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Vertical Distributions of pH and Fluorescence in the Western Tropical Indian Ocean–the INDIGO 2 Expedition

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ABSTRACT

A submersible pump and a continuous flow fluorometer were used to obtain the vertical pH and fluorescence profiles from the top 140 m of the seawater in the region between La Reunion, Seychelles and Djibouti in the western tropical Indian Ocean during the 1986 INDIGO 2 Expedition. The calculated chlorophyll *a* maxima are generally located near the nutracline, all within 50 m of the surface mixed layer and closer to the mixed layer at night but deeper in daytime. The chlorophyll *a* concentration in the mixed layer is uncorrelated with the concentration at the chlorophyll *a* maxima but is correlated with the integrated amount from surface to 116 m.

Continuous salinity, temperature and oxygen data from a CTD probe, and pH data from discrete samples collected by the submersible pump and by Rosette bottles are compared with the chlorophyll *a* profile.

(Key words: pH, Fluorescence, Chlorophyll *a*, Indian Ocean)

1. INTRODUCTION

Chlorophyll *a* measurements have historically provided a useful estimate of algal biomass and its spatial and temporal variability, which reflects primary productivity. Because satellites can cover a large area in a short time, more and more primary productivity (chlorophyll *a*) data will be collected by satellites. Suspended sediments, however, can mask the remote sensing signals and make readings too high. On the other hand, sensing only the top layer while missing the chlorophyll a below makes the readings too low. It is, therefore, still important to obtain ground-truth chlorophyll *a* distributions in the oceans (Lorenzen, 1970; Neville and Gower, 1977; Herbland and Voituriez, 1979; Cullen, 1982; Hayward and Venrick, 1982; Abbott *et al.*, 1984; Booda *et al.*, 1984; Feldman *et al.*, 1984; Eppley *et al.*, 1985; Bauerfeind, 1985; Dandonneau, 1986).

The vertical distribution of chlorophyll *a* is not uniform. There is usually, especially in the tropical regions, a 20-30 m thick layer of subsurface seawater that contains the maximum amount of chlorophyll *a* (Herbland, 1983; Chen, 1987). Conventional sampling with bottle

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casts often miss this thin layer. In order to overcome this difficulty, a submersible pump was used to sample the top 140 m of waters continuously during the INDIGO 2 Expedition (Expedition Etude des Gaz dans l'Ocean Indien, second expedition) in March and April, 1986. A Turner continuous-flow fluorometer was used to record the fluorescence signal, which was later converted to the chlorophyll *a* content.

This note describes the chlorophyll *a* signal and compares it with the pH and hydrographic data.

2. THE INDIGO 2 EXPEDITION

The INDIGO 2 Expedition is part of the INDIVAT and INDIGO programs (Chen, 1992; Chen and Poisson, 1986; Chen *et al.*, 1986 a, b; Poisson *et al.*, 1986). The French research vessel, Marion Dufresne, departed La Reunion on 29 March, 1986 and arrived at Mahe, Seychelles on 14 April. After a brief stopover, the vessel departed on the same day and arrived at Djibouti on 3 May. The cruise tracks and station locations are given on Figure 1 (Chen, 1993).

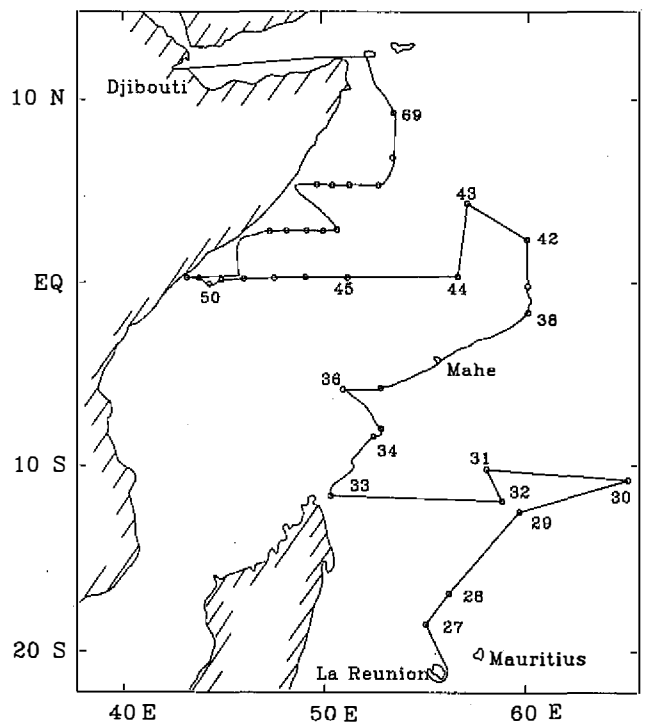

Fig. 1. The INDIGO 2 cruise track and station locations.

A submersible pump was used to pump large-volume seawater samples down to 140 m. Chlorophyll and pH samples were also taken. Since there was no pressure sensor attached to the pump, it was necessary to use the measured temperature and pH values to estimate the sampling depth, believed to be reliable to 5 m. Discrete pH samples were collected frequently from the outlet. In addition, pH samples were collected from the CTD/Rosette

system. Replicates of 4 pH samples were all analyzed within 30 minutes at 25 ± 0.02°C with a Radiometer combination electrode. NIST 4.004 and 7.415 buffers were used to calibrate the electrode. The reproducibility of the pH measurements was better than ± 0.003 units for replicate samples. The electrode drift (assumed to be linear) was determined at approximately 10-day intervals. The drift was approximately 0.002 unit/day, and the correction was made to the measured values.

The CTD-Rosette used to obtain deep samples malfunctioned once during INDIVAT 1, and all 11 bottles were closed at approximately 3400 m at GS 427. Four replicate samples were taken from each bottle. The standard deviation of the pH data (44 points) is 0.0027 pH units (1σ) which includes random error in both sampling and analysis.

At a test station (G O) during INDIVAT 1, 5 Rosette bottles were collected at 1000 m, the precision of 20 measurements was ± 0.0035 which also included measurement and sampling errors.

Precision and accuracy of pH measurements were further checked in an intercomparison of spectrophotometric and potentiometric methods performed during the INDIGO 1 expedition (Byrne *et al.*, 1988). No further tests were run during INDIGO 2.

Chlorophyll *a* fluoresces in the red wavelengths after extraction in acetone when it is excited by blue wavelengths of light. The fluorometer excites the extracted sample with a broadband blue light and the resulting fluorescence in the red can easily be detected by a photomultiplier. The fluorescence by phaeopigments is corrected for by acidifying the sample which converts all of the chlorophyll *a* to phaeopigments.

The submersible pump was used to obtain continuous samples down to 140 m. Chlorophyll *a* was determined with a Turner model 10-005 flow-through fluorometer with the scale "zeroed" for each door opening against a tube of 90% acetone. Discrete samples were filtered, extracted by 90% acetone and the chlorophyll *a* measured in order to check the continuous data. Coproporphyrin was used for calibration (Strickland and Parsons, 1972; Turner Designs, 1981).

In order to convert the fluorescence to the concentrations of chlorophyll *a* I used the following equation:

$$\text{chlorophyll } \underline{a} = F_0/F_a(F_m - 1) \cdot (F_0 - F_a) \cdot K_x \cdot Vol(ex)/Vol(sam)$$

where F_0 is the reading before acidification; F_a is the reading after acidification; K_x is the linear calibration door factor as the slope of the unacidified fluorometric reading vs the concentration of the standard; $Vol(ex)$ is the extraction volume and; $Vol(sam)$ is the sample volume. Once the fluorometer was calibrated, at each station, a simple factor was used to convert the in vivo fluorescence to the measured chlorophyll *a* concentration based on the calibration of the discrete samples. The factor varies from station to station.

The CTD/Rosette system was used to collect discrete samples from surface to bottom (Poisson *et al.*, 1986). This discussion is limited to data collected from the top 140 meters.

3. RESULTS AND DISCUSSION

The vertical profiles of temperature, salinity and oxygen obtained at a typical station (St. 30) by the CTD/O_2 are given in Figure 2. The surface wind-mixed layer is 30 meters thick where temperature, salinity, oxygen and seawater density are homogeneous and show no vertical gradient.

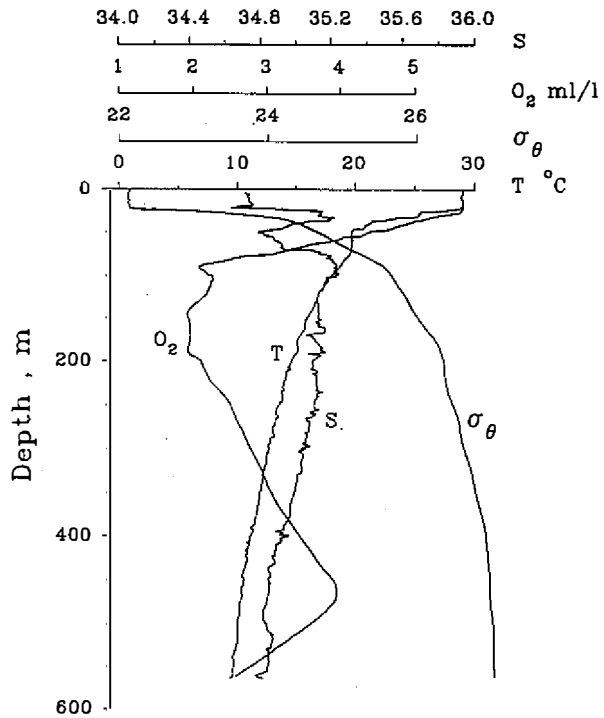

Fig. 2. The temperature, salinity, dissolved oxygen and σ_θ profiles at St. 30 (taken from shipboard data and Poisson *et al.*, 1986).

The temperature decreases below the mixed layer, rapidly first to 50 meters, more slowly between 50 and 80 m, then rapidly again below 80 m. The distributions of salinity and oxygen are quite irregular and show maxima and minima. The static stability, obtained from the density gradient, is high below the mixed layer.

Figure 3 shows the vertical distributions of chlorophyll *a* at St. 27-50, a typical tropical signal (Herbland and Voituriez, 1979). Taking St. 30 as an example, the distribution is homogeneous within the wind-mixed layer; a 20-30 m-thick maximum appears between 50 and 80 m, then the concentration decreases further down. Other stations show similar phenomena although there is slight station-to-station variability. For instance, St. 42 shows a broad maximum, or perhaps a double peak. On the other hand, St. 43 shows a small and narrow maximum. There is insufficient supporting information to explain these differences.

Preliminary analysis indicates that the surface chlorophyll *a* concentration is not related to the surface temperature. The maximum chlorophyll *a* concentration is also unrelated to the corresponding temperature. The chlorophyll a maximum is shallow at night and deep in the daytime based on the composite data (Figure 4). It seems that the depth of the maximum density gradient is always higher than the depth of the chlorophyll *a* maximum. The chlorophyll *a* maximum is very close to the depth of the maximum density gradient at night, but slightly deeper in the daytime. Regardless of the hours, however, the maximum layer is located within 50 m of the wind mixed layer.

In the open ocean the pH typically decreases below the mixed layer to a pronounced minimum at around 800 m due to the decomposition of organic matter. Sometimes a very

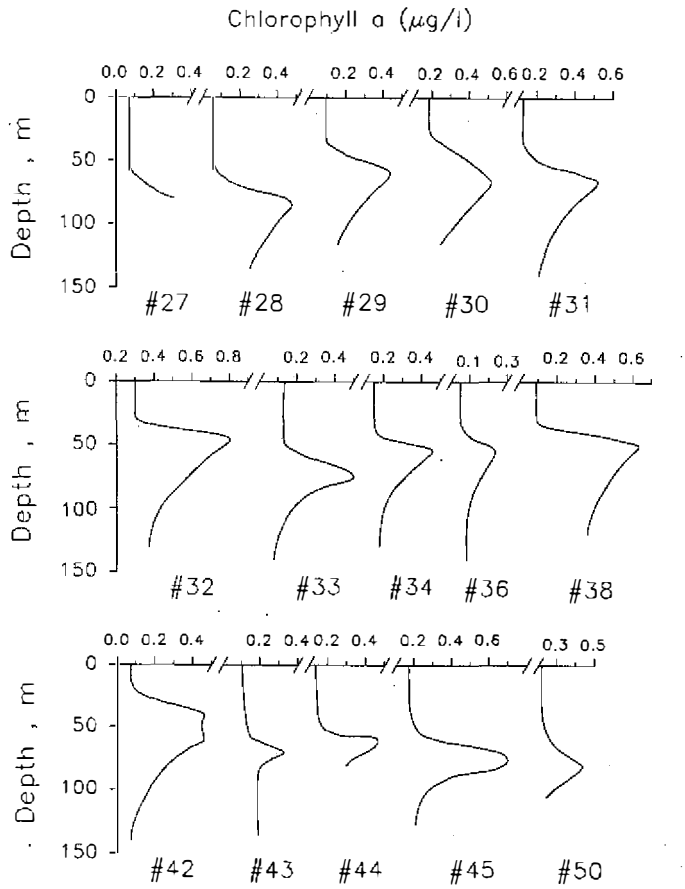

Fig. 3. The chlorophyll *a* profiles at St. 27-50.

weak maximum is found near surface due to photosynthesis (Chen *et al.*, 1986c). Figure 5 shows the vertical distributions of pH at St.27-69. Taking St. 30 as an example, the samples obtained from the pump, regardless of whether the pump was being lowered or raised, do not differ from the Rosette samples within the combined precision of the data. A notable exception occurs at St. 43 where different water masses might have been collected near 100 m due to drift of the ship.

The distribution of pH is homogeneous in the mixed layer. No maximum could be detected perhaps because the chlorophyll *a* maximum is generally located at the depth where pH already starts to decrease. The effect of photosynthesis on chlorophyll *a* (increasing chlorophyll *a* and pH) may be overwhelmed by the effect of respiration (decreasing pH). The pH values decrease rapidly in the first 20 m below the mixed layer but the slope decreases at a depth of 50 m. Most other stations show the same pattern although in some cases (i.e. St. 27-29) the pH values do not decrease as rapidly below the mixed layer (Chen, 1987).

The depths of maximum O_2, maximum salinity, minimum salinity, maximum chlorophyll *a*, and minimum O_2 for St. 30 are marked on Figure 5. Since photosynthesis increases dissolved oxygen and chlorophyll *a*, the chlorophyll *a* maximum layer is expected to be and

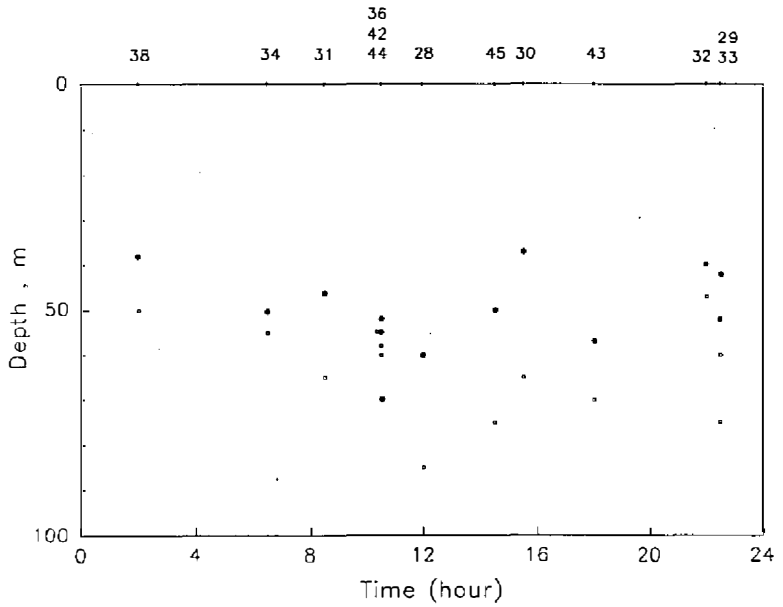

Fig. 4. The depths of the maximum density gradient (closed circles) and the maximum chlorophyll *a* concentration (open circles) at various hours.

is indeed located close to the depth where oxygen also shows a maximum. These extremes, however, are not clearly related to the pH signals. Only 3 stations (30, 31, 43) have a shallow O_2 minimum at roughly 100 m. The pH does not show a corresponding minimum at St. 30 but there is a distinctive pH minimum at the O_2 minimum at St. 31 and St. 43 (Figure 5). These are probably local features reflecting enhanced decomposition of organic matter. There is no pH maximum at the O_2 maximum for all stations. It should be pointed out that the O_2 data come from the CTD probe which is capable of showing small features. The pumped waters, however, may be somewhat mixed in the pipe, thus eliminating small pH signals.

There is an upwelling-like feature just south of the equator bringing cold, nutrient-rich subsurface water towards the surface to support new production (Figure 6). The 20°C temperature contour moves to only 80 m below surface creating a very sharp thermocline and a very high water-column stability. The nitrate and phosphate also show similar upwelling-like features (Poisson *et al.*, 1986). The nitrate and phosphate have maximum gradients at the same depth, which also shows a dome-like feature (Figure 6). Maximum stability of the water column near 50 m reflects minimum sinking rate for phytoplankton, which consume the maximum amount of nutrients near this depth. Since nutrients are brought up from the deep, are consumed mainly near the chlorophyll *a* maximum, and are all but used up above the thermocline, sharp nutraclines are created near the thermocline.

The depth of the chlorophyll *a* maximum is near the nutracline but shows no dome-like feature. There is only very weak correlation between the depth of the chlorophyll *a* maximum and the depth of maximum nitrate and phosphate gradients. This is not unexpected as the phytoplankton move up and down yet the nutraclines remain relatively steady (Cullen *et al.*, 1983). Grazing further complicates the relation between nutrient and chlorophyll concentrations (Minas and Minas, 1992).

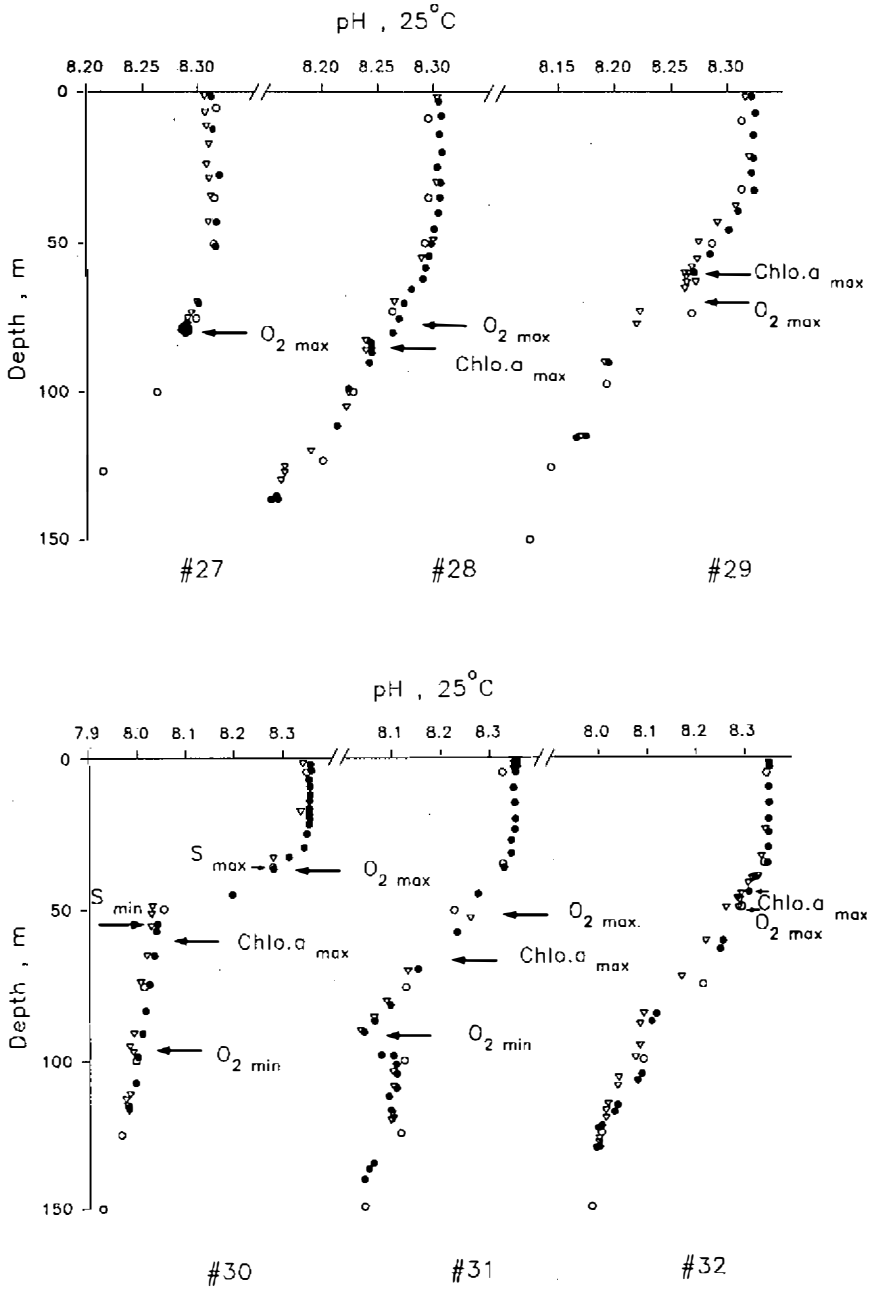

Fig. 5. The pH profiles at St. 27-69. The closed circles are pH values obtained while the pump was lowered; the crosses are the pH values obtained while the pump was raised, the open circles are pH values obtained by the CTD/Rosette system.

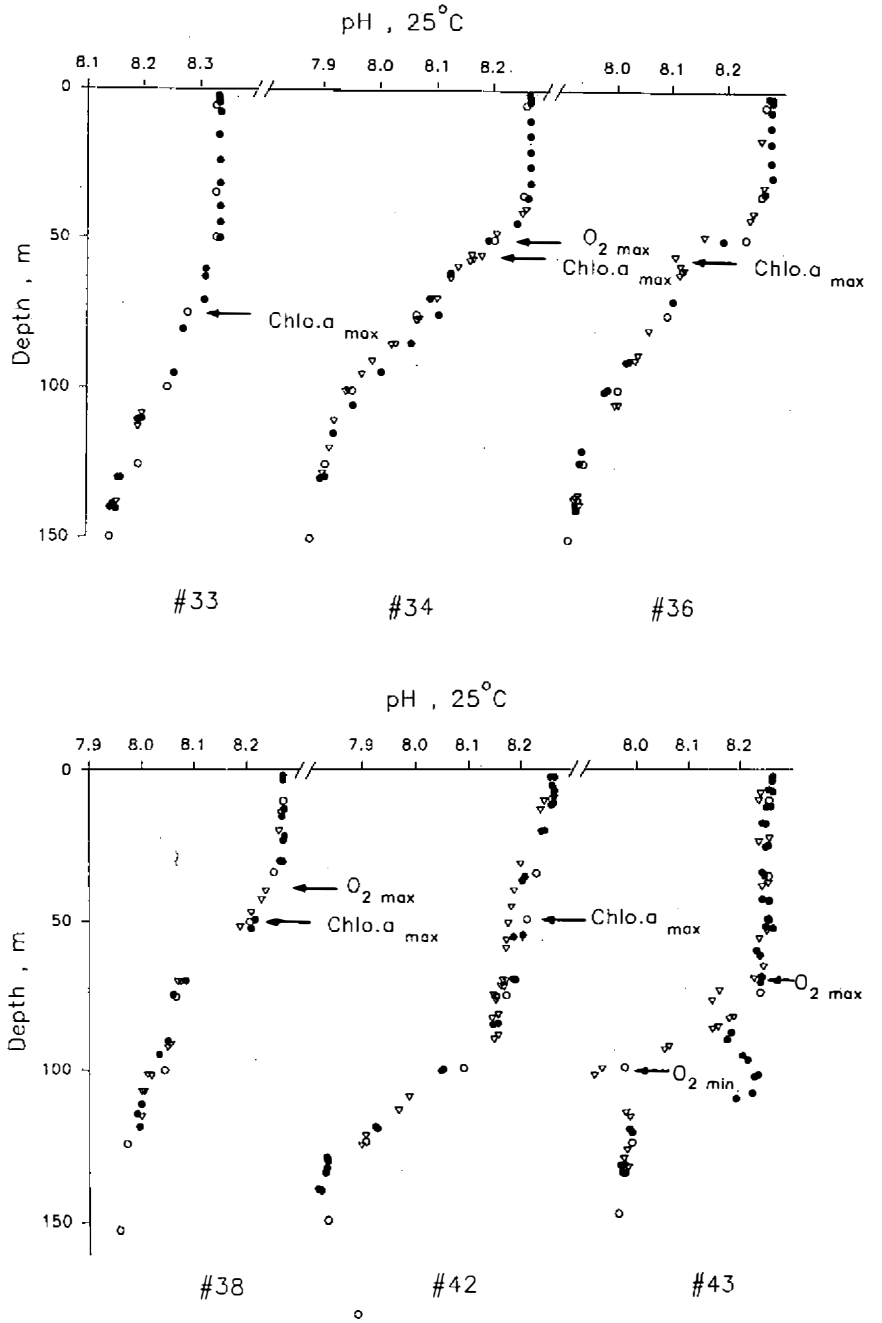

Fig. 5. (Continued.)

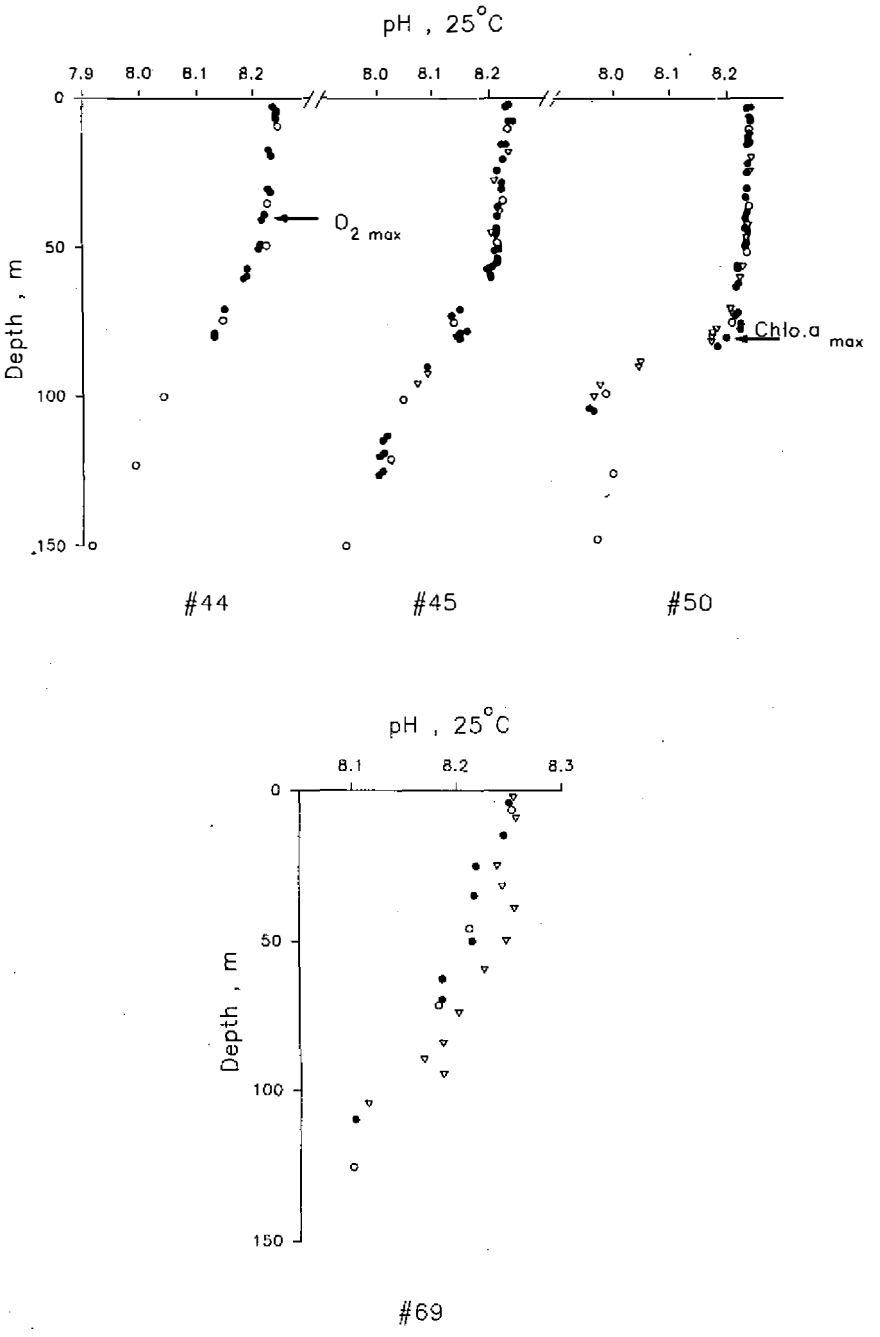

Fig. 5. (Continued.)

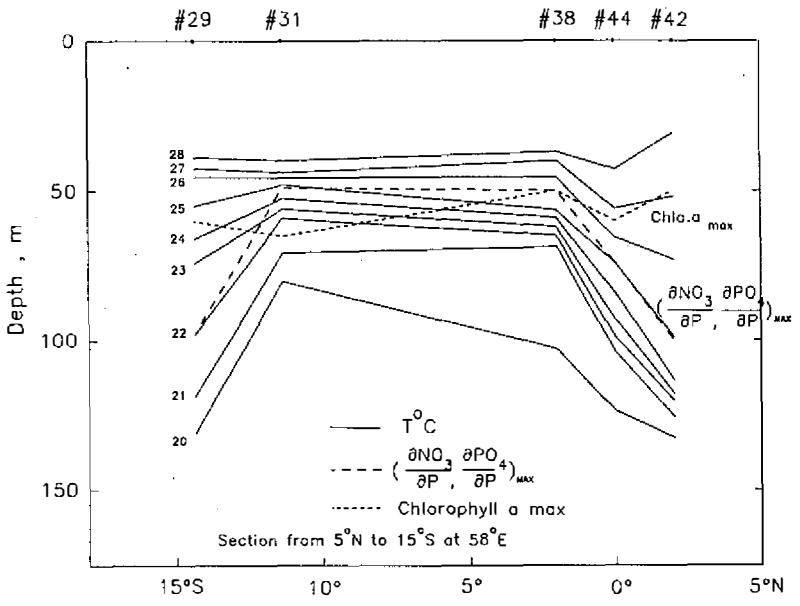

Fig. 6. The north-south temperature contours near the equator and the depths of maximum chlorophyll *a*, and maximum temperature, nitrate and phosphate gradients.

Surface chlorophyll *a* values fall between 0.05 and 0.15 $\mu g/l$, in agreement with the large data set of the tropical Pacific Ocean (Dandonneau, 1992). The maximum chlorophyll a values fall between 0.1 and 0.7 $\mu g/l$.

Figure 7 shows the surface chlorophyll a concentration plotted vs. the concentration at the maximum layer. There is no clear correlation. Since remote sensing can only detect the chlorophyll *a* concentration near the surface, the relation of the surface concentration to the total amount at each station deserves further study. Unfortunately, data do not extend to sufficient depth to do a proper integration in order to obtain the total chlorophyll *a* amount. Only the amount from surface to 116 m was integrated. It seems to correlate with the surface concentration (Figure 8).

4. CONCLUSION

The INDIGO 2 Expedition was perhaps the first to use a submersible pump to obtain the continuous fluorescence profile in the Indian Ocean. The preliminary data indicate that the vertical distribution is of the typical tropical type, i.e. the chlorophyll *a* concentration is low within the surface mixed layer; a 20-30 m thick maximum layer exists within 50 m beneath the mixed layer; and the concentration decreases again further down. Since mixing occurs in the pipe, small signals may be eliminated. As a result, although the pumping system is useful for obtaining large volume, or frequent samples, the in situ sensing and recording system is still the choice when continuous profiles are needed.

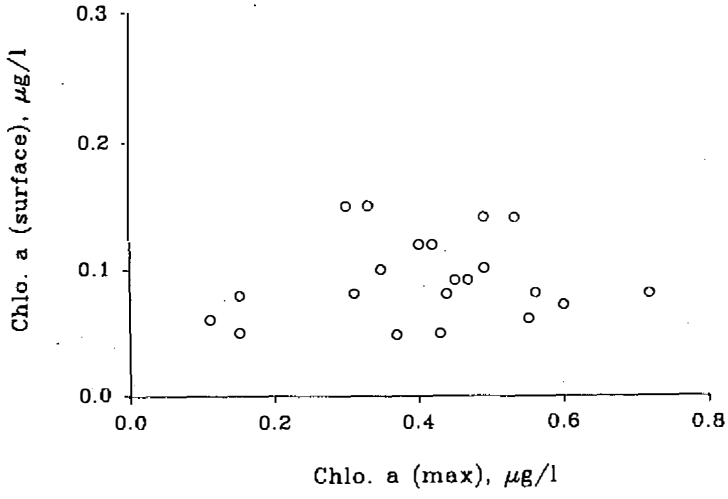

Fig. 7. The correlation of surface chlorophyll *a* concentration with the concentration at the chlorophyll *a* maximum.

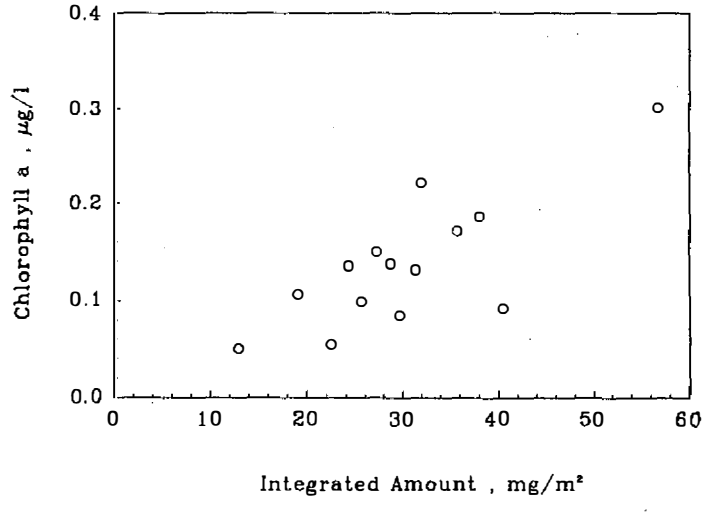

Fig. 8. The correlation of surface chlorophyll *a* concentration with the integrated chlorophyll *a* concentration from the surface to 116 m.

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