrite was measured by the method of Bendschneider and Robinson (1952). Data were filed in Preliminary Reports at the Scripps Institution of Oceanography (1961).

Since the presence of the secondary nitrite maximum appears to be related to very low concentrations of dissolved oxygen, particular attention was paid to determination of the reagent blank associated with the Winkler method employed. Two sources of error were considered: (i) oxidizing substances contained in the reagents; (ii) oxygen dissolved in the reagent solutions.

(i) Reagents were introduced into seawater in reverse sequence so that only oxidizing substances in reagents would react with the iodide solution to liberate iodine. No such oxidizing substances were detected.

(ii) For determination of the amount of oxygen dissolved in the reagent solutions, several liters of seawater were collected from the low-oxygen water off Callao. A series of ten aliquots of 250 ml was then treated with various

amounts of reagent solutions and the total dissolved-oxygen content determined (Table I). The reagent blank was about 0.02 ml/l — somewhat smaller than the value of 0.08 ml/l reported by Brandhorst (1959).

Surface Observations. The circulation at the time of the STEP-I Expedition has been discussed by Wooster and Gilmartin (1961) and Wyrski (1963). The general picture of weak north-westward flow at the surface is illustrated by the

TABLE I. REAGENT BLANK OF DISSOLVED OXYGEN DETERMINATION.

Reagent solutions added, ml			Total dissolved oxygen†
KOH + KI	MnSO ₄	H ₂ SO ₄	ml/l
0.10	0.10	1.00	0.08
0.10	0.25	1.00	0.07
0.10	0.50	1.00	0.08
0.25	0.25	1.00	0.09
1.00*	1.00	1.00	0.10
1.00*	1.00	1.00	0.10
2.50	0.10	2.50	0.14
2.50	0.10	2.50	0.12
5.00	5.00	5.00	0.18
5.00	5.00	5.00	0.18

† Includes oxygen dissolved in seawater (0.08 ml/l) in this case) plus that dissolved in reagents.

* Volumes of reagents used in routine determinations.

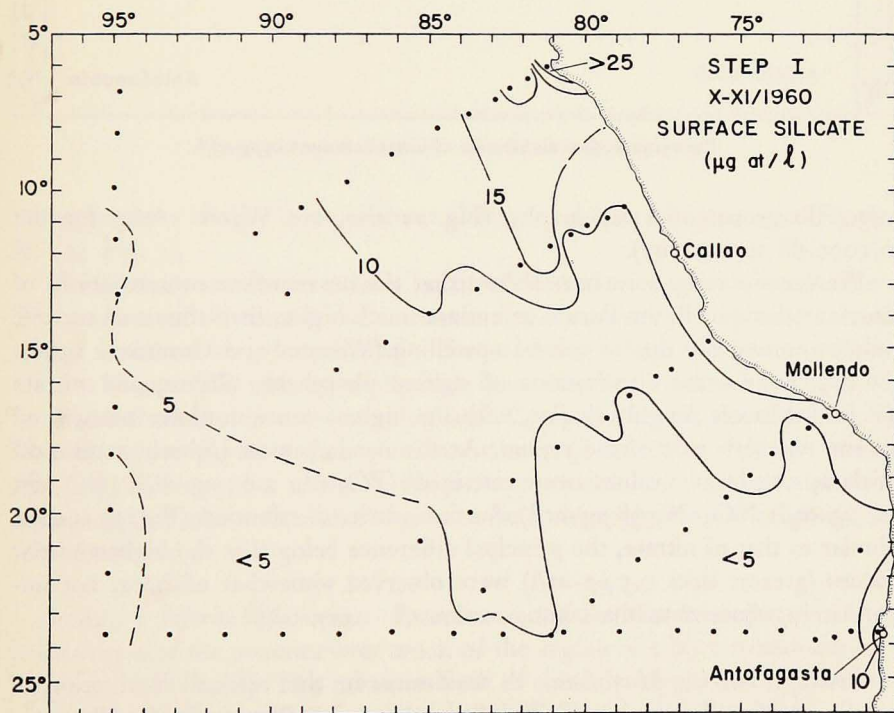


Figure 3. Surface distribution of silicate-silicon in $\mu\text{g-at/l}$.

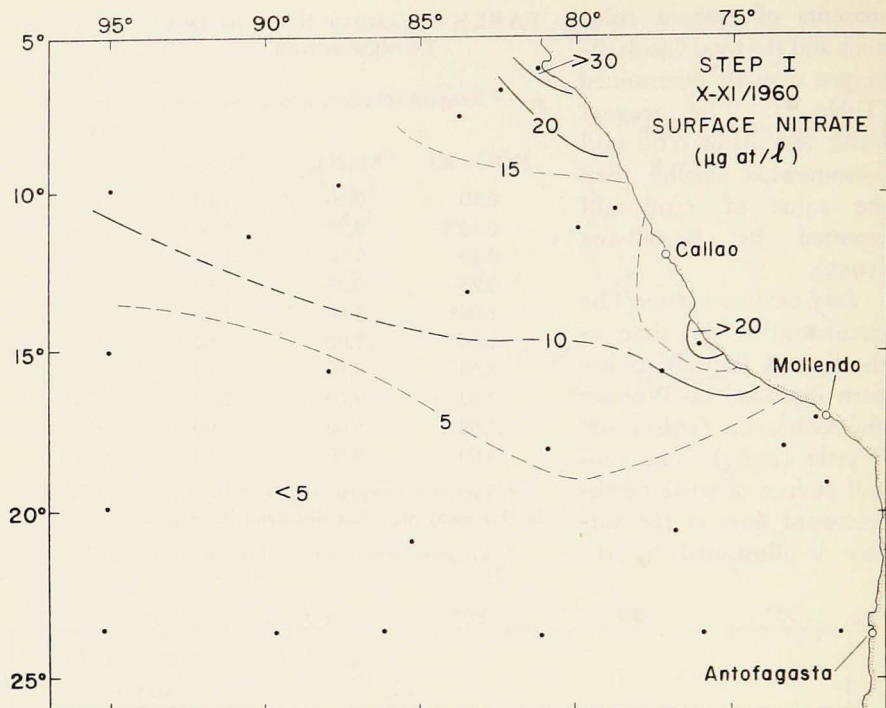


Figure 4. Surface distribution of nitrate-nitrogen in $\mu\text{g-at/l}$.

o/300 db geopotential topography (Fig. 1; also, see Wyrтки 1963 for the o/1000-db topography).

Previous investigations have shown that the near-surface concentrations of nutrient elements in the Peru Current are much higher than the usual oceanic values, presumably due to coastal upwelling (Wooster and Cromwell 1958). During STEP-I the distributions of surface phosphate, silicate, and nitrate (Figs. 2-4) were roughly similar, with the highest concentrations inshore and in the northern part of the region. At the northernmost inshore station, off Talara, maximum values were attained ($\text{PO}_4\text{-P}$, $2.05 \mu\text{g-at/l}$; $\text{SiO}_3\text{-Si}$, $28 \mu\text{g-at/l}$; $\text{NO}_3\text{-N}$, $38 \mu\text{g-at/l}$). Surface nitrite distribution (Fig. 5) is most similar to that of nitrate, the principal difference being that the highest nitrite values (greater than $0.5 \mu\text{g-at/l}$) were observed somewhat offshore, not immediately adjacent to the coast.

Primary Nitrite Maximum. A maximum in the vertical distribution of nitrite was found at almost all stations in the region (Fig. 6: St. 6). However, at six offshore stations in the northwest, nitrite was relatively high and uniform

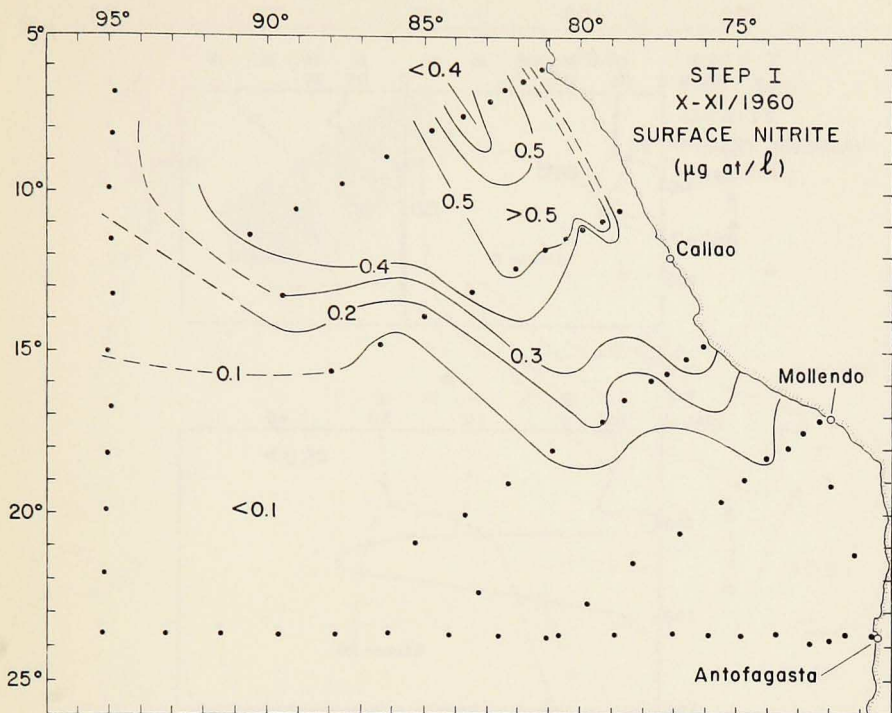


Figure 5. Surface distribution of nitrite-nitrogen in $\mu\text{g-at/l}$.

throughout the surface layer, without a clear maximum being present (Fig. 6: St. 12; Fig. 7).

The primary maximum usually occurred near the top of the thermocline. The horizontal distribution of nitrite in the maximum (Fig. 7) was related to that at the surface, the principal difference being a large offshore area (centered at about 16°S) with especially high concentrations, in which is imbedded the highest value observed— $2.25 \mu\text{g-at/l}$. Comparison with the distributions of surface chlorophyll *a* and zooplankton volumes (Forsbergh and Joseph 1964: figs. 3, 7) indicates that nitrite in the primary maximum is high (greater than $0.5 \mu\text{g-at/l}$) in about the same regions where chlorophyll *a* and zooplankton volumes are high.

Secondary Nitrite Maximum. Examination of the dissolved-oxygen distribution revealed the presence over much of the region of a layer containing less than 0.2 ml/l (Fig. 8). The northern limit of this low-oxygen pool appears to be $2\text{--}3^{\circ}\text{S}$ (Wooster and Cromwell 1958). The vertical extent of the layer decreases with increasing distance offshore, from 300 to 500 m nearshore to

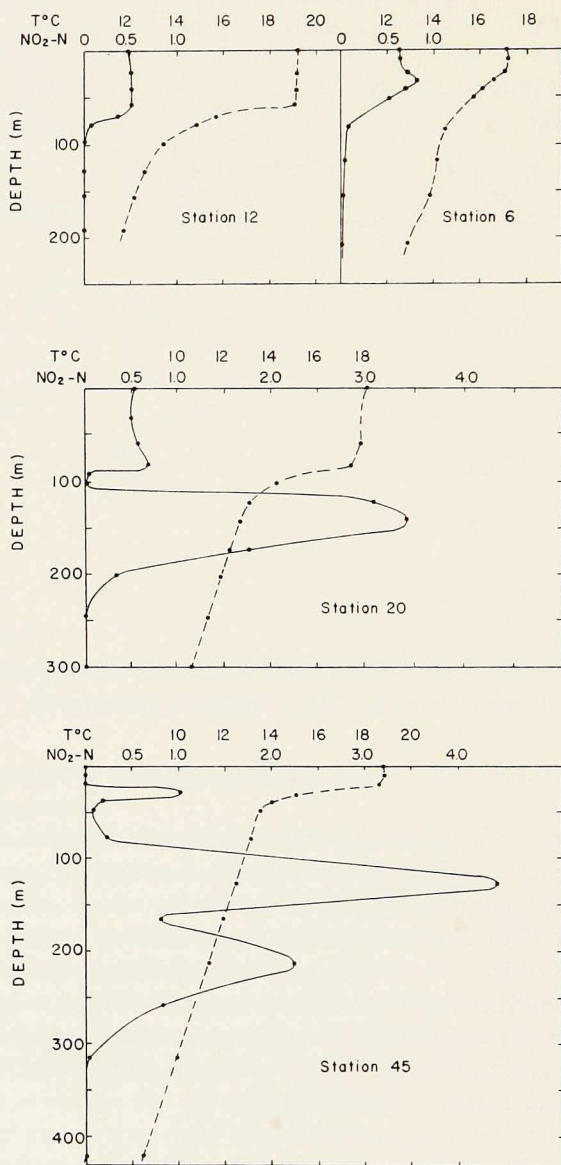


Figure 6. Vertical distribution of nitrite-nitrogen ($\mu\text{g-at/l}$), solid line, and temperature ($^{\circ}\text{C}$), dashed line, at selected stations:

St. 6— $6^{\circ}23'S$, $81^{\circ}54'W$; St. 12— $9^{\circ}47'S$, $87^{\circ}39'W$; St. 20— $12^{\circ}25'S$, $82^{\circ}08'W$; St. 45— $17^{\circ}34'S$, $72^{\circ}52'W$.

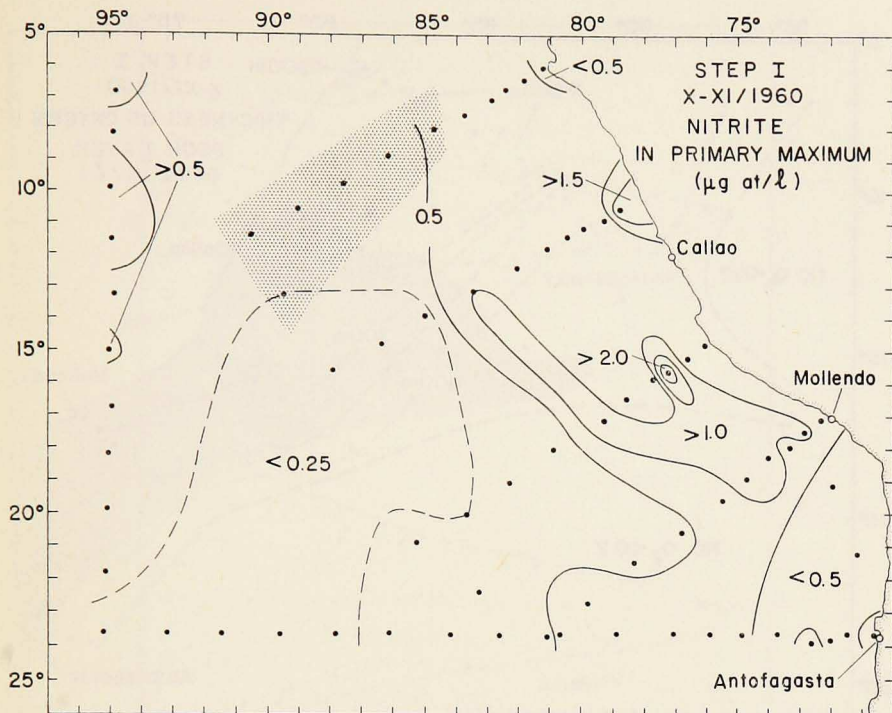


Figure 7. Horizontal distribution of nitrite-nitrogen ($\mu\text{g-at/l}$) in primary maximum. Shaded area includes stations with relatively high surface-layer concentrations but no clear-cut maxima.

less than 100 m at 500 km or more offshore. At the same time, the depth of the top of the layer increases offshore from 50 to 100 m near the coast to more than 200 m at 500 km or more offshore.

The secondary nitrite maximum was observed only within the upper half of this oxygen-poor layer, and there, only south of about 10°S (Fig. 8). The highest nitrite concentration observed was $9.04 \mu\text{g-at/l}$ at St. 30 ($16^{\circ}27'\text{S}$, $78^{\circ}38'\text{W}$). If this unusual station is excluded, the highest value was $4.66 \mu\text{g-at/l}$, with concentrations greater than $3 \mu\text{g-at/l}$ at nine stations (Fig. 6: St. 20). The depth of the maximum ranged from 67 m to 257 m, being less than 100 m on several stations near shore and greater than 200 m at the stations farthest offshore.

Significant concentrations of nitrite within the secondary maximum are restricted to narrow limits of temperature, salinity, and specific volume (Fig. 9). More than three-quarters of the observations, including all greater than $1.2 \mu\text{g-at/l}$, fall within the following limits: temperature, $11.0\text{--}13.5^{\circ}\text{C}$; salinity, $34.75\text{--}34.95\text{‰}$; thermobaric anomaly, $140\text{--}180 \text{ cl/ton}$. The highest values occur at about 12.3°C , 34.85‰ , 160 cl/ton .

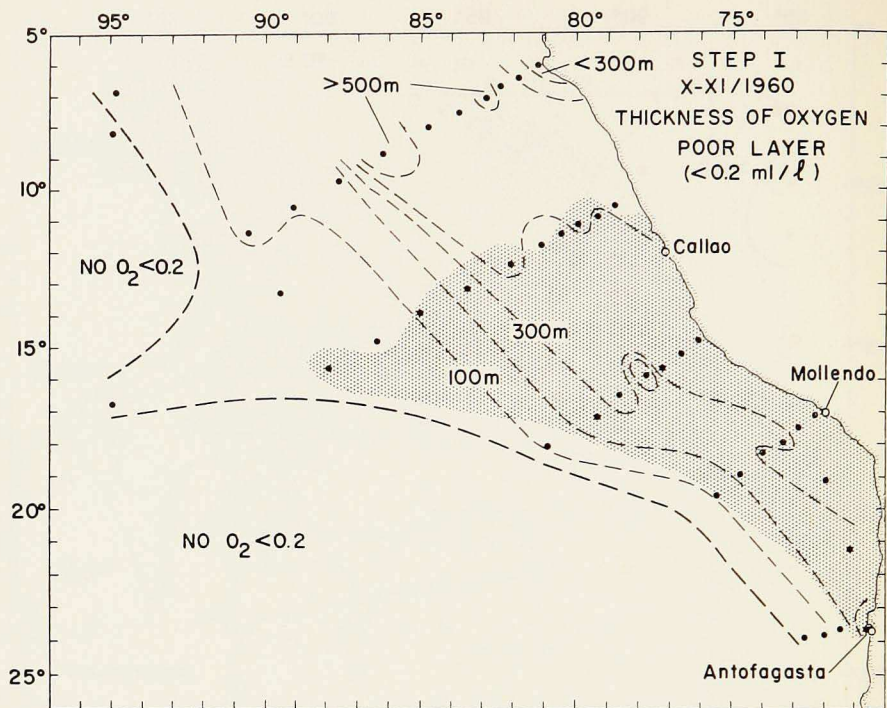


Figure 8. Thickness of layer containing less than 0.2 ml/l of dissolved oxygen. Shaded area includes all stations where secondary nitrite maximum was observed.

Characteristically, the vertical gradient of thermosteric anomaly near the secondary nitrite maximum is 2–5 cl/ton per 10 m, although values several times greater are observed above shallow nearshore maxima. If we take 4 cl/ton per 10 m as a representative value for the gradient, more than three-quarters of the significant nitrite values fall within a 50-m depth range. Thus, it is difficult to describe the maximum adequately unless sampling bottles are spaced much more closely than is customary, and the nonsystematic horizontal distribution of concentrations in the maximum may be attributed to inadequate sampling.

Because of this problem it is difficult to use the STEP-I data to portray the horizontal distribution of nitrite in the secondary maximum. There does appear to be an increase toward the south; all but two of the concentrations greater than $3.5\ \mu\text{g-at/l}$ were found south of Mollendo, and these high concentrations occurred at six of the nine southeastern stations where the secondary maximum was observed. It is also interesting to note that at six inshore stations south of Callao there is a double maximum in the low-oxygen layer (Fig. 6: St. 45) or high values of nitrite at several depths over a depth range of

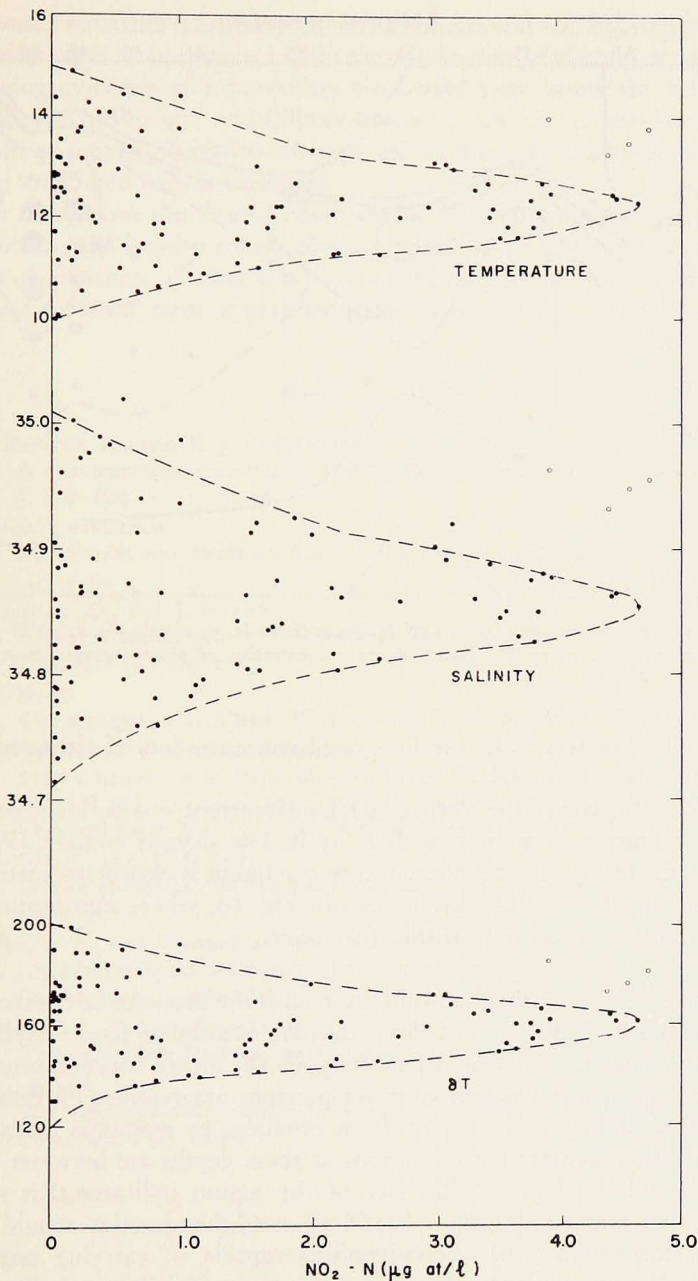


Figure 9. Nitrite-nitrogen in the secondary maximum as a function of temperature ($^{\circ}\text{C}$), salinity (‰), and thermocline anomaly (cl/ton). Dashed lines enclose most values; values for St. 30 are indicated by circles.

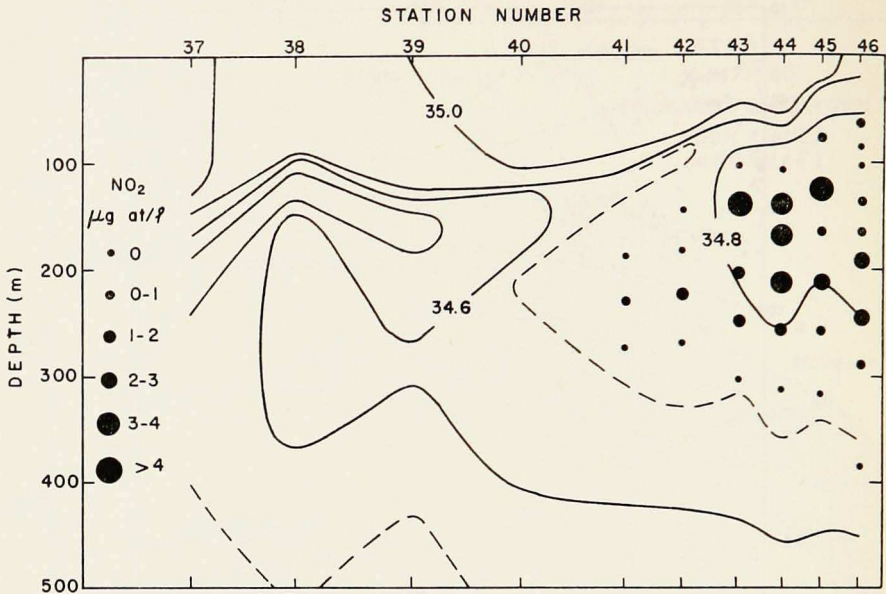


Figure 10. Salinity distribution on profile off Mollendo (from St. 37 at $23^{\circ}45'S$, $81^{\circ}07'W$ to St. 46 at $17^{\circ}12'S$, $72^{\circ}19'W$). Dots indicate concentration of nitrite-nitrogen in $\mu\text{g-at/l}$ in secondary maximum.

several hundred meters; thus the integrated concentration of nitrite-nitrogen at these stations is very high.

South of $15^{\circ}S$, where the Peru-Chile Undercurrent can be identified by a subsurface salinity maximum as well as by its low oxygen content (Wooster and Gilmartin 1961), the secondary nitrite maximum is closely associated with the high salinity layer. This can be seen in Fig. 10, where significant values of nitrite-nitrogen occur only within that layer.

Discussion. Although the STEP-I data establish the presence of the secondary nitrite maximum off the coast of Peru, they are inadequate for an explanation of this phenomenon. The association of significant nitrite concentrations with very low oxygen concentrations confirms previous observations by Brandhorst but throws no light on whether nitrite is produced by ammonia oxidation or nitrate reduction. Nitrate concentrations at these depths are between 20 and 30 $\mu\text{g-at/l}$, and the high productivity of the region indicates that reactive organic matter may be abundant. Clarification of this question would appear to require the isolation of microorganisms capable of carrying out either ammonia oxidation or nitrate reduction and a study of their metabolism under the conditions prevailing.

The relationship between the secondary nitrite maximum and characteristics

of the water structure (particularly specific volume and salinity) suggests that the circulation plays an important role in the distribution of nitrite-nitrogen. There is growing evidence of a prevailing southward flow below the surface layer (Wyrcki 1963, Wooster and Gilmartin 1961), and the accumulation of considerable quantities of nitrite-nitrogen off southern Peru and northern Chile may be attributed to this transport.

It is clear from the STEP-I observations that further studies of the nitrite distribution will require much closer vertical sampling than is customary as well as observations of other components of the nitrogen system and the quantities and turnover rates of pertinent organisms.

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