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Nitrogen fixation within a tropical upwelling ecosystem: Evidence for a Redfield budget of carbon/nitrogen cycling by the total phytoplankton community

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Abstract. Recent measurements and paradigms suggest that (1) the uptake of dissolved carbon and nitrate by phytoplankton may be greater than the Redfield ratio of 6.6 and (2) the oceans may be losing nitrogen from an imbalance in the global rates of nitrogen fixation and denitrification. An analysis of concurrent $\Delta\text{DIC}/\Delta\text{NO}_3$ depletion ratios within the Venezuelan and Peruvian upwelling ecosystems, indeed, suggests that values of 10.1–28.6 may pertain to these tropical eutrophic habitats. Nitrogen fixation may provide a Redfield balance in at least the former system, with 34–77% of the new production attributed to assimilation of N_2 . Independent confirmation of such new production on the Venezuelan shelf is provided by the interannual increases of H_2S and DIC within the adjacent Cariaco Trench.

Introduction

With the exception of Cooper's [1933a, b] observations during 1930–1932 in the English Channel, few time series of total dissolved inorganic carbon (DIC) ($\text{CO}_2 + \text{HCO}_3 + \text{CO}_3$) and nitrate depletion by phytoplankton were available, when the Redfield ratio of element utilization was formulated in the same time period, from 1933 data on DIC/ NO_3 regeneration in the Sargasso Sea [Redfield, 1934]. Despite Cooper's mean $\Delta\text{DIC}/\Delta\text{NO}_3$ depletion ratio of 20.4 at three stations during February–August and citation of his first paper by both Redfield [1934] and Redfield *et al.* [1963], early and more recent models of carbon/nitrogen (C/N) cycling by marine plankton continued to invoke a “standard” C/N ratio of 6.6 by atoms [Richards, 1975; Walsh and Dieterle, 1994]. It was thus somewhat of a “surprise” [Sambrotto *et al.*, 1993; Banse, 1994] when field studies of the 1980s found the same high ratios of the DIC/ NO_3 stocks left behind in the water column.

The modern time series of in situ $\Delta\text{DIC}/\Delta\text{NO}_3$ depletion ratios were first taken within polar regions of the Bering and Bellingshausen Seas [Codispoti *et al.*, 1986; Karl *et al.*, 1991], where all types of cyanophytes are thought to be rare at temperatures of $<10^\circ\text{C}$ [Bidigare *et al.*, 1992; Azam *et al.*, 1991]. These high-latitude field estimates suggested atomic C/N uptake ratios of ~ 12.2 during new production, similar to a mean of 10.2 encountered during diatom blooms on Georges Bank and in the North Atlantic [Sambrotto and Langdon, 1994], that is, almost twice the Redfield ratio. Previous discrepancies in $^{14}\text{C}/^{15}\text{N}$ estimates of element assimilation by phytoplankton had been rationalized by invoking either other sources of organic nitrogen [Walsh and Howe, 1976] or uptake of nitrogen at lower light levels [Walsh and McRoy, 1986].

Since the DIC left throughout the water column during a diatomaceous bloom is mainly a balance of what is removed in photosynthesis and the amount respired during recycling of ammonium and urea, the $\Delta\text{DIC}/\Delta\text{NO}_3$ ratio is considered to be

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that of new production; calcite formation, nitrification, and air-sea exchange should then all be relatively small factors. Organic sources of nitrogen and depth-dependent photosynthesis are thus also unimportant, leaving open the possibility of phytoplankton excretion with high dissolved organic carbon (DOC)/dissolved organic nitrogen (DON) ratios; unfortunately, the usual release rates are $\sim 5\%$ of those of primary production [Walsh, 1995].

Another time series in a subtropical region of a mean surface temperature of 23°C yields even larger in situ C/N uptake ratios of >100 at undetectable nitrate concentrations of $<0.05 \mu\text{g-atoms}$ at $\text{NO}_3 \text{ kg}^{-1}$ in the Sargasso Sea [Michaels *et al.*, 1994; Bates *et al.*, 1996]. Nitrogen fixation is invoked as a source of new production around Bermuda, in the absence of much nitrate and with dismissal of significant atmospheric deposition of DON [Cornell *et al.*, 1995]. The large colonial diazotroph *Trichodesmium thiebautii* is thought to be rare here [Carpenter and Romans, 1991], however, but the smaller cyanophyte *Synechococcus* spp. does fix nitrogen, at least in laboratory cultures [Mitsui *et al.*, 1986, 1987].

Within oligotrophic tropical waters of 25°C around Hawaii, recent increases of primary production and of dissolved organic matter have been attributed to greater abundance and nitrogen fixation of *T. thiebautii* [Karl *et al.*, 1995]. This diazotroph is common at $>20^\circ\text{C}$ and reaches its maximal growth rates at $25^\circ\text{--}30^\circ\text{C}$ [Carpenter and Romans, 1991]. If nitrogen fixation is also important in eutrophic tropical waters, where $>5 \mu\text{g-atoms NO}_3 \text{ kg}^{-1}$ can be found at the surface, we must change our past views of nitrogen limitation in marine ecosystems, even on the continental shelves [Walsh, 1991].

One last time series of $\Delta\text{DIC}/\Delta\text{NO}_3$ depletion has also been ignored within coastal waters, those off Venezuela [Okuda, 1975; Avila-Meleán, 1976]. Most importantly, it was located (station 1 of Figure 1) next to a natural sediment trap of the Cariaco Trench [Richards, 1975], which will provide us with an independent assessment of the new production during this time series. More recent carbon dioxide and nutrient data provide an assessment of the reliability of these early observations as well [Hastings and Emerson, 1988; Zhang and Millero, 1993; M. Bacon, personal communication, 1996].

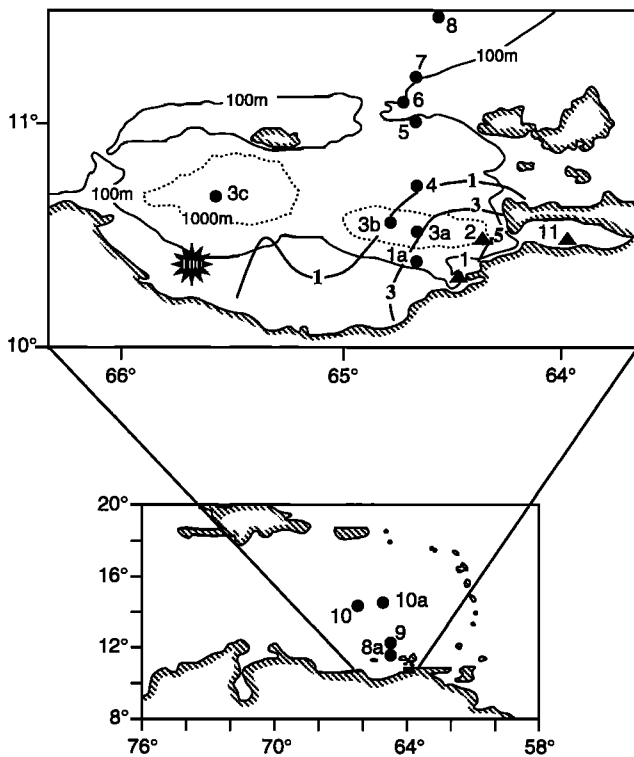


Figure 1. The location of time series (solid triangles) and stations (solid circles) within the coastal upwelling ecosystem of the southern Caribbean Sea, with respect to an upwelled plume of nitrate ($>1 \mu\text{g-atom NO}_3 \text{ L}^{-1}$) at 20 m during November 1982 [Garcia et al., 1983] and a bloom of *Gymnodinium splendens* ($>100 \text{ cells } 50 \text{ mL}^{-1}$) during October 1982 [Ferraz-Reyes, 1983].

Methods

Within tropical upwelling waters of the southern Caribbean Sea (Figure 1), surface temperatures range seasonally, from 23° to 28°C, with an annual mean of 25°C, about 2°C lower than offshore waters. Here one time series (Figure 2) of in situ $\Sigma\text{CO}_2/\text{NO}_3$ depletion during 1973–1974 [Okuda, 1975; Avila-Meleán, 1976] is available from the coastal upwelling ecosystem on the inner Venezuelan shelf, south of the Cariaco Trench, where additional information exists on the distributions of DIC [Deuser, 1973], nutrients [Richards, 1960, 1975; Garcia et al., 1983], nitrogen gas [Richards and Benson, 1961; Cline, 1973], and phytoplankton species composition [Margalef, 1965; Ferraz-Reyes, 1983].

During 18 sampling periods between April 1973 and March 1974, nitrate was measured at 10-m depth intervals above the 90-m isobath of the Gulf of Santa Fe by a spectrophotometric method [Strickland and Parsons, 1972]. The concurrent DIC stocks were indirectly estimated [Postma, 1964] by alkalinity and a pH meter with a precision of 0.01 [Strickland and Parsons, 1972]. Another 20 stations were taken here for additional nutrient analyses between August 1972 and April 1975 [Okuda, 1975].

During 1982, nitrate was again measured with both the same method [Garcia et al., 1983] and by autoanalyzer (M. Bacon, personal communication, 1996). DIC was then measured directly with potentiometric titration [Hastings and Emerson,

1988], compared to a coulometric technique employed later in 1990 [Zhang and Millero, 1993].

Prior measurements of nitrate in 1963–1965 used a similar cadmium column method [University of Washington (UW), 1970], while DIC was observed in 1971 with a direct volumetric method [Deuser, 1973]. I used the 1965 measurements of alkalinity and pH [UW, 1970] to calculate DIC and $p\text{CO}_2$ with more recent solubility and dissociation coefficients [Peng et al., 1987], instead of the Buch et al. [1932] equations and tables of the UW [1970] data report. Finally, dissolved organic phosphorus (DOP) was measured in the Venezuelan and Peruvian upwelling systems by the respective methods of Ketchum et al.

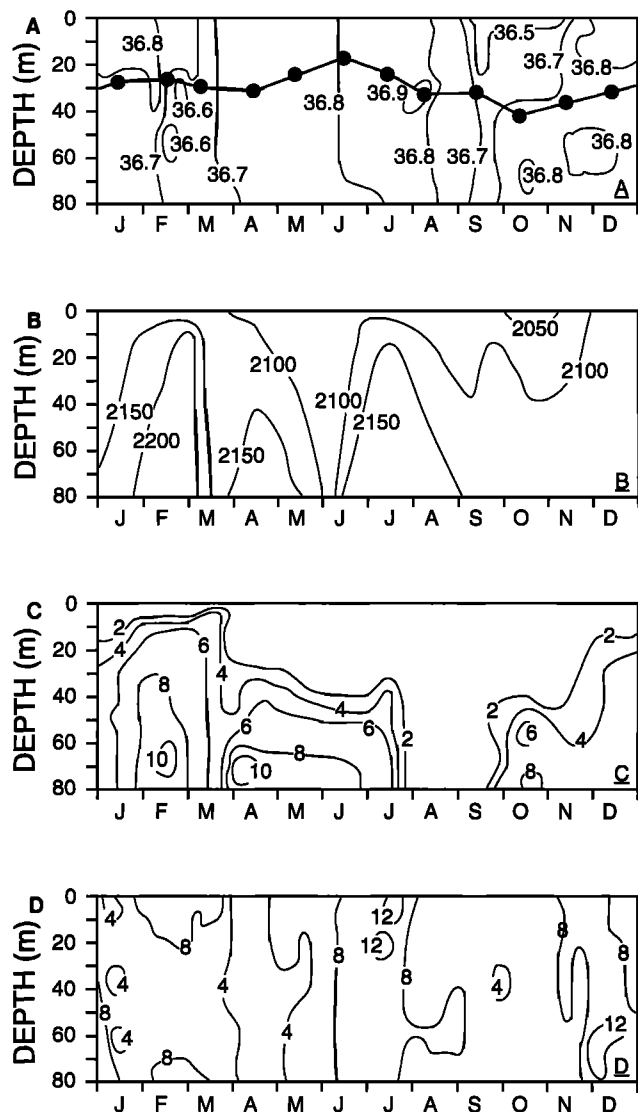


Figure 2. Times series of (a) salinity and depth of the euphotic zone (1% isolume, solid circles), (b) total dissolved inorganic carbon ($\mu\text{g-atoms } \Sigma\text{CO}_2 \text{ kg}^{-1}$), (c) nitrate ($\mu\text{g-atoms NO}_3 \text{ kg}^{-1}$), and (d) dissolved organic nitrogen ($\mu\text{g-atoms DON kg}^{-1}$) above the 90-m isobaths on the inner Venezuelan shelf, south of the Cariaco Trench, at 10°18'N, 64°29'W (time series 1 of Figure 1) and in the Gulf of Cariaco at 10°28'N, 63°58'W (times series 11 of Figure 1) during 1973–1974 [Okuda, 1975; Avila-Meleán, 1976; Benitez-Alvarez and Okuda, 1985].

[1955] and Menzel and Corwin [1965]; all analysts used the phosphate technique of Murphy and Riley [1962].

Offshore at stations 10a and 10 (Figure 1) during November 1965 and 1982, respectively, the different nitrate methods yielded a mean ($n = 13$) difference of $0.82 \mu\text{g-atoms NO}_3 \text{ kg}^{-1}$ over depths of 150 m to 1300 m, that is, 10% of the nitrate content of upwelling source waters at 200 m. The differences were random, with the 1965 data larger than the 1982 observations in 54% of the cases and smaller in 46%; thus no corrections were made to these nutrient data. The two DIC estimates over the same depth interval at $\sim 14^\circ 35' \text{N}$ and over the upper 200 m at $\sim 10^\circ 35' \text{N}$ differed by only a mean ($n = 20$) of $12.5 \mu\text{g-atoms } \Sigma\text{CO}_2 \text{ kg}^{-1}$, about 0.6% of the DIC stock at 200 m in the Caribbean Basin. The differences were again random (35% negative, 65% positive), such that the data from all of these stations were used to form a consistent view of fall upwelling conditions within the composite November section.

Similarly, $2200 \mu\text{g-atoms } \Sigma\text{CO}_2 \text{ kg}^{-1}$ were found both at a depth of 75 m during July 1973 at station 1 on the 90-m isobath, with the indirect DIC method of the time series [Avila-Meleán, 1976], and at 100 m in the adjacent Cariaco Trench during July 1971, with the direct DIC method [Deuser, 1973]. At a deeper depth of 800 m in the trench, we will also find that the different direct DIC methods give results which are consistent with sulfide data, measured the same way over a 25-year period [Cline, 1969]. I use these original data sets to assess the impact of nitrogen fixation on a Redfield balance of carbon/nitrogen cycling from the perspectives of (1) nitrate formation, (2) $\Delta\text{DIC}/\Delta\text{NO}_3$ depletion, (3) N_2 removal, (4) diazotroph abundance, (5) DON release, and (6) export utilization on the Venezuelan shelf and slope.

Results

Nitrate Formation

In response to seasonal migration of the Intertropical Convergence Zone [Muller-Karger and Aparicio, 1994], the weakest upwelling occurs along the Venezuelan coast during the rainy season of September–November [Okuda, 1975]. At the end of this period, only $1 \mu\text{g-atom NO}_3 \text{ kg}^{-1}$ and $2087 \mu\text{g-atoms } \Sigma\text{CO}_2 \text{ kg}^{-1}$ occur at a depth of 15 m (Figure 2) on the 90-m isobath of the inner shelf, upwelling from a shallow depth of 50 m within the trench. At a depth of 20 m a plume of $>1 \mu\text{g-atom NO}_3 \text{ kg}^{-1}$ extends westward (Figure 1) along the shelf break [Garcia et al., 1983].

Upwelling of dense ($\sim 26.3 \sigma_t$), nutrient-rich ($\sim 8.0 \mu\text{g-atoms NO}_3 \text{ kg}^{-1}$), and carbon-laden ($\sim 2157 \mu\text{g-atoms } \Sigma\text{CO}_2 \text{ kg}^{-1}$) waters then also occurs along the outer Venezuelan shelf, from source depths of 150–200 m within the salinity maximum (>36.5) of Subtropical Underwater in the Caribbean Basin (Figure 3). After passage over sill depths of 135–146 m the core of Subtropical Underwater penetrates the Cariaco Trench to shallow depths [Holmen and Rooth, 1990], where local nitrification occurs [Ward and Kilpatrick, 1991]. On the same $26.3 \sigma_t$ isopycnal surface in the trench, $\sim 12.0 \mu\text{g-atoms NO}_3 \text{ kg}^{-1}$ and $\sim 2180 \mu\text{g-atoms } \Sigma\text{CO}_2 \text{ kg}^{-1}$ are found at a depth of 150 m (Figure 3). A mean $\Delta\text{DIC}/\Delta\text{NO}_3$ increment of 5.8 at stations 3a, 3b, and 3c (Figure 1) approximates both the Redfield ratio of 6.6 and the body C/N of 6.1 for *Trichodesmium* colonies [McCarthy and Carpenter, 1979].

An increase of $4.0 \mu\text{g-atoms NO}_3 \text{ kg}^{-1}$ and a Redfield N/P ratio of 16 require a phosphorus source of $0.25 \mu\text{g-atoms P kg}^{-1}$ during this transit from basin to trench. Each element can

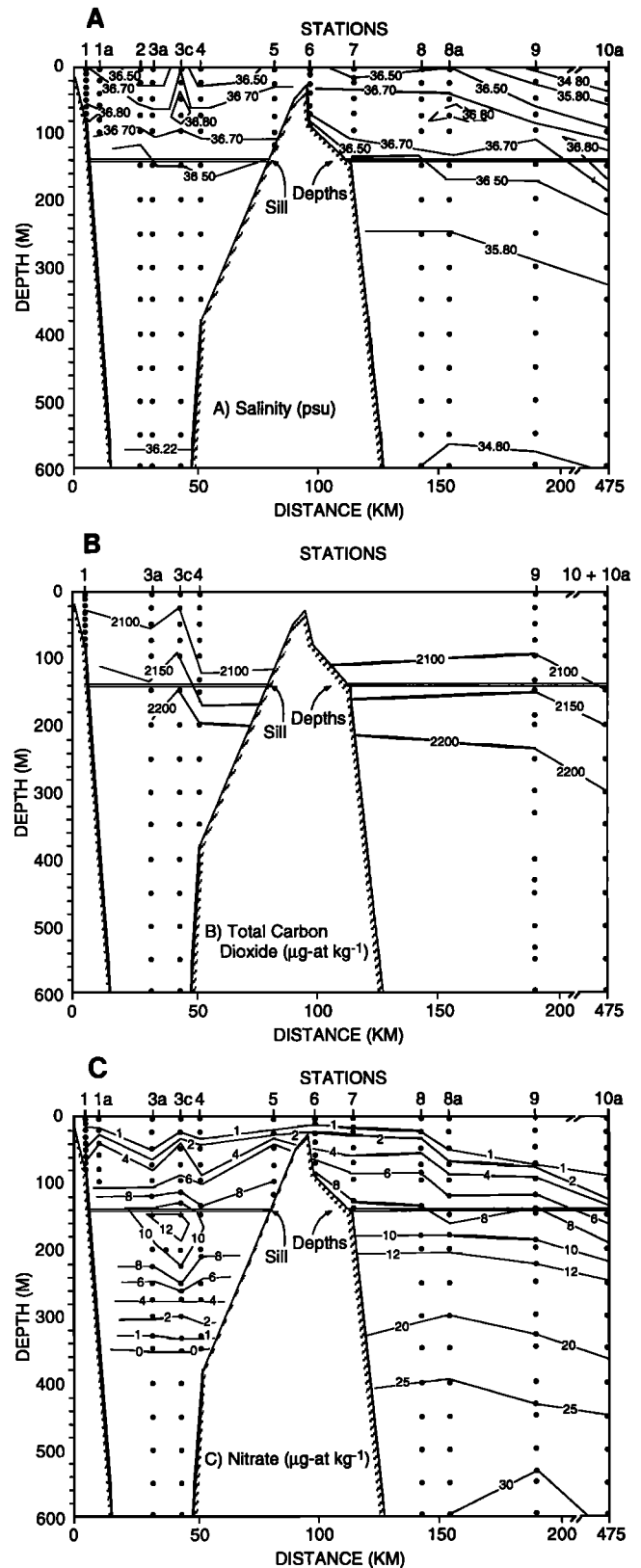


Figure 3. A composite November section of (a) salinity, (b) total dissolved inorganic carbon ($\mu\text{g-atoms } \Sigma\text{CO}_2 \text{ kg}^{-1}$), and (c) nitrate ($\mu\text{g-atoms NO}_3 \text{ kg}^{-1}$) along $\sim 64^\circ 40' \text{W}$, from $\sim 10^\circ 15' \text{N}$ to $\sim 14^\circ 30' \text{N}$ (see Figure 1), during November 1958 (stations 6 and 8), November 1963 (station 2), November 1965 (stations 3a, 4, 8a, 9, and 10a), November 1973 (station 1), and November 1982 (stations 1a, 3c, 5, 7, and 10).

Table 1. A Redfield Budget for Nitrogen Fixation Above the 90-m Isobath of the Inner Venezuelan Shelf at 10°18'N, 64°29'W During 120 Days of February–June and 45 Days of July–August 1973–1974

	February–June	July–August
Total Δ DIC loss	80.3	69.0
Δ NO ₃ loss	4.0	2.1
Total Δ C/ Δ N ratio	20.0	32.9
Δ CaCO ₃ loss	40.0	9.0
Organic Δ C/ Δ N ratio	10.1	28.6
Δ DIC ₀ – 6.6 Δ NO ₃ alternative new production	13.9	46.1
Δ N needed	2.1	7.0
Daily fixation	0.02	0.16
Percent new production	34	77

The total Δ DIC and Δ NO₃ losses are the observed differences in carbon and nitrogen stocks (μ g-atoms kg⁻¹) between February 15 and June 15 during strong upwelling and from July 17 to August 31 during weaker upwelling. The Δ CaCO₃ loss is the computed depletion of carbonate ion over the same periods and depths. The organic Δ C/ Δ N ratio and the Δ DIC₀ loss reflect subtraction of the inorganic uptake of carbonate from the total Σ CO₂ depletion. The total N₂ increment of Δ N and the daily fixation rate are those needed to allow a Redfield ratio (C/N of 6.6/1) during net photosynthesis attributed to new production, that is, the amount of growth based on nitrate and the alternative nitrogen gas.

be provided by diazotrophs within the overlying surface waters, since *Trichodesmium* displays alkaline phosphatase activity [Yentsch et al., 1972] and a high affinity for phosphomonoesters [McCarthy and Carpenter, 1979]. Within the upper 50 m of the Cariaco Trench and the Caribbean Basin, for example, DOP amounts to 83% of the total dissolved phosphorus. In the trench a mean ($n = 8$) of 0.26 μ g-atoms DOP kg⁻¹ is found over 0–50 m, compared to 0.04 μ g-atoms DOP kg⁻¹ ($n = 6$) at depths of 100–200 m [UW, 1970].

Water column production rates of biogenic CO₂ in the trench may be maximal in this oxic zone of particle decomposition [Fry et al., 1991] at depths of 100–200 m, where the vertical gradient [Zhang and Millero, 1993] of DIC is the largest, $\sim 1.13 \mu$ g-atoms Σ CO₂ kg⁻¹ m⁻¹. Over anoxic depths of 350 m to 1400 m, the vertical gradient of DIC is instead only a mean of 0.31 μ g-atoms Σ CO₂ kg⁻¹ m⁻¹. An average ammonium oxidation rate of $\sim 0.025 \mu$ g-atoms NO₃ kg⁻¹ d⁻¹ over depths of 70–230 m [Ward and Kilpatrick, 1991] suggests that the 4 μ g-atoms NO₃ kg⁻¹ increment within the trench may be formed within 160 days, that is, on the same seasonal timescale of nitrogen fixation during net depletion of carbon dioxide.

Δ DIC/ Δ NO₃ Depletion

In the strongest upwelling period of February the mean nitrate stock is $\sim 6.4 \mu$ g-atoms NO₃ kg⁻¹ over the water column on the inner Venezuelan shelf (Figure 2), with a NO₃/PO₄ ratio of 16.6 [Okuda, 1975]. At the onset of the intermediate upwelling season in July the average new nitrogen is instead $\sim 3.0 \mu$ g-atoms NO₃ kg⁻¹, with a similar NO₃/PO₄ ratio of 16.3. At the end of the upwelling seasons in June and August the respective NO₃/PO₄ ratios are instead 13.8 and 7.2, perhaps reflecting the increasing importance of cyanophyte utilization of DOP.

These two periods of February–June and July–August are when a net depletion of DIC occurs off Venezuela (Figure 2), like in the English Channel [Cooper, 1933a, b]. To account for diffusive and upwelling resupply of nutrients to the euphotic

zone [Walsh and McRoy, 1986], I have averaged the total Δ DIC/ Δ NO₃ depletion ratio over the 90-m water column (Table 1). Between February and June this mean ratio is 20.0, compared to 32.9 during July–August.

Within offshore source waters of the Caribbean Basin at $\sim 14^\circ 35'N$, however, the vertical gradients of Σ CO₂ and nitrate instead yield a mean ($n = 6$) Δ DIC/ Δ NO₃ regeneration ratio of 6.3 over oxygenated depths of 150–700 m. Similarly, the Δ DIC/ Δ NH₄ regeneration ratio is 7.4 over anoxic depths ($n = 5$) of 350–800 m in the Cariaco Trench [Zhang and Millero, 1993]. Since these ratios and that of the increment during transit from the basin to the trench approximate the Redfield relation, the sources of organic matter should have a similar elemental composition. The larger depletion ratios of 20.0–32.9 may instead indicate a neglect of the different uptake processes of the diverse tropical phytoplankton, whose body C/N ratios are all about 6.6.

Within the second time series of the Cariaco Trench at 10°31'N, 64°23'W (station 2 of Figure 3), for example, diatoms predominate only during the dry season [Margalef, 1965], amounting to $\sim 70\%$ of the total phytoplankton abundance in March–April, compared to $\sim 15\%$ in October here and along the Venezuelan shelf [Hulburt, 1963, 1966; Hulburt and Corwin, 1969; Ferraz-Reyes, 1983]. Over the upper 20 m the March bloom of small *Nitzschia fragilissima* is followed (Figure 4) by summer-fall pulses of the large diatoms, *Rhizosolenia stolterfothi* and *Hemiaulus hauckii*. They can host the cyanophyte endosymbiont *Richelia intercellularis*, whose nitrogen fixation rivals that of *T. thiebautii* [Carpenter and Romans, 1991].

We must first consider the consequences of calcification by other phytoplankton, since inorganic precipitation of calcium carbonate by coccolithophores would also lower the DIC stocks in the euphotic zone. Indeed, the surface sediments are 15–22% CaCO₃ in the trench, compared to 30–50% on the

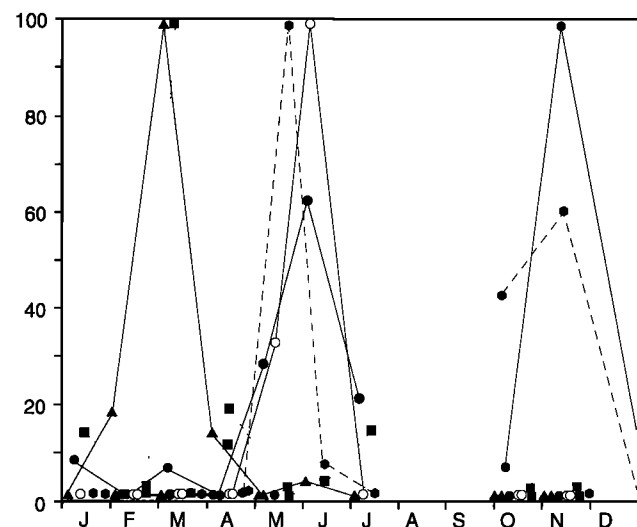


Figure 4. Time series of the relative seasonal abundance (percent of the maximum cells 50 mL⁻¹) within the upper 20 m of *Nitzschia fragilissima* (solid triangles), *Rhizosolenia stolterfothi* (solid circles), *Hemiaulus hauckii* (open circles), *Emiliana huxleyi* (solid squares), and *Trichodesmium thiebautii* (solid hexagons) above the 1100-m isobath in the Cariaco Trench, at 10°31'N, 64°23'W (time series 2 of Figure 1) during 1963–1965 [Margalef, 1965].

outer Venezuelan slope, adjacent to the basin [Lidz *et al.*, 1969].

All species of coccolithophores constitute only ~8% of the cell counts in both March and October above the trench [Margalef, 1965], however, compared to >50% of offshore populations [Hulbert, 1963, 1966; Hulbert and Corwin, 1969]. The seasonal abundance of *Emiliania huxleyi* within the upper 20 m of the trench peaks during March (Figure 4), reflecting the depletion of carbonate ion (Table 1) by $40 \mu\text{g-atoms CO}_3 \text{ kg}^{-1}$ during February–June, compared to $9 \mu\text{g-atoms CO}_3 \text{ kg}^{-1}$ in July–August on the adjacent shelf [Avila-Melean, 1976]. After subtraction of the inorganic deposition of CaCO_3 , the mean organic $\Delta\text{DIC}_0/\Delta\text{NO}_3$ depletion ratio within Venezuelan coastal waters is 10.1 during February–June and 28.6 in July–August (Table 1); these are similar to those found in temperate waters [Cooper, 1933a, b; Sambrotto and Langdon, 1994].

N₂ Removal

To maintain a Redfield balance during fixation of carbon and nitrogen, respective N₂ demands of 2.1 and $7.0 \mu\text{g-atoms N kg}^{-1}$ are required to support the rest of the DIC₀ decrements during the two periods (Table 1). Different sets of measurements of N₂/argon ratios in the trench indeed suggest that after bouts of nitrogen fixation, depletions of 2.9–4.0 $\mu\text{g-atoms N kg}^{-1}$ still remained over the upper 5 m during the rainy seasons of October 1972 and November 1957 [Richards and Benson, 1961; Cline, 1973].

During 120 days of February–June and 45 days of July–August, such N₂ demands imply daily fixation rates of 0.02–0.16 $\mu\text{g-atoms N kg}^{-1} \text{ d}^{-1}$, which would contribute ~34% of the winter-spring new production and ~77% of the summer one (Table 1). An associated phosphorus requirement of the Venezuelan upwelling ecosystem might be 0.0013–0.0094 $\mu\text{g-atoms P kg}^{-1} \text{ d}^{-1}$, to be met perhaps by an inshore stock of at least $0.57 \mu\text{g-atoms DOP kg}^{-1}$, found at a depth of 26 m on station 3a (Figure 1). The surface concentration had been stripped to $0.15 \mu\text{g-atoms DOP kg}^{-1}$ in November 1965, implying a prior residence time of 44–323 days, based on the cyanophyte P demands and the DOP decrement.

The Peru upwelling system is fourfold to eightfold more productive [Walsh, 1988] than the Venezuelan one of 172–356 $\text{g POC m}^{-2} \text{ yr}^{-1}$ [Ballester and Margalef, 1965; Moigis, 1986], as a result of greater nitrate additions to the euphotic zone (Figure 5b). Consequently, the surface DOP stocks were a mean ($n = 16$) of $0.42 \mu\text{g-atoms DOP kg}^{-1}$ in April 1969 but only 28% of the total phosphorus pool at higher PO_4 concentrations (N. Corwin, unpublished data, 1970) than those of Venezuelan coastal waters [Okuda, 1975]. A higher mean ($n = 6$) of $0.72 \mu\text{g-atoms DOP kg}^{-1}$ was found in surface waters off Peru in April 1966 [Strickland *et al.*, 1967], and we shall find that cyanophytes may indirectly effect significant depletions of CO_2 (Figure 5a) here. In contrast, more recent measurements found only $0.20 \mu\text{g-atoms DOP kg}^{-1}$ within surface waters of another upwelling ecosystem off California [Jackson and Williams, 1985], where the primary production is at most $150 \text{ g C m}^{-2} \text{ yr}^{-1}$ [Walsh, 1988] and sea surface $p\text{CO}_2$ of only 298–438 μatm prevails [Friederich *et al.*, 1995].

Diazotroph Abundance

So where are these cyanophytes? The sampling techniques of the 1960s preclude an estimate of nitrogen fixation by chroococoid cyanobacteria within the Cariaco Trench, but they amount to 60–80% of carbon uptake in other subtropical and

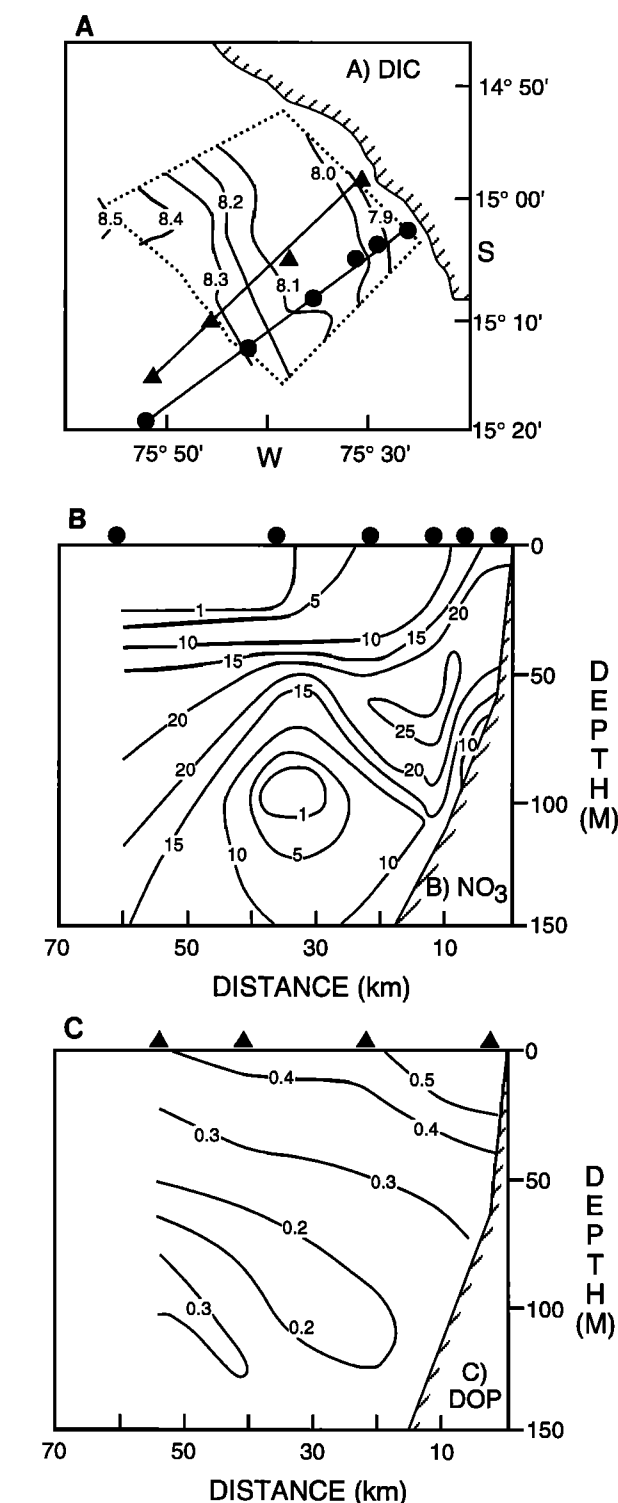


Figure 5. The stocks (ρH , $\mu\text{g-atoms kg}^{-1}$) of dissolved (a) carbon, (b) nitrate, and (c) organic phosphorus during May 1976 (solid circles) and April 1969 (solid triangles) off the Peru coast at ~15°S [Codispoti *et al.*, 1976; Simpson and Zirino, 1980; N. Corwin, unpublished data, 1970].

tropical ecosystems [Li *et al.*, 1983; Platt *et al.*, 1983]. An analysis of the large blue-green and endosymbiont abundances thus provides a minimal estimate of nitrogen fixation in Venezuelan waters.

Separate net samples at the Cariaco Trench time series

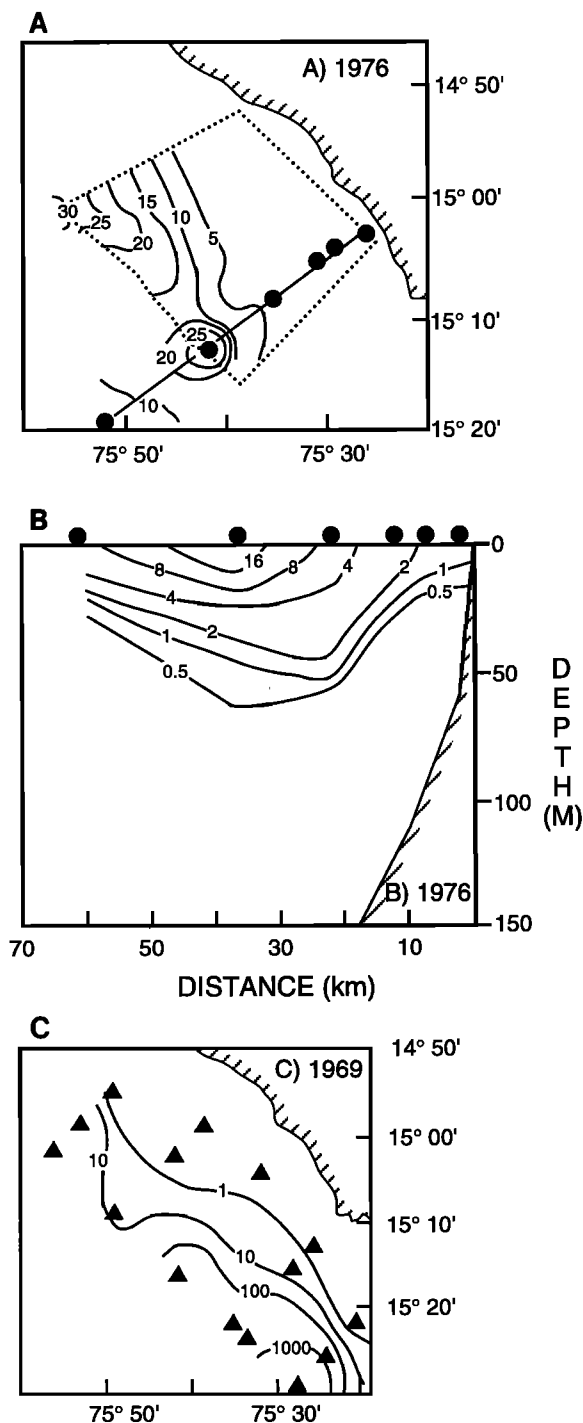


Figure 6. The distribution of total phytoplankton biomass ($\mu\text{g chl L}^{-1}$) (a) at the surface and (b) over the water column during May 1976 (solid circles) in relation to (c) the abundance (cells 50 mL^{-1}) of *Gymnodinium splendens* over the euphotic zone in April 1969 (solid triangles) off the Peru coast at $\sim 15^\circ\text{S}$ [Blasco, 1971; Codispoti *et al.*, 1976; Simpson and Zirino, 1980].

station (Figure 4) indicate that none of the surface population of phytoplankton was *Trichodesmium* during March 1963, compared to 84% in May–June and 92% in November [Margalef, 1965]. Near-surface abundances of these large blue-green algae of $25.8 \text{ cells mL}^{-1}$ in May and $15.2 \text{ cells mL}^{-1}$ in October amount to *T. thiebautii* colonies of $632\text{--}1075 \text{ m}^{-3}$ in the trench,

similar to prior observations in the southern Caribbean Sea [Carpenter and Romans, 1991]. The relatively low amount of ^{15}N within particulate organic nitrogen (PON) of trench surface waters, that is, a $\delta^{15}\text{N}$ of 1‰ [Fry *et al.*, 1991], may reflect the isotopic signature of -1.7‰ to 0.5‰ for *Trichodesmium* [Wada and Hattori, 1979]. At population growth rates of 0.1–1.0 doublings d^{-1} , $1000 \text{ colonies m}^{-3}$ could fix [Carpenter and Romans, 1991] as much as $0.01\text{--}0.10 \mu\text{g-atoms N kg}^{-1} \text{ d}^{-1}$ on the Venezuelan shelf.

At smaller populations of $1\text{--}2 \text{ cells mL}^{-1}$ of *H. hauckii* and *R. stolerfothi* during June (Figure 4), the endosymbionts could also fix [Villareal, 1990; T. A. Villareal, unpublished data, 1992], respectively, $0.003\text{--}0.030 \mu\text{g-atoms N kg}^{-1} \text{ d}^{-1}$. The potential N_2 assimilation by the large cyanophytes and small endosymbionts might thus sum to at least $0.04\text{--}0.13 \mu\text{g-atoms N kg}^{-1} \text{ d}^{-1}$, compared to the results of the Redfield balance of $0.02\text{--}0.16 \mu\text{g-atoms N kg}^{-1} \text{ d}^{-1}$ (Table 1). Unknown picoplankton assemblages of *Synechococcus* could add to such nitrogen fixation within the trench and on the adjacent shelf as well.

DON Release

As a consequence of nitrogen fixation by *T. thiebautii*, DON accumulates in the water column [Karl *et al.*, 1995], since as much as 50% of the assimilated N_2 is released as DON [Glibert and Bronk, 1994]. During the same months of 1973–1974 above the 90-m isobath at station 11 in the nearby Gulf of Cariaco (Figure 1), another time series was obtained [Okuda *et al.*, 1978; Benítez-Alvarez and Okuda, 1985]. The seasonal vertical structure of nitrate, in response to upwelling within the upper 60 m, at station 11 replicated that of station 1 (Figure 2c) and is not shown.

The pulse of $\sim 9 \mu\text{g-atoms DON kg}^{-1}$ during March in the gulf (Figure 2d) is associated with the diatom bloom in the adjacent trench (Figure 4), where $64\text{--}73 \mu\text{g-atoms DOC kg}^{-1}$ were found within surface waters in March 1972 [Karl *et al.*, 1977]. Redfield ratios of DOM [Jackson and Williams, 1985] suggest a similar labile stock of $59 \mu\text{g-atoms DOC kg}^{-1}$ and $0.56 \mu\text{g-atoms DOP kg}^{-1}$ in the gulf, as measured at station 3a in the trench [UW, 1970]. The observed species succession (Figure 4) may, in part, be affected by winter release of DOP by diatoms, with smaller excretion rates of $\sim 5\%$ [Walsh and Dieterle, 1994].

The larger stocks of $>12 \mu\text{g-atoms DON kg}^{-1}$ in June and December (Figure 2d) instead follow the *Trichodesmium* pulses of abundance (Figure 4) within Venezuelan waters. Nutrient releases have been found after premonsoon blooms of these cyanophytes in the Arabian upwelling ecosystem at $\sim 15^\circ\text{N}$ as well [Devassy *et al.*, 1978]. Within the Peru upwelling ecosystem at $9^\circ\text{--}16^\circ\text{S}$, where the dinoflagellate *Gymnodinium splendens* is an abundant red tide organism [Walsh *et al.*, 1980], a mean ($n = 6$) of $31.0 \mu\text{g-atoms DON kg}^{-1}$ was found in surface waters, compared to $2.8 \mu\text{g-atoms DON kg}^{-1}$ at 100 m [Strickland *et al.*, 1967]. The DON/DOP ratio at a depth of 100 m was 14.9, in contrast to 43.1 at the surface, reflecting presumed cyanophyte release of DON, which may be a nitrogen source for blooms of *G. splendens* in an otherwise oligotrophic habitat (Figure 6).

Such DON also serves as a substrate for ammonium regeneration in the euphotic zone, nitrate formation in the aphotic zone, and N_2 evolution above the anoxic interface of the trench, as part of the recycling processes associated with respiration of DOC to CO_2 . The remaining POC/PON, which

reflects separate new productions of diatoms, coccolithophores, cyanophytes, and dinoflagellates, instead falls out of the water column.

The net organic depletion of DIC stocks of 68 μg -atoms particulate organic carbon (POC) kg^{-1} during 120 days of February–June and of 63 μg -atoms POC kg^{-1} over 45 days of July–August at depth of 15 m (Figure 2b) is considered to be a total new production of 131 μg -atoms POC $\text{kg}^{-1} \text{yr}^{-1}$. Over a mean euphotic zone of 30 m on the shelf (Figure 2a), similar to those of 27 m in the Gulf of Cariaco and 34 m within the trench [Ballester, 1965; Moigis, 1986], the depth-integrated new production is thus 48.3 g POC $\text{m}^{-2} \text{yr}^{-1}$. The total annual photosynthesis of 172–356 g POC $\text{m}^{-2} \text{yr}^{-1}$, estimated from ^{14}C incubations, then suggests a range in total f ratio of 0.14–0.28 for uptake of $(\text{N}_2 + \text{NO}_3)/(\text{N}_2 + \text{NO}_3 + \text{NH}_4)$, compared to a standard nitrate-based f ratio of 0.07–0.14.

Export Utilization

In the absence of sediment trap data to validate estimates of export production [Michaels *et al.*, 1994], the increasing accumulation of elements below sill depth of the trench [Scranton *et al.*, 1987] is instead exploited to assess my estimate of total new production of 48.3 g POC $\text{m}^{-2} \text{yr}^{-1}$. Since there is little indication of CaCO_3 dissolution within the anoxic water column of the trench [Hastings and Emerson, 1988], the interannual increments of DIC here are attributed to decomposition of organic export, that is, the amount of new production derived from both nitrate assimilation and nitrogen fixation.

Within the deep (>1200 m) waters of the trench, for example, the measured increments of hydrogen sulfide over 35 years are $\sim 1.12 \mu\text{g}$ -atoms $\text{H}_2\text{S} \text{kg}^{-1} \text{yr}^{-1}$ [Zhang and Millero, 1993]. A stoichiometric model of sulfate reduction of organic matter [Richards, 1975], that is, an atom ratio of 2.0 for C/S, then suggests that 2.24 μg -atoms $\Sigma\text{CO}_2 \text{kg}^{-1} \text{yr}^{-1}$ are also formed. At a shallower depth of 800 m, DIC stocks in 1971 (2237 μg -atoms $\Sigma\text{CO}_2 \text{kg}^{-1}$), 1982 (2247 μg -atoms $\Sigma\text{CO}_2 \text{kg}^{-1}$), and 1990 (2372 μg -atoms $\Sigma\text{CO}_2 \text{kg}^{-1}$) similarly suggest a mean decomposition rate of 2.02 μg -atoms $\Sigma\text{CO}_2 \text{kg}^{-1} \text{yr}^{-1}$ [Deuser, 1973; Hastings and Emerson, 1988; Zhang and Millero, 1993]. Extrapolation of an average particle degradation rate of 2.13 μg -atoms $\Sigma\text{CO}_2 \text{kg}^{-1} \text{yr}^{-1}$ over the 1365-m aphotic zone, through both the 315-m oxic region of nitrification (35–150 m) and denitrification (150–350 m) and the 1050-m anoxic regime of sulfate reduction (350–1400 m), yields a depth integral of POC demand within the trench of at least 35.8 g POC $\text{m}^{-2} \text{yr}^{-1}$, similar to a prior maximal estimate of oxidation in deep water [Deuser, 1973].

The ^{210}Pb sedimentation rate in the trench is $\sim 0.05 \text{cm yr}^{-1}$ where carbon contents of 3% dry weight (dw) prevail [Wakeham and Ertel, 1988]; the geological estimate of the long-term sedimentation rate in the trench is similarly 0.05cm yr^{-1} [Heezen *et al.*, 1959]. A porosity of 67% [Jacobs *et al.*, 1987] and these sediment properties yield a carbon burial rate [Walsh *et al.*, 1985] of 12.9 g POC $\text{m}^{-2} \text{yr}^{-1}$ at the bottom of the trench. Such a total export demand of 48.7 g POC $\text{m}^{-2} \text{yr}^{-1}$ within the aphotic zone of the trench confirms the above estimate of new production derived from import of nitrogen from both the shelf break and the atmosphere.

Discussion

Prior estimates of carbon sequestration in both oligotrophic and eutrophic ecosystems over 30°N – 30°S , outside of anoma-

lous equatorial upwelling regimes, assumed that a polar paradigm of nitrate-driven new production also determined export of tropical carbon to the deep sea [Taylor *et al.*, 1991; Walsh and Dieterle, 1994]. Such hubris reflects the dearth of ecosystem studies in tropical waters, compared to those in temperate, or even, polar waters. Analysis of disparate data sets from the Venezuelan upwelling ecosystem now suggests that nitrogen fixation may instead account for 34% of the new production during strong upwelling and 77% during weaker influxes of nitrate. Nitrogen fixation may also explain the unexpected observations of undersaturated CO_2 conditions at seven of nine stations within upwelled waters along the Chile coast [Kelley and Hood, 1971].

During May 3, 1976, an underway map of surface pH [Simpson and Zirino, 1980] and a nitrate section [Codispoti *et al.*, 1976] were taken off the Peru coast at $\sim 15^\circ\text{S}$ (Figure 5), where prior DOP data were collected in April 1966 and 1969 [Strickland *et al.*, 1967; N. Corwin, unpublished data, 1970]. Assuming an alkalinity of 2335 $\mu\text{eq kg}^{-1}$ at a constant salinity of 34.96 yields [Peng *et al.*, 1987] $p\text{CO}_2$ values of 291–1091 μatm for endpoints of 7.8–8.3 pH (Figure 5a) and of 19.5° – 20.5°C temperature, similar to Simpson and Zirino's [1980] calculations. The associated surface DIC stocks are 2001–2244 μg -atoms $\Sigma\text{CO}_2 \text{kg}^{-1}$, which, together with a nitrate gradient of 0.1–17.0 μg -atoms $\text{NO}_3 \text{kg}^{-1}$ (Figure 5b), generate a $\Delta\text{DIC}_0/\Delta\text{NO}_3$ depletion ratio of 14.4 for this sampling of the Peru upwelling ecosystem.

A Redfield utilization of just the upwelled DIC and NO_3 stocks would have led to supersaturated $p\text{CO}_2$ conditions off Peru, instead of the undersaturation found here (Figure 5a). Such a Redfield balance requires a total nitrogen depletion of 36.8 μg -atoms N kg^{-1} , of which the needed 19.9 μg -atoms DON kg^{-1} can be obtained from the observed surface pool of $\sim 31.0 \mu\text{g}$ -atoms DON kg^{-1} along the Peru coast [Strickland *et al.*, 1967]. A similar total phosphorus demand of 2.30 μg -atoms P kg^{-1} can be met by the stocks of $\sim 0.42 \mu\text{g}$ -atoms DOP kg^{-1} (Figure 5c) and 2.18 μg -atoms $\text{PO}_4 \text{kg}^{-1}$ [Codispoti *et al.*, 1976].

Blooms of *G. splendens* were found in offshore Peruvian waters (Figure 6) during both April 1969 [Blasco, 1971] and May 1976 [Simpson and Zirino, 1980; Walsh *et al.*, 1980], and they, like *Ptychodiscus brevis* (*Gymnodinium breve*), may utilize DOP [Vargo and Shanley, 1985]. They do not fix nitrogen, however, and a biomass of $\sim 30 \mu\text{g chl L}^{-1}$ (Figure 5) represents an equivalent PON accumulation of $\sim 18 \mu\text{g}$ -atoms N kg^{-1} , without consideration of grazing losses. *G. splendens* is a favorite prey of anchovy larvae, and various estimates of zooplankton ingestion suggest a grazing loss of $\sim 52\%$ of the daily primary production within waters off Peru [Walsh *et al.*, 1980]. If 50% of the May 1976 phytoplankton population had been consumed, the total PON production would have been $\sim 36 \mu\text{g}$ -atoms N kg^{-1} , similar to the Redfield budget of $\Delta\text{DIC}/\Delta$ total N depletion.

The biomass maxima of 25–30 $\mu\text{g chl L}^{-1}$ were found at near-noon and near-midnight positions of 2- to 5-m depths (Figure 6b) [Barber *et al.*, 1978], however, exhibiting little evidence of diurnal migration to nutrient-rich layers of $\sim 5 \mu\text{g}$ -atoms $\text{NO}_3 \text{kg}^{-1}$ at 30 m (Figure 5b). With dinoflagellate swimming speeds of 1–2 m h^{-1} [Eppley *et al.*, 1968; Walsh *et al.*, 1974], a daily round-trip of 60 m would be difficult. We are thus left with the hypothesis that DON released by nitrogen fixers is partly responsible for both blooms of *G. splendens* and undersaturated $p\text{CO}_2$ conditions off Peru.

The same element transfer may occur between cyanophytes and red tide dinoflagellates in the weaker tropical upwelling ecosystem off Venezuela. Within the eastern Cariaco Trench, populations of *G. splendens* were not observed at the 1963–1965 time series [Margalef, 1965], similar to the flora of upwelling loci off Peru (Figure 6c). Instead, they were found downstream of the upwelling plume in October 1982 (Figure 1), when cyanophytes and dinoflagellates were the codominants of the phytoplankton community [Ferraz-Reyes, 1983]. At cell concentrations of 113/50 mL the Venezuelan populations of *G. splendens* are more than tenfold less than those off Peru, reflecting the range in upwelled nitrate stocks of <1 to >15 $\mu\text{g-atoms N kg}^{-1}$ in surface waters near the coast (Figures 3c and 5b).

Within Cooper's time series in the English Channel, a second drawdown of DIC occurred during July–August, when nitrate stocks were negligible [Cooper, 1933a]. Cyanophytes then constitute 20–30% of the phytoplankton biomass [Friate and Purdie, 1993] and primary production [Joint et al., 1986] of such stratified waters and are codominants with populations of the episodic red tide dinoflagellate, *Gyrodinium aureolum* [Hochman et al., 1995], which can utilize DON [Carlsson and Graneli, 1993]. Widespread fixation of the most abundant form of nitrogen in the sea may lead perhaps to (1) closure of presently unbalanced global nitrogen [Codispoti, 1995] and carbon [Walsh, 1991] budgets and (2) initiation of red tides within local oligotrophic habitats.

Indeed, the future biological uptake of atmospheric carbon dioxide in the sea may not proceed via the usual Redfield calculations of nitrate supply, since in situ stocks of N_2 are $\sim 800 \mu\text{g-atoms N kg}^{-1}$ in surface waters. At future global warmings of only $1^\circ\text{--}2^\circ\text{C}$, the areas of most likely impact would be subtropical and tropical regions of the ocean at temperatures $>20^\circ\text{C}$ between 30°N and 30°S , where *Trichodesmium* spp. now persist [Carpenter and Romans, 1991], if this large cyanophyte is the major diazotroph. A greater role for the small, ubiquitous *Synechococcus* spp. may lead to increased nitrogen fixation within temperate regions as well. In diatom-dominated polar areas, where a recent estimate of the $\Delta\text{DIC}/\Delta\text{NO}_3$ depletion ratio is only ~ 8.6 within the Bellingshausen Sea [Turner and Owens, 1995], global warming may have little impact on nitrogen fixation, unless the endosymbionts are a significant factor of the nitrogen economy at high latitudes.

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