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# Nutrients and mixing, chlorophyll and phytoplankton growth

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**Abstract**—During a cruise to the Sargasso Sea in April 1985, we observed an event of wind-induced mixing during a 4-day sequence of observations while operating in a Lagrangian sampling mode. The sharp increase in wind stress was followed by a sharp increase in nitrate concentration in the euphotic zone. The nitrate declined rapidly, and over the next 2 days the quantity of chlorophyll *a* in the euphotic zone increased by a factor of three. The phytoplankton community was dominated by diatoms; this and other evidence indicates that the events observed were part of the spring bloom in the north Sargasso Sea.

These observations are interpreted in terms of laboratory models for nutrient-dependent phytoplankton growth. The cell-quota model of Caperon and Droop provides an internally consistent explanation of the observed data. The data also suggest the notion of "nutrient switching" (rather than a multiplicative form of nutrient interaction) in the interaction of nitrate and silicate, although this could not be verified.

## INTRODUCTION

RELATIONSHIPS between phytoplankton and environmental nutrients have developed to the point where satisfactory descriptions of steady-state growth rates are possible for single-species populations in laboratory culture vessels. The Michaelis–Menten model, which relates uptake of an ambient-limiting nutrient to growth (MONOD, 1942; DUGDALE, 1967), has been modified to include the effect of varying cellular nutrient content (DROOP, 1968; CAPERON, 1968). Here, population growth is more closely related to the quantity of limiting nutrient within the cells rather than available in the surrounding medium. Later work has indicated the limitations of this model (see GOLDMAN and GLIBERT, 1981). For example, transient conditions between steady states are often not well-described by the cell-quota model (CUNNINGHAM and MAAS, 1978; BURMASTER, 1979; CUNNINGHAM, 1984).

Another limitation to this research effort is that none of the models developed in the laboratory have been tested with respect to growth in natural phytoplankton populations, although application to the field must be an eventual prospect. To be sure, the Michaelis–Menten model forms the basis of the growth term in environmental simulation models (e.g. DITORO *et al.*, 1971; WALSH, 1975; WROBLEWSKI, 1977), and TETT *et al.* (1985) have employed the extended cell-quota model. But these models are usually used to represent large-scale changes or distribution in biomass, and the details of growth and nutrient removal are not considered.

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The issue remains, therefore, whether any of the models applied to growth of laboratory populations, be they batch-culture (WILLIAMS, 1971), Michaelis–Menten, or cell-quota models, apply to the growth of natural populations. As suggested above, several problems exist. The apparent necessity for steady state in the laboratory is a simplification that may have no reality elsewhere. In natural populations, it is possible that more than one nutrient is important to growth dynamics. Finally, there is no assurance that the single-species approach used in laboratory culture is a useful experimental method for eventual application to natural, multi-species, populations (WILLIAMS, 1973).

During a cruise to the North Sargasso Sea (April 1985; Biowatt I), while operating in a drifter-following sampling regimen, we observed a wind event, erosion of the seasonal thermocline and rapid cooling of the upper layer. This was followed by a sharp increase in nitrate in the euphotic zone over a period of 12 h. Over the 2 days following this event, chlorophyll in the euphotic zone tripled while nitrate once again became depleted. These events and their explanation in terms of laboratory models of phytoplankton growth are the subject of this paper. They are similar to the observations reported recently by GLOVER *et al.* (1988) and EPPLEY and RENGER (1988), except that the biological signals here are larger and we attempt to deal with them in terms of phytoplankton growth kinetics.

## METHODS

Details of the methods used during this experiment can be found in SMITH *et al.* (1989) and BIDIGARE *et al.* (1989). Here we provide a brief summary.

Wind velocities were computed as true wind from the ship's anemometer. Hourly wind stress was calculated according to the relationship presented in GILL (1982), that is,

$$\tau = C_D \rho_a U^2, \tag{1}$$

where $\tau$ is the wind stress (in N m$^{-2}$), $C_D$ is the neutral drag coefficient ($1.1 \times 10^{-3}$), $\rho_a$ is the air density (1.26 kg m$^{-3}$), and $U$ is the wind speed in m s$^{-1}$ at 10 m above the ocean surface.

Hydrographic measurements were performed with a conductivity–temperature–depth (CTD) profiling system. A Sea Data model 650 submersible data logger consolidated the sensor signals for onboard computer logging. The CTD also had an *in situ* fluorometer (SeaMarTec) and a 12 bottle rosette mounted with Niskin samplers for water collection. The *in situ* fluorometer was calibrated on each cast using samples from the Niskin bottles which were analysed fluorometrically for Chl *a* (see below). CTD casts were performed at 6 h intervals to a depth of 200 m. Lowering speeds and data logging specifications permitted a depth resolution of 1 m. Rosette samplers were tripped at 10 m intervals from 0 to 60 m, and at 75, 100, 125, 150 and 200 m.

The surface buoy of the Multi-Variable Profiler (MVP) was used as a drifter in this study. The MVP supplied temperature, conductivity and irradiance (PAR) for this observational period (DICKEY *et al.*, 1985). The MVP was tethered to the surface buoy and automatically ascended and descended at 15–25 cm s$^{-1}$ through the upper 200 m of the water column, and recorded observations every 20 s giving profile data each hour of the operation. The data were recorded internally and transmitted via radio to the ship for real-time data acquisition. To improve statistics and to minimize aliassing, the raw data

were averaged over depth bins of 10 m. Further details concerning the MVP can be found in DICKEY *et al.* (1985) and DICKEY (1988). The temperature and conductivity data from the MVP agree with the CTD data; however, the MVP data is used, because of the better temporal resolution obtained.

Nutrient analyses were performed with a six-channel Alkem auto-analyzer. Phosphate, ammonium, nitrate and nitrite were determined using the methods described by WHITLEDGE *et al.* (1981). Silicate and urea were measured according to the techniques outlined in TECHNICON (1973) and KEROUEL (1982), respectively. The methods were slightly modified to enhance system stability and sensitivity (J. D. GUFFY, personal communication).

Chlorophyll *a* was determined by the method of SMITH *et al.* (1981), using a Turner model 111 fluorometer. This fluorometer was calibrated at sea with pure Chl *a* (from Sigma Chemical Co., and purified by high performance liquid chromatography), as a reference standard. Enumerations for phytoplankton were done on an inverted microscope using samples preserved in (acid) Lugol's solution.

Primary production experiments were conducted using the $^{14}C$ method (SMITH *et al.*, 1989) on 5 and 7 April. These experiments were performed *in situ* from dawn to dusk. Concurrent samples for particulate organic carbon (POC) were also collected and analysed on a Perkin–Elmer 240D Elemental Analyzer.

## RESULTS

### *Observations*

The observations, near 35°N, 70°W, were made within a few hundred meters of the buoy used for tethering the MVP. The MVP was launched on 4 April and recovered on 7 April. The system drifted first slowly northeast, and then southeast at greater speed (Fig. 1). During the course of the observations, the buoy drifted approximately 42 km with a mean speed of 17 cm $s^{-1}$ (DICKEY *et al.*, 1985).

Wind stress ($\tau$) during the period of study (Fig. 2) increased during 5 April 1985 from less than 0.02 N $m^{-2}$ (~3 m $s^{-1}$) to greater than 0.12 N $m^{-2}$ (~8 m $s^{-1}$), and succeeded shortly thereafter by rapid changes in water column structure and erosion of the seasonal thermocline. For the purpose of the subsequent discussion of the changes observed in the water column, we have defined the wind event as the period from the afternoon of 5 April (when the effects of the wind became apparent in the water column) until the afternoon of 6 April (Fig. 2). Although the cessation of the wind event is ill-defined, this makes little difference to the biological changes observed on 6–7 April (described below).

North Atlantic 18°C water (WORTHINGTON, 1959), dominates the water column at this time of year; vernal warming brought surface temperatures to ~20°C (Fig. 3a). Although the general trend is toward warming of the surface layer and restratification in the seasonal thermocline, wind (and sometimes convective) events often lead to entrainment of water from beneath the mixed layer, and temporary cooling, a type of situation believed to be encountered here (Fig. 3a).

The mixed layer depth (MLD) is defined in two ways: the depth at which the difference from surface temperature is 0.5°C (MLD2 in Fig. 2), and in which this temperature difference is 0.1°C (MLD1). MLD was relatively constant until the late afternoon of 5 April when it deepened rapidly to ~150 m in about 12 h. This deepening may have resulted from the sudden increase in wind stress during 5 April. Following

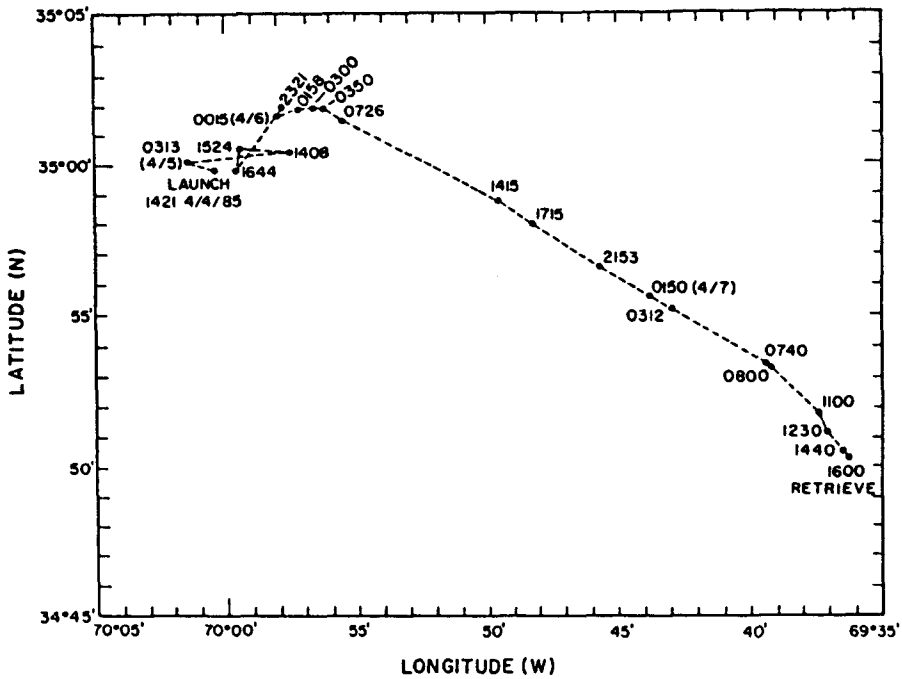


Fig. 1. The trajectory of the buoy to which the Multi-Variable Profiler (MVP) was tethered during the observational period. Hours and dates (month/day/year) are given for positions.

this episode, the MLD remained relatively deep until the end of the observational period.

The MVP also collected profiles of photosynthetic available radiation (PAR) (Fig. 3b) and the diurnal variation and nearly exponential decay of PAR with depth are apparent. While there was little change between 5 and 6 April, on 7 April (based on the half-day data available), the depth of the euphotic zone (depth of 1% of surface irradiance)

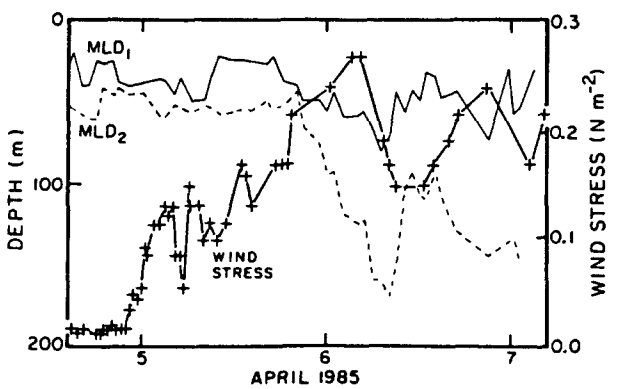


Fig. 2. Wind stress, $\tau$ (N m$^{-2}$), over the observational period, calculated using equation (1) in the text. Wind data are from the ship's anemometer. Two mixed layer depths are shown: MLD1 (solid line) is defined as a temperature difference of 0.1°C, and MLD2 (dashed line) is defined as a temperature difference of 0.5°C. The data are somewhat noisy in part because of repositioning the ship for over-the-side operations. For the purposes of this analysis "wind event" is defined as the period from 1200, 5 April to 1200, 6 April.

decreased by about 15 m. The decreasing absolute PAR values on this day were probably caused by increasing cloudiness, and perhaps, secondarily, by the increase in Chl *a* concentration beginning on 6 April (see below).

Nitrate, silicate and Chl *a* distributions for the drifter-following experiment are shown in Fig. 3c–e. Since these variables are observed at much less frequent intervals than temperature from the MVP, the contours in these figures cannot be verified by the temperature data. (Nitrate and silicate have more limited depth resolution as well.) We cannot determine whether some features are real or are functions of the contouring routine employed. The major features of interest, however, remain conspicuous.

During the initial portion of the observations, Chl *a* was relatively high (about 0.5–1.0 μg $l^{-1}$) and uniformly distributed in the euphotic zone (~55 m). This same time period was marked by low nitrate concentrations. Coincident with the onset of higher winds on 5 April, average Chl *a* concentration in the near-surface water declined. As we

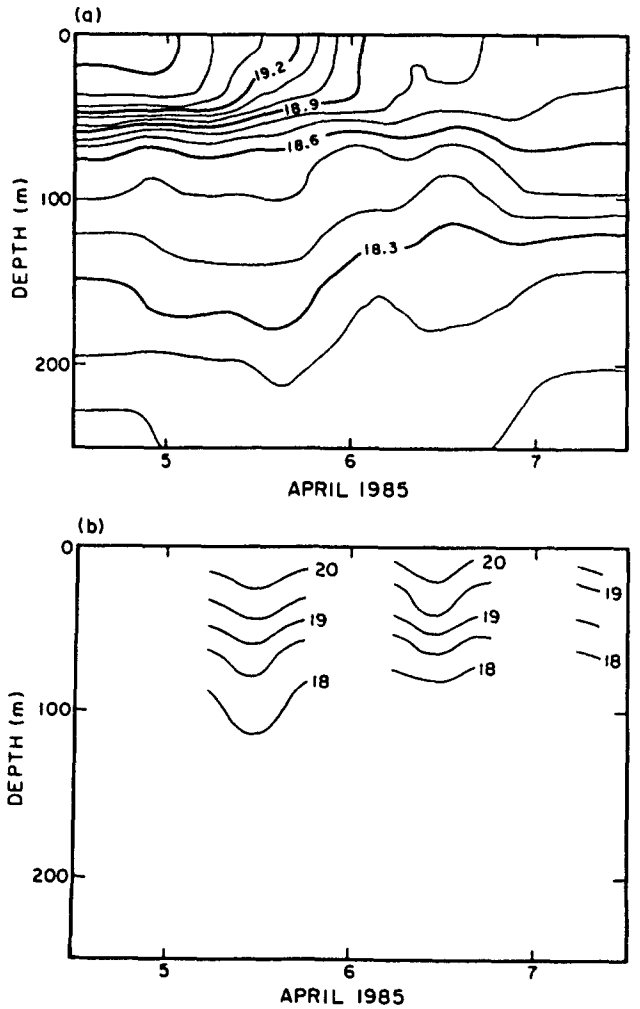


Fig. 3a, b.

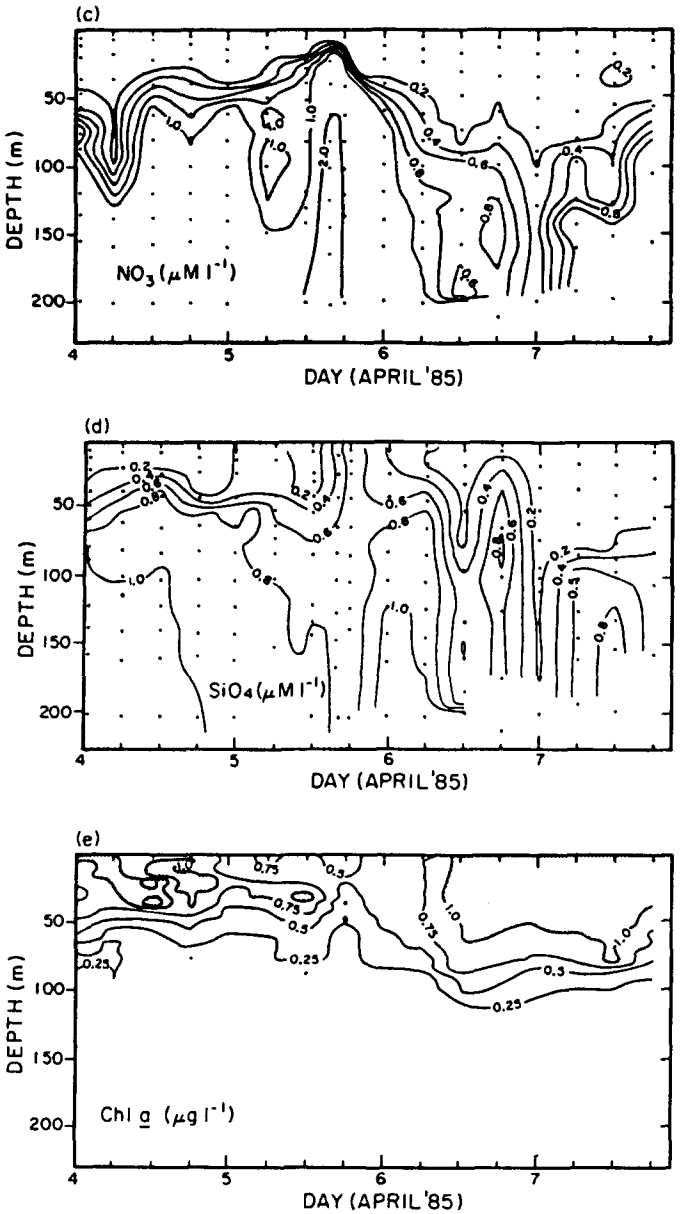


Fig. 3. Time–depth distributions of (a) temperature (°C); (b) $\log_{10}$ (photosynthetically available radiation) (where PAR is in quanta $m^{-2}$ $s^{-1}$); (c) nitrate (μmol $l^{-1}$), (d) silicate (μmol $l^{-1}$); and (e) Chl *a* (μg $l^{-1}$). The contours in these plots were generated from computer routines after creating gridded data points from the profile data. Dots in the nutrient data plots represent sampling depths. We assumed a linear interpolation between nutrient data points to create the gridded data set for contouring. Salinity never varies more than 0.05 psu from a mean of 36.50 psu, thus it does not contribute significantly to density variability and is not shown. Phosphate and ammonium showed little dynamic behavior and are not considered in our analysis. The depth of the euphotic zone in (b) is indicated approximately by the $10^{19}$ quanta $m^{-2}$ $s^{-1}$ isopleth. Since PAR isopleths are absolute values but with finite sensitivity, day-to-day variations in solar intensity will have the effect of changing daylength slightly.

discuss below, this appears to be a decline in the quantity of chlorophyll in the euphotic zone and not just a redistribution. Nitrate, in contrast to chlorophyll, increased dramatically. The increase in near-surface nitrate, noticeable on the afternoon of 5 April (see Fig. 3e) was coincident with the lowest chlorophyll concentrations in the water column.

Silicate (Fig. 3d) exhibited similar behavior to nitrate and chlorophyll; however, before the wind event, silicate was always measurable throughout the euphotic zone. The wind event produced an increase; but since it was already present in the surface layer, the changes were less dramatic. After the increase in wind, nitrate declined even faster than it appeared. Meanwhile, Chl *a* concentrations (Fig. 3e) increased to average values $>1$ μg $l^{-1}$. After the nitrate decline during 5–6 April, silicate remained in the euphotic zone, but was subsequently removed. The difference in the timing of the removal of the two potentially limiting nutrients, silicate and nitrate, will be discussed below.

The phytoplankton populations during this time were dominated by diatoms. This was established by microscopic examination of water samples from 5 and 7 April (F. Reid, personal communication) and from analysis of accessory pigments. The fucoxanthin-to-Chl *a* ratio was measured to be 0.6 (w:w) and remained constant through the time of chlorophyll increase during 5–7 April.

To simplify the analysis of these data, we have integrated nitrate, silicate and chlorophyll over the depth of the initial euphotic zone (~55 m) (Fig. 4). The dynamics of the nutrients and chlorophyll are more pronounced than depicted in the time–depth distributions, although the primary features remain the same: a sharp increase in nitrate and a decrease in Chl *a* (cf. Fig. 3c, e) following the sharp increase in wind stress (Fig. 2). This is followed by depletion of nutrients, and an increase in Chl *a* (Fig. 3e).

During the period we have identified as the wind event, integrated Chl *a* declined about two-fold, that is, from ~40 to ~25 mg $m^{-2}$. Over the next 2 days, integrated Chl *a* concentrations increased by a factor of three. Also, much of the initial nitrate removal occurred during the night. If there is a light dependence to the assimilation of nitrate in phytoplankton, it is not evident in our data.

The change in chlorophyll computed from the $^{14}C$ experiments (5 and 7 April) and using the carbon:chlorophyll ratio (estimated from the regression of POC on Chl *a* to be 55), is noted on the chlorophyll time course (Fig. 4). The change in chlorophyll predicted by the $^{14}C$ experiment on 5 April is greater than the observed change; however, it is difficult to detect any trend in the water column chlorophyll during this time. The 7 April experiment provides a prediction closer to the observations. Primary production on these 2 days was actually similar, at 600–700 mg C $m^{-2}$ $day^{-1}$. However, the very different chlorophyll levels lead to different predicted growth rates.

*Biological changes*

Since the observations were near a drifting buoy, the distributions shown in Figs 2 and 3 in principle should represent changes in water column structure for a particular water mass. Analysis of these data with respect to changes caused by biological rates requires the assumption that the MVP is a perfect (or near-perfect) drifter, that is, a drifter with no slippage relative to the mean current. (In fact, no drifter will achieve that criterion.) We believe that the changes in the water column we observed on the afternoon of 5 April involve a redistribution of heat and other properties in the water column rather than the effects of an advection event. Contrary evidence to this supposition is from two obser-

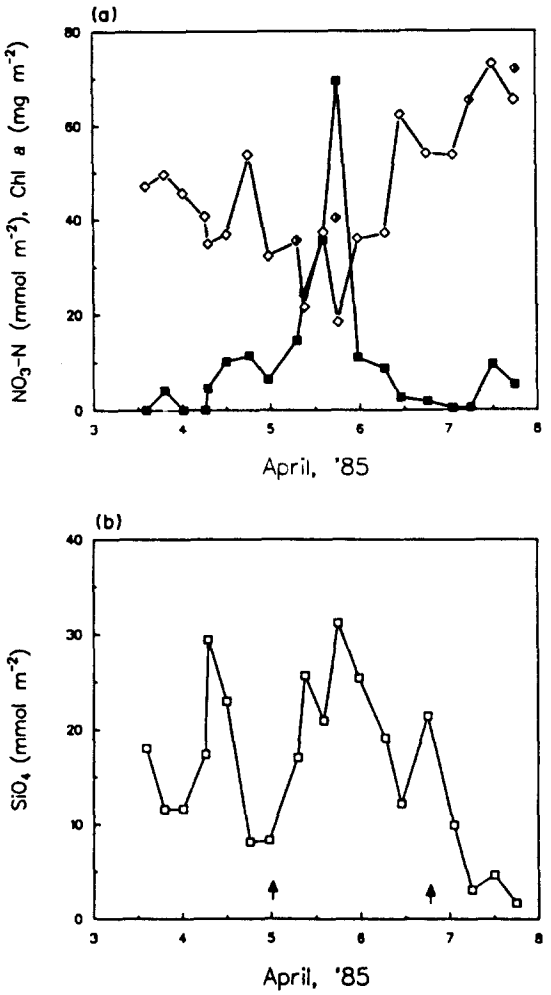


Fig. 4. (a) Integrated nitrate (mmol $m^{-2}$) (filled symbols) and Chl *a* (mg $m^{-2}$) (open symbols), and (b) silicate (mmol $m^{-2}$) measured during the observation period. The depth of integration is 55 m. Superimposed on the chlorophyll time course is the increase in chlorophyll predicted from the assimilation of $^{14}C$-labeled $HCO_3^-$, (EPPLEY, 1972) for 5 and 7 April (half-filled symbols). The arrows in (b) enclose a period in which silicate may be more limiting to growth than nitrate (see Discussion).

vations during the afternoon of 5 April. First is the decline of the quantity of chlorophyll in the euphotic zone (Figs 3e and 4a). This seems to be more than a redistribution of phytoplankton; integrations over a deeper depth interval do not correct the loss.

The second observation is the appearance of the high nitrate values (Fig. 3c). The concentrations of nitrate measured deeper in the water column, 2–3 μmol $l^{-1}$, are in agreement with wintertime values for this region of the Sargasso Sea (MENZEL and RYTHER, 1960). However, the appearance of these values in the data is puzzling since it is a singular episode. It could indicate a change in water mass, not otherwise revealed in the temperature or salinity fields.

Other than these two observations, no changes could be detected in heat content of the water column (integration of temperature from 0 to 200 m) over the duration of the experiment. The currents measured by the MVP were not significantly different from zero at 10 m depth, which suggests that the drifting buoy was probably tracking surface water reasonably well. This implies that there was in fact little slippage between the buoy and the water mass we were attempting to track. Also, the nitrate and chlorophyll data during 6–7 April indicate that the same water mass was being sampled. This latter point requires explanation.

The changes in Chl *a* (in $\mu g\ l^{-1}$) from 5 to 7 April are well-correlated with the changes observed in the values of nitrate (in $\mu mol\ l^{-1}$) during the wind event. That is, about 1 $\mu mol\ l^{-1}$ of nitrate removed from the water column produces about 1 $\mu g\ l^{-1}$ of Chl *a*. Assuming a C/N ratio (atomic) of 6.6, this would occur if the carbon-to-chlorophyll (C/Chl) ratio (by weight) was 80. A regression of our data for particulate organic carbon on chlorophyll for this station gives a slope of 55 ($n = 20$, $r^2 = 0.72$). This lower value is compensated by the fact that nitrate is never the sole source of inorganic nitrogen during growth in natural populations. To achieve the C/Chl ratio requires that the nitrate be assimilated in proportion to the total nitrogen demand, giving the so-called "*f*-ratio" (Eppley and Peterson, 1979; Eppley, 1981) a value of 0.7. This is not unreasonable for the Sargasso Sea during the period of the spring bloom (Menzel and Ryther, 1960; Platt and Harrison, 1985), and given the statistical analysis of Harrison *et al.* (1987), it may be typical where nitrate concentrations exceed 1 $\mu mol\ l^{-1}$. McCarthy and Nevins (1986) determined an *f* of 0.6 for a warm-core ring for a similar time of year, also including urea as part of the total nitrogen assimilated. These authors also assumed this value to be conservative because of the methods used to estimate the assimilation of regenerated forms of nitrogen. Of course, the explanation for the ratio (atom/weight) of N/Chl $\approx$ 1 set forth here implies that if $f = 0$, no net chlorophyll production would occur. (A speculative but intriguing possibility is that the C/Chl ratio may be diagnostic for new production.) Evidence to support N/Chl $\approx$ 1 has been observed in field studies (Dugdale and Goering, 1970; Saksaug *et al.*, 1981; Barlow, 1982; Takahashi *et al.*, 1986) and in experiments in mesocosms (Takahashi *et al.*, 1975; Malone *et al.*, 1975; Parsons *et al.*, 1978) for healthy, growing populations of diatoms. It also has been demonstrated in laboratory investigations of diatoms (Caperon and Meyer, 1972a; Laws *et al.*, 1983).

While it is not possible to verify precisely N/Chl = 1 for these data, the evidence of the relationship between nitrate and chlorophyll reinforces the supposition that we are sampling the same water mass as tracked by the drifter, or that the process of removal and uptake was stationary in the water traversed by the drifter. That N/Chl = 1 is also a reasonable assumption for modeling purposes. Thefefore, we assume a C/Chl ratio equal to 55 and an *f* of 0.7 to simplify the model analysis presented below, which considers the kinetics producing this outcome.

As a final point, while we acknowledge zooplankton grazing as a factor in plankton dynamics, we do not believe it is an important consideration for these data. Grazing is generally a broader scale phenomena than phytoplankton growth for the springtime Sargasso Sea. If grazing were important in preventing phytoplankton growth, then we should have seen a decline in biomass (i.e. chlorophyll) prior to the wind event as well, when in fact the quantity of chlorophyll in the upper layers remained constant.

## DISCUSSION

The data presented in Figs 2–4 will now be discussed in terms of laboratory models of phytoplankton growth in response to nutrients. These models include one for batch-culture growth, a cell-quota model, and, briefly, an outgrowth of the cell-quota model which considers the interactions of two nutrients (e.g. RHEE, 1978). Since we neglect physical processes in these models, a three-point running mean is used in the observational data to remove some of the variability that is presumed to have resulted from physical processes (internal waves, etc.) or because the MVP buoy behaved as an imperfect drifter. Also, a constant depth, 55 m, was used, over which to integrate nutrients and chlorophyll, as representative of the mixed layer. Based on the data of Fig. 3, this is a reasonable assumption.

### *"Batch-culture" growth*

The simplest means to describe the nitrate removal and consequent growth of phytoplankton is to assume "batch-culture" increase of the chlorophyll in response to the nitrate perturbation, where the nutrient is taken up as the phytoplankton grow. Assume, therefore, a closed system, such as phytoplankton growing in a flask where nutrients and biomass are conserved through time, $t$. This type of model has been examined by WILLIAMS (1971) for laboratory cultures. The balance between nitrate removal and chlorophyll growth after the nitrate injection during 5–7 April suggests that this assumption might be valid. We have,

$$P_t + N_t = P_0 + N_0, \tag{2}$$

where $P_t$ is phytoplankton biomass at time $t$, and $N$ is the corresponding nutrient (nitrate) concentration. The subscript 0 refers to the initial concentration of phytoplankton and nutrient, $P$ and $N$ are averages over the euphotic zone. The change in the concentrations will be described by a rate constant, k, or

$$dN/dt = -kNP,$$

$$dP/dt = kNP.$$

This is functionally the same as logistic growth. The solutions are

$$P = \frac{(N_0 + P_0)}{1 + (N_0/P_0)\exp[-kt(N_0 + P_0)]}, \tag{3}$$

$$N = \frac{(N_0 + P_0)}{1 + (P_0/N_0)\exp[kt(N_0 + P_0)]}. \tag{4}$$

The results from this model of phytoplankton growth along with the observations from the time of the nitrate perturbation (which defines $N_0$ and $P_0$) to the end of the observations are shown in Fig. 5. The initial values were chosen from three-point running means of the chlorophyll and nitrate values at the time of the mixing event. The mid-point of this running mean, or time-zero, is 1200 on 5 April.

As can be seen in Fig. 5, a given choice of k (in this case, 0.7) can provide a trajectory of chlorophyll increase consistent with the data. However, the nitrate removal is poorly represented. Figure 5 also shows an acceptable fit to the observed nitrate data, but the

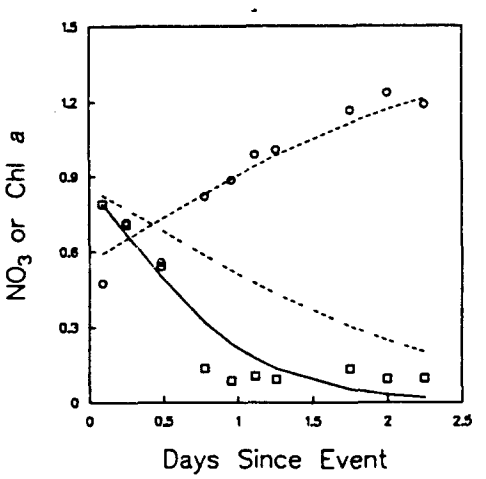


Fig. 5. Three-point running means of nitrate (squares) and Chl *a* concentrations (circles) averaged over 0–55 m, plotted as a function of time since the mixing event (time = 0 is 1200 on 5 April), and compared to the output from the batch-culture growth model described in the text. Dashed line: predicted chlorophyll for k = 0.7; triple dashed line: predicted nitrate for k = 0.7; solid line: predicted nitrate for k = 1.5.

rate constant for nitrate removal must be set at two times the rate constant for chlorophyll growth (k = 1.5). In other words, nitrate is taken up faster than the phytoplankton are growing. This kind of result has been observed in laboratory investigations (e.g. CAPERON and MEYER, 1972a,b; EPPLEY and RENGER, 1974; DROOP, 1977; CUNNINGHAM and MAAS, 1978; MCCARTHY and GOLDMAN, 1979; COLLOS, 1982b; DORTCH, 1982; PARSLOW *et al.*, 1984). The lack of agreement between the kinetics of nutrient uptake and the instantaneous transformation into growth is strong evidence that nutrient uptake and cell growth are uncoupled, thus leading to the inadequacy of this model.

*Model based on the cell quota*

The uncoupling of the nutrient uptake and algal growth implies that models of phytoplankton dynamics in nutrient-limited systems require a delay mechanism. This delay can be expressed in terms of a convolution integral, that is, weighting nutrient uptake according to past values of nutrient (CAPERON, 1969). Or, the delay can be expressed by postulating that nutrient uptake is governed by ambient concentration of nutrient, but that growth is governed by nutrient already assimilated. This latter expression of delay has more meaning physiologically. Growth governed by internal cellular pools of nutrient is incorporated in the cell-quota model (CAPERON, 1968; DROOP, 1968).

The governing equations describing the change in nitrate, chlorophyll and cell quota for this model are given by,

$$[\text{Chl } (\mu g)] \equiv [N(\mu\text{g-at.})],$$

$$dN/dt = -V_N \cdot (\text{Chl}), \tag{5}$$

$$d(\text{Chl})/dt = \mu \cdot \text{Chl}, \tag{6}$$

$$dQ/dt = V_N - (\mu \cdot Q). \tag{7}$$

Nitrate uptake ($V_N$) and growth ($\mu$) are given by

$$V_N = V_N\text{max}[N/(K_N + N)]; \quad (8)$$

$$\mu = \mu\text{max}[(Q - kq)/Q]; \quad (9)$$

where $K_N$ is the Michaelis constant for nitrate uptake. This model requires two new pieces of information not readily available from field observations: the maximum growth rate ($\mu$max) and the minimum cellular quota (kq), the internal nitrogen concentration in the cells below which growth cannot occur. The model generates the cell quota (the amount of nutrient in the cell), $Q$, a parameter not measured in this field study. In the application of this model we have used literature values for the former two parameters (CAPERON and MEYER, 1972a; GOLDMAN and GLIBERT, 1981), and set initial values of kq and $\mu$max to 0.2 $\mu$mol and 0.6 day$^{-1}$, respectively. The other initial conditions are given by the observations, with the zero time for the simulation given as 1800 on 5 April. The uptake rates for nitrate are found by non-linear regression of the disappearance of nitrate after the mixing event (e.g. CAPERON and MEYER, 1972b), using the integral form of equation (8) above,

$$t(V_N\text{max}) = (N_0 - N) + K_N[\ln(N_0/N)], \quad (10)$$

where $N_0$ is the nitrate concentrations at time zero. $V_N$max was found to be 0.82 $\mu$mol l$^{-1}$ day$^{-1}$ and $K_N$, 0.21 $\mu$mol l$^{-1}$ using this technique on the smoothed data. Chlorophyll is assigned a growth rate based on the $^{14}$C-uptake experiment conducted on 5 April, and the observed C/Chl ratio of 55, using the equation (EPPLEY, 1972),

$$\mu = (1/t)\ln\{[(C/Chl) + (\Delta C/Chl)]/(C/Chl)\}, \quad (11)$$

where $\Delta$C/Chl is the carbon assimilation from the $^{14}$C-uptake experiment normalized to chlorophyll. Equations (5), (6) and (7) were solved numerically with a time-step of 1 h.

Figure 6 shows the results of this model for the time period following the onset of mixing. The simulation adequately predicts the end-points for both chlorophyll and nitrate; however, there is a period at day 1 of the simulation where both growth and nitrate removal are underestimated by this model. This may be because additional factors affect the short-term growth variations. For example, irradiance variability, both diurnally and from day-to-day, may be responsible for short-term variations in growth. Alternatively, even in laboratory chemostats, the cell-quota model has been found to be inconsistent with observed behavior of phytoplankton biomass and nutrient concentration (e.g. BURMASTER, 1979). Even if the details of the time-course are in error, the important result here is that the derived nutrient uptake and growth parameters provide a consistent explanation for the behavior of both nitrate and chlorophyll.

Alternatively, it could be that the delay we have postulated through the cell-quota model occurs simply as a result of uptake occurring during the night (Fig. 4). Nitrate uptake is generally thought to be strongly light-dependent (COLLOS and SLAWYK, 1980); however, in several investigations day–night variations in uptake do not occur. Diatoms have been shown to assimilate nitrate at night, particularly under conditions of nitrogen deficiency (EPPLEY and COATSWORTH, 1968; EPPLEY and RENGER, 1974; MALONE *et al.*, 1975; COLLOS, 1982a). There is evidence for dark uptake of nitrate from natural populations as well (DORTCH *et al.*, 1985). Operationally, dark uptake of nitrate is no different than how the cell-quota model manages the delay, but it could provide the delay

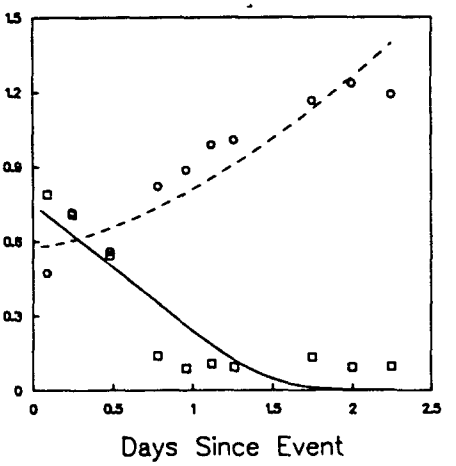


Fig. 6. Same as Fig. 5, except that the comparison is with the cell-quota model. Symbols as in Fig. 5.

mechanism. Indeed, EPPLEY and COATSWORTH (1968) concluded that nitrate taken up in the dark was not as readily assimilated as that taken up in the light.

*Interactions between two nutrients*

Consideration of earlier times than the wind-generated nitrate event requires that the changes observed in the silicate distributions be explained as well. Detectable concentrations of silicate are found prior to the time of the mixing event, when nitrate is absent or low, and while chlorophyll exhibits no appreciable net change. Given the subsequent production, apparently, growth of the phytoplankton prior to the mixing event was sufficient only to balance losses from grazing and sinking. After the mixing event, first nitrate is removed (Fig. 4a), then silicate (Fig. 4b), while Chl *a* increases (Fig. 4a). Thus the data suggest a possible switch in nutrient limitation between these two nutrients over the course of the observations.

The concept of a switch in nutrient limitation, that is, that the phytoplankton populations can be limited by only one nutrient at a time, has support from laboratory investigations. RHEE (1978), for example, has demonstrated conclusively that phytoplankton growth rates for different nutrients should be calculated separately. In other words, growth is regulated by the nutrient in shortest supply rather than by two nutrients together. This idea is implicit in the data of TERRY (1982) as well. These studies, however, concern nitrate and phosphate. Although there have been studies of the interaction of ammonium and silicate (or ammonium and nitrate), we are unaware of similar studies describing the interaction of nitrate and silicate. As pointed out by TERRY (1982) and others, nitrate uptake and assimilation requires significantly more energy than other nutrients because of the required steps to form amino-nitrogen. The concept of the nutrient switch supports Liebig's Law of the Minimum (REDFIELD *et al.*, 1963).

The cell-quota model has been elaborated to include silicate and to calculate the minimum growth rate between nitrate and silicate. Unlike the previous simulation (Fig. 6), however, we cannot treat the change in nutrients and chlorophyll in a dynamical way. For example, we would have to make further assumptions about the relationship between

silicate uptake and chlorophyll produced. Hence, we can only calculate a growth potential for each observational pair (silicate, nitrate) and illustrate the use of this model by identifying growth during the observational period as being regulated by nitrate or silicate.

For the purposes of illustration, we have determined the kinetic parameters for silicate in a similar manner to nitrate, applying equation (10) to the period of silicate removal on 6–7 April. The half-saturation constant and $V_{max}$ for silicate are 0.17 μmol $l^{-1}$ and 0.30 μmol $l^{-1}$ $day^{-1}$, respectively. As for nitrate, the same ratio of maximum cell quota of 5 was assumed. The outcome of the nutrient-switching model suggests that growth might be limited by silicate within the time frame noted by the arrows in Fig. 4b. That is, before and after the mixing event, growth of the phytoplankton population would be limited by nitrate rather than silicate, consistent with the relative distributions of the nutrients in the euphotic zone. The differences in growth rate predicted by this model are small enough ($<0.05$ $day^{-1}$) such that consistency of this model with the data must be regarded as tentative.

## CONCLUSIONS

The observed events can be summarized as follows. Because early in the time series, nitrogen is too low to allow net growth of the phytoplankton populations, silicate concentration remains detectable in the water column. The mixing event increases nitrate, and once the phytoplankton demand for nitrate is met, the cells are prepared to grow, and they assimilate silicate while doing so. Ultimately, nitrogen appears to limit the accumulation of biomass (and new production) here. For other locales [e.g. upwelling areas: see KAMYKOWSKI and ZANTARA (1985), DUGDALE *et al.* (1981), and others], silicate can be the more important nutrient for explaining biomass changes.

For modeling of phytoplankton-nutrient dynamics, the data suggest that over time scales of a few days or less, additional information regarding cellular nutrient quotas and maximum growth rates are required to simulate local dynamics. However, accepting the proviso that N/Chl $\approx$ 1, the data also show a balance of nitrate removal and chlorophyll increase over time scales longer than this. Therefore, at longer time scales, the simpler models (i.e. those which assume growth of phytoplankton biomass proportional to nutrient loading) will serve adequately. In this category are, for example, the seasonal models of phytoplankton production and loss (KIEFER and KREMER, 1981) and the basin-scale model reported by WROBLEWSKI *et al.* (1988).

On shorter time scales, there is an increased cost in modeling due to the additional parameters employed in the cell-quota model. From a practical standpoint, it is not clear that the increased realism we have attained at the day-to-day time scale will be generally applicable if there is little confidence in the kinetic parameters required.

Finally, we emphasize the transience of the event we observed. The nitrate appeared and was removed in less than a day, and had the sampling been any less frequent, the event would have appeared as noise rather than signal. EPPLEY and RENGER (1988) also report an event such as that observed here, of smaller magnitude but similar transience, that is about a day. This consideration supports the need for high frequency sampling in the ocean environment (DICKEY, 1988) to understand the processes regulating phyto-plankton growth and loss.

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