4-15-1999

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Walsh, John J.; Dieterle, Dwight A.; Muller-Karger, Frank E.; Bohrer, Richard; Bissett, W. Paul; Varela, Ramon J.; Aparicio, Ruben; Diaz, Rafael; Thunell, Robert; Taylor, Gordon T.; Scranton, Mary L.; Fanning, Kent A.; and Peltzer, Edward T., "Simulation of Carbon-Nitrogen Cycling During Spring Upwelling in the Cariaco Basin" (1999). *Marine Science Faculty Publications*. 17.  
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Simulation of carbon-nitrogen cycling during spring upwelling in the Cariaco Basin

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Abstract. Coupled biological-physical models of carbon-nitrogen cycling by phytoplankton, zooplankton, and bacteria assess the impacts of nitrogen fixation and upwelled nitrate during new production within the shelf environs of the Cariaco Basin. During spring upwelling in response to a mean wind forcing of 8 m s⁻¹, the physical model matches remote-sensing and hydrographic estimates of surface temperature. Within the three-dimensional flow field, the steady solutions of the biological model of a simple food web of diatoms, adult calanoid copepods, and ammonifying/nitrifying bacteria approximate within ~9% the mean spring observations of settling fluxes caught by a sediment trap at ~240 m, moored at our time series site in the basin. The models also estimate within ~11% the average ¹⁴C net primary production and mimic the sparse observations of the spatial fields of nitrate and light penetration during the same time period of February–April. Stocks of colored dissolved organic matter are evidently small and diazotrophy is minimal during spring. In one summer case of the model with weaker wind forcing, however, the simulated net primary production is 14% of that measured in August–September, while the predicted detrital flux is then 30% of the observed. Addition of a cyanophyte state variable, with another source of new nitrogen, would remedy the seasonal deficiencies of the biological model, attributed to use of a single phytoplankton group.

1. Introduction

Complex ecological models, like the “real world,” are difficult to interpret. At the other extreme, simple nutrient-phytoplankton-zooplankton models may provide little insight into the consequences of altered composition of the phytoplankton bases of the marine food web. Coastal upwelling ecosystems of diatom-based short food webs, for example, were thought to be some of the most productive in the sea [Ryther, 1969], producing high fish yields from annual carbon fixation rates of >2000 g C m⁻² yr⁻¹ [Walsh, 1981]. Such neritic paradigms have been recently questioned, however, with perhaps important roles for large cyanophytes, dinoflagellates, and picopelagia [Walsh, 1996]. Here we address how adequately a simple biological model of diatom production and copepod grazing represents the observed measurements of carbon fixation and detrital losses from the euphotic zone of the Venezuelan upwelling ecosystem, when forced by another simple physical model of the wind- and buoyancy-induced circulation patterns.

Upwelling of dense water occurs along northeastern South America (Figure 1a) in response to both local winds and western boundary currents. Slope source waters at depths of 125–150 m within the salinity maximum (>36.5 practical salinity units, psu) of Subtropical Underwater [Wust, 1964] contain ~6–8 mol NO₃ kg⁻¹ over a density interval of 24.0–26.3 off French Guiana [Ryther et al., 1967; Gibbs, 1980], Suriname [Hulbert and Corwin, 1969], Guyana [Van Bennekom and Tjsen, 1978], Venezuela [Richards, 1960; Bonilla et al., 1993], and Colombia [Corredor, 1979]. At times, this amount of nitrate was found within the upper 10–20 m of coastal waters of 36.8 psu in a prior times series (Figure 2) on the inner central Venezuelan shelf at the 90-m isobath [Okuda, 1975].

Alongshore zonal winds are favorable for coastal upwelling year-round off Venezuela, with some seasonal variation (Figure 3a), as a result of north-south migration of the Intertropical Convergence Zone [Herrera and Febres-Ortega, 1975; Pellegri and Padron, 1988; Müller-Karger and Aparicio, 1994]. Maximal coastal upwelling occurs after onset of the dry season in December, when the stronger mean ENE trade winds of ~8 m s⁻¹ usually dominate until the end of April; optimal production of fish in upwelling regimes occurs under such wind forcing [Cury and Roy, 1989]. Within the summer-fall rainy season of May–November, weak upwelling, or even downwelling, instead occurs, in response to mean SSE winds of ~5 m s⁻¹.
Below a depth of ~300 m, the Cariaco Basin (Figure 2) is an anoxic habitat within the central Venezuelan shelf [Richards, 1975], which serves as a natural sediment trap to record the interannual consequences of primary production in the overlying euphotic zone [Walsh, 1996]. With a sill depth of ~150 m, nutrients can be imported from the southern Caribbean during upwelling, but their by-products at greater depths of the basin are not exported, as a result of rare ventilation events. In contrast, the Sea of Japan subthermocline waters, enclosed by the same sill depth, are renewed at 3- to 10-year intervals at a higher latitude [Chen et al., 1996]. No ventilation over the last 50–75 years [Zhang and Millero, 1993] and interannual increases of remineralized CO₂ have led to dissolved inorganic carbon (DIC) stocks at a depth of 330 m, which are thus >150 μmol ΣCO₂ kg⁻¹ larger in the basin, than in offshore Caribbean waters to the north.

As a consequence of wind forcing and bathymetry, local upwelling provides an east-west gradient (Figure 1) of the supply of nutrients, of satellite-sensed pigments [Müller-Karger and Aparicio, 1994] and of phytoplankton abundance [Hulburt,
1966] towards the less productive waters of the western Cariaco Basin [Curl, 1960; Ballester and Margalef, 1965]. In response to different productivities of the water column, the $^{210}$Pb sedimentation rate is $\sim 0.10$ cm yr$^{-1}$ below the more productive regions of the eastern basin, where the organic carbon content of surficial sediments is 4% dry weight [Lidz et al., 1969]. Beneath the more oligotrophic western part of the basin, the $^{210}$Pb sedimentation rate is $\sim 0.05$ cm yr$^{-1}$ where carbon contents of 3% dw prevail [Wakeham and Ertel, 1988].

Within the spatially heterogeneous surface waters of this natural sediment trap, the Cariaco Basin, we wished to know which trophic state of the coastal upwelling ecosystem was mainly represented by the site of field measurements within the Carbon Retention in a Colored Ocean (CARIACO) project of the U.S. National Science Foundation (NSF), NASA, and the Venezuelan Consejo Nacional de Investigaciones Científicas y Tecnológicas (CONICIT), at 10°30'N, 64°40'W (the solid square in Figures 1 and 2). Here we installed a sediment trap array, around which monthly hydrographic and biochemical measurements were made over the $\sim 1400$-m water column for the two years 1996-1997. We also wished to know how important diatom utilization of upwelled nitrate might be in the N economy of this ecosystem, since an analysis of the 1973-1974 inner shelf time series had suggested that 34-77% of the new production could be attributed to assimilation of $N_2$ by cyanophytes during February-June and July-August, respectively [Walsh, 1996].

Any ecological model is a simple version of the real world, of which aliased observations must provide an assessment of the model's fidelity. In such a hypothesis testing cycle, validation of our present coupled model assumptions and predictions consists of satellite and in situ temperature data for comparison with the results of the physical model. Our and other in situ measurements of (1) light penetration [Ballester, 1965], (2) nutrients [Garcia et al., 1983], (3) dissolved inorganic and organic carbon, (4) chlorophyll [Ferraz-Reyes, 1983], (5) 14C-estimated net primary production, (6) bacterial biomass, and (7) particulate carbon and nitrogen caught by a sediment trap at $\sim 240$ m arc used to test the food web model, driven by the physical one.

We have no time series data of zooplankton abundance at the CARIACO site, however. A few prior observations suggest a tenfold seasonal change in total zooplankton carbon stocks of $\sim 2-20$ mg C m$^{-3}$ (1 mg C m$^{-3} = 4.5\%$ (mg wet weight)$^{-3}$) within the eastern Cariaco Basin between October and March [Urosa, 1983]. Biological closure [Steele and Henderson, 1992] is thus obtained with a constant grazing pressure by copepods for a steady state solution to "typical" March wind forcing and zooplankton biomass during early spring. In this boundary value problem, the conditions of the state variables in the aphotic zone thus represent those of prior "intermediate" upwelling, found in late December. Finally, we explore one late summer case of weaker wind forcing with no prior upwelling, typical of oligotrophic conditions in August-September.

2. Methods

The governing equations and parameter values for the circulation and biochemical models are given in Appendices A and B. We coupled a prior model of shelf plankton dynamics [Walsh and Dieterle, 1994] to a primitive equation circulation submodel, fashioned after the coastal upwelling model of O'Brien and Heburn [1983]. Since our initial simulation studies in the CARIACO program focus on the relevance of simple ecological assumptions about the minimal diversity of the base of the food marine web, we first use the results from this relatively simple two-layered, depth-integrated formulation of the physical habitat to test the adequacy of one functional group of spring diatoms. Our previous studies [e.g., Pribble et al., 1994], suggested that much greater effort and computer resources would have been expended in implementation of either a z level [Bryan, 1969], or sigma coordinate [Blumberg and Mellor, 1987], finite-difference model of the local shelf-basin circulation. Either of these models would require very fine vertical and horizontal grid spacing [e.g., Haney, 1991] to resolve the complex geometry of the Venezuelan coast and the sharp topography of the Cariaco Basin (Figure 2). Steep topography, in general, does not cause numerical difficulties for the present two-layered formulation. The bottom depth is a model surface, and integration over the depth of each layer essentially removes those terms, which cause this particular numerical error.

With only two layers the vertical stratification is crudely represented, however, and formulating bottom stresses with depth-averaged velocities, using classical empirical formulas, may not always be appropriate [Nihoul, 1982]. In addition, numerical instabilities develop as either layer thickness approaches zero, which normally results in an artificial constraint on the depth to which the interface between the layers is allowed to shoal or deepen. Nevertheless, given these limitations it is still possible, when the model is used in conjunction with a one-dimensional Ekman model, to adequately represent the flow in the upper layers of the water column [O'Brien and Heburn, 1983].

Building upon a previous simulation study of the Gulf of Mexico [Walsh et al., 1989], a term for the heating of the upper layer of the water column, due to the net flux of heat across the air-sea interface, has been introduced in the two-layer circulation model. Following the results of Thompson [1974], a parameterization for mass and momentum transfer between layers, due to turbulent mixing processes, has also been included.
The steady solution of the model's biochemical variables are thus obtained from boundary conditions of light \( L(z) \), nitrate \((\text{NO}_3)\), ammonium \((\text{NH}_4)\), DIC \((\Sigma\text{CO}_2)\), monomeric dissolved organic carbon \((\text{DOC})\), macromolecular DOC \((\text{DOC}_2)\), phytoplankton biomass \((P)\), zooplankton fecal pellets \((Z_f)\), and bacteria \((B)\) within constant three-dimensional flow and temperature fields, forced by the same buoyancy field in three different cases of 6, 8, and 10 m/s winds. Local vertical mixing at each grid point of the ecological model is computed from a Mellor-Yamada turbulence closure scheme used by, among others, Walsh and Dieterle [1994].

The spatial domains of both the two-layered circulation model and the embedded biochemical one (10 layers in the upper 50 m of the water column and 20 layers stretched from depths of 50 m to 1450 m) extend east-west over \(-350\) km at \(4.4\)-km resolution between \(63.2^\circ\)W and \(66.4^\circ\)W (Figure 2). The northern boundary of the circulation model extends to \(-23^\circ\)N, while the seaward boundary of the biochemical model is set at \(12^\circ\)N. The north-south grid resolution is \(4.5\) km to \(23^\circ\)N and thence stretched, reaching a maximum of \(107\) km near \(23^\circ\)N. The model's bathymetry is shown in Figure 2.

2.1. Physical Submodel

The no-slip condition and zero exchange of advective and diffusive fluxes across the northern boundary in the central Caribbean Sea is of sufficient distance [O'Brien and Heburn, 1983] that solutions for the flow on the shelf and within the Cariaco Basin are minimally impacted. These flow fields and lateral eddy viscosities of \(-5 \times 10^6\) cm\(^2\)s\(^{-1}\) (Table A1) are obtained by first computing the layer-averaged flow, forced by winds, interfacial stresses, bottom stresses, and heating within the upper layer. Equations (A1)–(A5) for the \(u\) and \(v\) components of such horizontal flow, density, and layer thickness, with a net surface heat flux into the upper layer at a constant rate of \(40\) W m\(^{-2}\) [Oberhuber, 1988] are given in Appendix A.

At the eastern inflow boundary (Figure 2) we apply (A1) with all alongshore \((x)\) derivatives set to zero. An exception occurs if the flow is out of the domain at this boundary, in which case the alongshore advective term is calculated. Equation (A1) is also applied along the western outflow boundary. At this boundary a constant alongshore pressure gradient is calculated for each layer with the constraint that the total outflow exactly balances the inflow at the eastern boundary [Hurlburt and Thompson, 1980]. We note that the density and
the tangential component of the flow just outside the eastern and western boundaries are set equal to their corresponding values at adjacent interior grid cells.

The full, three-dimensional circulation patterns of the physical model are next found from (A6)–(A7) for the departure of the horizontal velocity components from their vertical mean in Appendix A. The continuous analytical solutions of these equations at each grid point have top and bottom Ekman layers and a geostrophic interior. The vertical velocity (w) field at the interface of the two layers of the circulation model is computed from the time rate of change of the upper layer thickness. A linear variation was assumed to interpolate w from the depth of the interface to the sea surface, and below the interface to the bottom, subject to the constraints that w is zero both at the surface and the bottom, or at depths of >120 m within the Cariaco Basin. With a Lagrange multiplier technique [Stoddard and Walsh, 1986] the total horizontal flow field of the biochemical model was then adjusted to satisfy continuity within each grid cell. To avoid discontinuities of flow at the northern boundary, we did not compute the vertical velocity at this boundary.

2.2. Ecological Submodel

2.2.1. Phytoplankton. The measured primary production in March, the chlorophyll (chl) stock, and a C/chl ratio of 50 [Morris et al., 1981] yield a carbon-based growth rate of 0.11 hour⁻¹ over the upper 15 m at 22.8°C. This realized estimate of growth is identical to the upper limit of Eppley’s [1972] compilation of batch culture growth at 23°C under presumably no other limitation. Similarly, in the equatorial Pacific the chlorophyll-normalized maximum photosynthesis was ~0.46 mg-at C (mg chl)⁻¹ hour⁻¹ over the upper 15 m at temperatures of ~25°-26°C [Lindley et al., 1995]. The same C/chl ratio of 50 again yields a maximum carbon-based growth rate of 0.11 hour⁻¹. The maximal diatom growth rate c₁ in equation (B10) of 0.12 hour⁻¹ is the same used at 25°C in a prior model of the Gulf of Mexico [Walsh et al., 1989], providing a Q₁₀ of ~2.1 in relation to another study, which employed a c₁ of 0.026 hour⁻¹ at 5°C in the Mid-Atlantic Bight [Walsh et al., 1988]. No additional explicit thermal regulation of metabolism is included in this study, but we do consider solubility effects of CO₂.

Our prior analysis of possible N fixation of ~34% of the new production during strong upwelling in February–June along the Venezuelan shelf assumed a Redfield ratio for DIC utilization during nitrate uptake by phytoplankton [Walsh, 1996]. To be consistent with this nutrient budget, we again assume that primary production is Redfieldian, albeit by only diatoms of our numerical model at a ratio of 7.0 for both nitrate and ammonium uptake (Table B1).

2.2.2. Zooplankton. The dominant calanoid copepods in the Cariaco Basin during spring 1964 and 1965 were Eucalanus pileatus and Clausocalanus arcuicornis [Cervigon and Marcano, 1965]. We thus assume that their fecal pellets have a mean sinking rate wₛ of 100 m d⁻¹ [Paffenhofer and Knowles, 1979] in (B3) for the copepod herbivores of our model. To allow penetration of DOC to depth, these fecal pellets have a lysis rate of 0.132 day⁻¹ (Table B1) to DOC₁₂⁰, compared with 0.033 day⁻¹ in a prior model of the Bering and Chukchi Seas [Walsh et al., 1997], i.e. another implicit Q₁₀ of 2.0.

We assume that these small copepods graze 100% of their body weight each day, amounting in one scenario to a ubiquitous, constant value of 10 μg C L⁻¹ over the upper 100 m of the basin. In most cases of higher grazing stress, the biomass of zooplankton is instead 20 μg C L⁻¹. If their diatom prey is below a grazing threshold of 2.5 μg C L⁻¹ (Table B1), i.e., 0.05 μg chl L⁻¹, no grazing occurs in (B17), ensuring numerical stability [Walsh, 1975]. The copepods are sloppy herbivores [Jumars et al., 1989; Banse, 1992] in (B3), such that 50% of the grazed material is released as DOC, partitioned further into 40% DOC₁ and 60% DOC₂ [Walsh and Dieterle, 1994].

Of the prey that is ingested by nominal E. pileatus, 70% is then assimilated [Paffenhofer and Knowles, 1979], to be respired as CO₂ in (B8) and to be excreted as NH₄ in (B7). Thus 30% of the ingested food, or 15% of the grazed particulate organic carbon (POC)/particulate organic nitrogen (PON), is converted to fecal pellets of macrozooplankton in (B3) for exit from the upper water column. Since the zooplankton biomass is constant, the remaining 35% of the diatom losses to herbivores is recycled as excreted NH₄ and respired CO₂. With only one functional group of phytoplankton of the model, the ammonium of zooplankton and bacterial origin is utilized by just the diatoms.

2.2.3. Bacterioplankton. We partition the bacterial substrate into labile DOC, and refractory DOC, whose loss is both photolytic destruction [Keiber et al., 1990], X₂, to DOC, within the upper 5 m in equations (B4) and (B5), and inefficient utilization by the bacteria [Walsh and Dieterle, 1994]. A half-saturation constant of 0.83 μmol DOC kg⁻¹ (Table B1) and a maximum bacterial growth rate c₅ of ~1.35 day⁻¹ are used in (B18). After passage through nanoflagellate and ciliate predators of an implicit microbial web at a mortality rate of 0.24 day⁻¹ (Table B1), only 1% of the bacterial secondary production is converted to zooplankton fecal pellets in (B3). The bacterial growth and death rates are based on prior sensitivity analyses of the microbial loop of the Gulf of Mexico [Walsh and Dieterle, 1994]. The rest of the bacterial predation, as well as their own respiration at a growth efficiency of 50%, are converted to CO₂ and NH₄ at the approximate Redfield C/N ratio R, in (B6)–(B7), of 7.0 (Table B1).

In this simple biological model, we assume that phytoplankton assimilate NH₄ more efficiently than bacteria, so that their bacterial nitrogen demands are met instead by dissolved organic nitrogen (DON). A maximal nitrate stock of ~12 μmol NO₃ kg⁻¹ was found by us and prior investigators [Richards, 1975; M. Bacon, personal communication, 1995] at a nominal depth of 150 m at the CARIACO time series site, after local increment of the original shelf break supply of nitrogen [Walsh, 1996]. Such nitrification in the aphotic zone [Ward and Kilpatrick, 1991] is represented by X₁ in (B6) and (B7), at a rate of 0.025 μmol NO₃ kg⁻¹ d⁻¹ for NH₄ ≥ 0.1 μmol NH₄ kg⁻¹ and L(t, z) < 0.1 L(t, 0).

2.3. Boundary Conditions

We begin with the buoyancy field of the circulation model, with prevailing densities of 24.0 σₘ in the upper layer and 26.0 σₘ in the lower one, reflecting prior weak upwelling of the rainy season [Walsh, 1996]. An ocean at rest, with an initial interface depth of 35 m, has an upper layer temperature of 25.5°C, i.e., typical of the end of December (Figure 3a), while the lower layer has a mean temperature of 18.5°C. After computation of "typical" thermal and velocity fields that match available data, these results are applied to the separate ecological model, which has other boundary conditions of the biochemical state variables.

Since we are not concerned with hypoxic processes of denitrification in this model, we assume a spatially varying bound-
ary condition of a uniform 12.5 μmol NO₃ kg⁻¹ from a depth of 150 m to the bottom of the model (Figure 2), outside a baroclinic radius of deformation of ~30 km from the shelf break. By late January, however, ~10 μmol NO₃ kg⁻¹ [Okuda, 1975] and ~2180 μmol Σ CO₂ kg⁻¹ [Avila-Meleán, 1976] are instead found at a depth of 60 m on the 90-m isobath. Following Yoshida [1955], for example, the model's reduced gravity of 0.019 m² s⁻¹, interface depth of 35 m, and Coriolis parameter (Table A1) yield a Rossby radius of 31 km for prior weak upwelling. Thus in most cases of the model, we considered upward sloping isopleths of nitrate and DIC (Figure 4) within one radius of deformation during spring to simulate the impact of western boundary currents at the edge of the shelf. In one summer case we instead imposed no slope to mimic prior downwelling, or absence of an offshore current.

Accordingly, within the slope region of 30 km width from the shelf break, we assumed vertical profiles of NO₃ and DIC at these grid points, like those of the upstream boundary (Figure 4), such that there was initially ~10 μmol NO₃ kg⁻¹ and ~2170 μmol Σ CO₂ kg⁻¹ at 80 m on the 100-m isobath, with an exponential decay offshore. Here, at depths of >150 m in the biological model, the conditions of the other variables are similar to simplify matters: an alkalinity of 2400 μeq kg⁻¹, DIC of 2250 μmol Σ CO₂ kg⁻¹, ammonium of 0.10 μmol NH₄ kg⁻¹, phytoplankton biomass of 0.05 μg chl L⁻¹, zooplankton fecal pellets of 3.0 nmol C kg⁻¹, bacterial stocks of 0.10 μmol C kg⁻¹, and zero amounts of monomeric labile DOC and macromolecular refractory DOC₂.

Within these source regions of upwelled water, the biological model's inert background stock of DOC, is assumed to be 55.0 μmol C kg⁻¹, the same as that found at 18.5°C within upwelling waters in the equatorial Atlantic [Thomas et al., 1995]. At 12°N, 52°W, this ~18.5°C water at a salinity of 36.5 psu and a depth of 150 m also contains a nitrate stock of 8.9 μmol NO₃ kg⁻¹, with a N/P ratio of 15.1 and a density of 26.3 σ₀ [Knapp and Stommel, 1985], i.e., about the same as that found just north of the Cariaco Basin at 12°N [Walsh, 1996].

During passage along the continental slope off South America, we assume that there is no change in total DOC stocks but that the colored dissolved organic carbon (CDOC) component may have two sources of different optical properties: deep water and the near-surface layers. An absorption coefficient \( a_c \) of 0.061 m⁻¹ for DOC at 3000 m in the Sargasso Sea [Green and Blough, 1994], for example, where ~45 mmol DOC m⁻³ prevail [Guo et al., 1995], yields a DOC-specific coefficient \( a_{dc} \) of 11.3 x 10⁻⁵ mg⁻¹ DOC m⁻² at 375 nm. This is about half the Gordon et al. [1988] surface estimate, or 25% of that found in the subsurface maximum [Siegel and Michaels, 1995].

In shallow waters above the 70-m isobath of our Bering Sea model, we just considered the CDOC attenuation of light at 441 nm, since mainly blue light penetrates the euphotic zone of polar coastal waters [Mitchell and Holm-Hansen, 1991]. We then estimated the specific absorption coefficient of CDOC, \( a_c(441) \), at 441 nm from

\[
a_c(441) = 0.565 \exp(0.020[375 - 441])
\]
where $a_c$ (375) is $56.5 \times 10^{-5}$ mg$^{-1}$ CDOC m$^{-2}$ in surface waters of the Sargasso Sea [Gordon et al., 1988], i.e., an assumed total DOC coefficient $a_d$ of $25.4 \times 10^{-5}$ DOC m$^{-2}$ at 375 nm, with 0.020 nm$^{-1}$ as the spectral slope of mainly marine CDOD absorption [Carder et al., 1989]. With a cosine of the subsurface solar zenith angle $\theta$ of 0.82 [Walsh et al., 1992], we obtained a specific attenuation coefficient $k'_c$ (441) of $18.4 \times 10^{-5}$ mg$^{-1}$ CDOC m$^{-2}$, employed by Walsh and Dieterle [1994] with a CDOD/DOC ratio of 0.45. We now consider two light attenuation scenarios of near-surface and deep CDOD, with respective ratios of 0.45 and 0.22, i.e., half of our prior value.

As a result of coastal upwelling along the Araya-Paria Peninsula, we have found an offshore gradient of 0.5-5.0 $\mu$g chl L$^{-1}$ during prior studies in April 1986 to the east of Cariaco Basin (Figure 1b). Near-bottom DIN stocks of $-2.0 \mu$mol NO$_3$ kg$^{-1}$ and $-2.0 \mu$mol NH$_4$ kg$^{-1}$ are then observed here at the 40-m isobath [Gomez and Chanut, 1993]. Accordingly, we use this information to set the upstream, cross-shelf boundary conditions to the east of Margarita Island (Figure 4). At the downstream western boundary of the model near Cape Codera, a Dirichlet condition prevails at the few inflow points of the grid mesh; i.e., we specify values of the state variables rather than their gradients.

Finally, at the surface of the model, light penetrates the sea, and air-sea exchange of CO$_2$ occurs, the form of which is shown in equation (B8b). The atmospheric $p$CO$_2$ is now the 355 ppm value of the 1990s, rather than 345 ppm of the 1980s [Walsh and Dieterle, 1994] (at Mauna Loa, 358 ppm was found in 1994). At the benthic boundary the influx of fecal pellets to the bottom is converted at the Redfield ratio [Chen et al., 1996; Hopkinson et al., 1997] to dissolved forms without the time lag of our prior polar model. Of the POC/PON influx to the sediments, 25% is returned to the near-bottom water column in the form of DOC and NO$_3$, and 75% is returned as DIC and NH$_4$.

3. Results

The mean February-April winds at Margarita Island during 1994–1997 were 7.8 m s$^{-1}$ (Figure 3a). Accordingly, a quiescent ocean was first subjected to a wind forcing of 8 m s$^{-1}$ (stress of 0.116 N m$^{-2}$) from ENE (068°) after 1 day, followed by the same stress for another 7 days. The other circulation scenarios under weaker and stronger winds were explored similarly, except the winds were then 6 and 10 m s$^{-1}$ (0.060 N m$^{-2}$ and 0.198 N m$^{-2}$). In any wind forcing of the simple physical model, one must constrain the upper layer thickness to be $\geq 10$ m for stability criteria of the two-layered formulation [O'Brien and Heburn, 1983] if the circulation model is run for more than a few days, however.

Our "typical" flow pattern of spring upwelling thus comes from day 3 of the 8 m s$^{-1}$ wind scenario, so that we can determine the vertical velocity field without the constraint that the upper layer thickness be $\geq 10$ m. This period is at the end of the initial spin-up timescale of the order of 2-3 days [Hamilton and Rattray, 1978]. For example, the model's response in this wind case is a mean upper layer flow from the SSE at the site of 10 cm s$^{-1}$ after 1 day, increasing to 31 cm s$^{-1}$ from ENE after 5 days and decreasing to 26 cm s$^{-1}$ from the ENE after 8 days, as the density field begins to compensate the barotropic pressure field. The solution after 8 days became contaminated with numerical noise, beginning first in the density field near Margarita Island, so that the integration was halted. See Appendix A for more details.

3.1. Circulation

On day 3 of the 8 m s$^{-1}$ wind case, the model's upwelling velocity is a maximum of 8 m d$^{-1}$ at the western end of the Araya Peninsula and 3 m d$^{-1}$ at the CARIACO site (Figure 5a). A downwelling cell prevails in the less productive, western part of the Cariaco Basin, near Tortuga Island. Additional
upwelling loci of 4–5 m d⁻¹ are simulated at Cape Codera and north of Margarita Island, where cold plumes have been observed by satellite [Müller-Karger and Aparicio, 1996].

At the site, the simulated horizontal currents of the Ekman layer are ~30 cm s⁻¹ at 1.3 m (Figure 6a) and ~10 cm s⁻¹ at 25 m, flowing mainly to the west near the surface as was found by Febres-Ortega [1974] in April 1974. He measured a westward flow at the surface of 24–28 cm s⁻¹ in the eastern half of the basin. At a depth of 46 m, the model’s flows slow down to a southward speed of ~3.2 cm s⁻¹ (Figure 6b); at 50 m, Febres-Ortega [1974] estimated a similar onshore flow of 1–6 cm s⁻¹ across the basin. At greater depths of 100–150 m, the model predicts eastward speeds of ~1.4 cm s⁻¹ (Figure 6c). Of the three wind scenarios, these results of the 8 m s⁻¹ wind case best approximate the sparse current data.

Within such a steady three-dimensional circulation pattern (Figures 5a and 6), a water parcel would take 10.8 days to upwell from a depth of 49.5 m at the western tip of Margarita Island (Figure 5c), move along the 100-m isobath, thence to the southwest, and arrive at 12.1 m within the site’s euphotic zone over a distance of ~75 km, as indicated by the daily trajectory (asterisks). It would exit the Cariaco Basin past Cape Codera on day 18. Farther offshore, another parcel above the sill entrance between Tortuga and Margarita Islands (Figure 1) would also take 10.9 days to reach the CARIACO site (trajectory is not shown), but it would upwell only from a depth of 49.5 m to 32.6 m at the bottom of the euphotic zone.

In the strongest upwelling center off the Araya Peninsula, a third water parcel (squares in Figure 5c) would instead upwell from 49.5 to 12.1 m within just 5.9 days of a southward translation of ~10 km along the coast. It would then move west on the shelf and exit the basin on day 15. This latter trajectory appears to move downstream along the axis of a spring upwelling plume, demarcated by the few observations of cold temperatures of <22°C (Figure 7a) and high nitrate stocks of >4 μmol NO₃ kg⁻¹ (Figure 7c) at 20 m.

3.2. Temperature

The thermal response of our model to the intermediate wind case of 8 m s⁻¹ is minimal on day 3, with little spatial gradient. By day 6, however, a northwestward movement of the 23°–24°C isopleths of the surface layer is simulated past the CARIACO site, with lowest values of 19.5°C computed off the Araya Peninsula (Figure 5b). During February–April 1996–1997, the satellite advanced very high resolution radiometer (AVHRR) and hydrographic surveys both detected such surface temperatures at the site (Figure 3b). Earlier in February 1983, the 20-m temperature was also ~23°C at the site (Figure 7a), while lower values of 21°C were found at 20 m above the 90-m isobath in February 1974 [Okuda, 1975]. The weaker upwelling loci at Cape Codera and Margarita Island, demarcated in our model by temperatures of <23.5°C (Figure 5b), are also observed in field studies (Figure 7a).

Temperatures of only 25.0°–25.5°C are instead simulated on day 6 at the CARIACO site under the 6 m s⁻¹ wind forcing, mimicking both the SST and in situ hydrographic observations of December 1996–1997 (Figure 3b). With a 10 m s⁻¹ wind, much colder temperatures of 19.5°–20.0°C are predicted at the CARIACO site. Only the daily AVHRR images may have detected such intense transients of cold temperatures at the surface in response to rare 10 m s⁻¹ wind events (Figure 3a), since the less frequent hydrographic surveys instead show minimal temperatures of ~22°C at the site during winter-spring upwelling (Figure 3b).

On the basis of the predicted and observed fields of both currents and temperature, we conclude that the model’s non-equilibrium flow fields under a wind forcing of ~8 m s⁻¹ may be a “reasonable” description of the physical habitat during February–April. We now employ the one snapshot of currents on day 3 of the undeniably simple circulation model to ask what are the biochemical consequences of such implied nutrient delivery and simple food web transfers in an upwelling region, where mainly biological validation data are derived from the CARIACO program.

Furthermore, to explore the thermal impacts on CO₂ solubility in two scenarios of the ecological model, we use (1) a
constant surface temperature of 25.4°C for computation of $pCO_2$ [Peng et al., 1987] at a single salinity of 36.5 psu, since salt variability is small in the Cariaco basin, and then (2) the temperature field of Figure 5b and the same salinity. Only the results of the latter scenario are shown.

### 3.3. Biological Response

Solutions to this boundary value problem are independent of initial conditions at the 2- to 3-month timescale of interest. To speed convergence, however, we began each case with an initial state derived from a two-dimensional analysis of the upstream boundary conditions (Figure 4). The cross-isobath solutions were the result of an approximately 6-year spin-up of the model in the absence of local wind-forced upwelling. Initial conditions at the interior grid points of the model were specified using the values at the corresponding isobath of the upstream boundary. The model was then integrated without the advective terms for an additional 240 days, followed by 45 days with the imposed flow fields. This procedure yielded solutions that are free of the effects of arbitrary along-isobath asymmetries, or strongly imbalanced conditions in the vertical. We discuss the results of each case after 45 days, although little change was found after 30 days.

#### 3.3.1. Baseline food web

The higher grazing stress and a deepwater source of smaller amounts of refractory CDOC represent the baseline spring scenario. A steady solution after 45 days of integration yields an alongshore nitrate plume (Figure 8e), demarcated by the 4 μmol NO₃ kg⁻¹ isopleth, that resembles the sparse observations [Garcia et al., 1983] of February 1983 (Figure 7c). The model's prediction of 7.5 μmol NO₃ kg⁻¹ at 25 m within the Gulf of Santa Fe waters (see plus symbol in Figure 2) is the same as that found at this depth above the 90-m isobath in February 1975 [Okuda, 1975]. Similarly, a simulated DIC stock of 2150 μmol CO₂ kg⁻¹ at 25 m in the Gulf (Figure 8d) somewhat underestimates the 2175 μmol DIC kg⁻¹ found at this depth and time during a prior study of the Venezuelan shelf [Avila-Melean, 1976].

The model's phytoplankton respond with maximum near-surface biomass of 10.0 μg chl L⁻¹ (Figure 8a) and net primary production (gross photosynthesis − respiration − excretion) of 4.4 g C m⁻² d⁻¹ (Figure 8b) within a shallow euphotic zone of ~19 m (Figure 8c) near the coast. At the CARIACO site, 1% of the model's surface radiation penetrates to a depth of 40 m, as was also observed. The measured oceanic euphotic zones of ~75-m depth, where the simulated and observed phytoplankton biomasses become <0.5 μg chl L⁻¹, are also replicated by this case of an offshore CDOC of 22% of the DOC, but not in the alternative scenario of 45% DOC discussed below.

Within a cross-plume section (see location in Figure 2), 4 μg
chl L$^{-1}$ are simulated at 10 m on the shelf (Figure 9d), as was found in patches during March 1984 (Figure 7e). At the location of the CARIACO time series (indicated by plus symbols in Figure 9), moreover, the model's results yield a mean diatom biomass over the upper 25 m of 2.7 μg chl L$^{-1}$. Here during February–April 1996–1997, a similar mean biomass of all phytoplankton was 2.1 μg chl L$^{-1}$ over this depth interval (Figure 10c). We define fidelity of the model as 1 - |(observation - model)/observation|, so that for our numerical estimation of the spring algal stock it is 71%.

All assessments of the model's fidelity are restricted to the CARIACO site, since the prior aliased spatial surveys can only confirm the general pattern of the three-dimensional results of the biochemical model. At the site the model's net carbon fixation of 4–8 mg C m$^{-2}$ h$^{-1}$ (Figure 9e) mimics that observed in near-surface loci of net photosynthesis (Figure 10d). The depth-integrated net primary production of 2.0 g C m$^{-2}$ d$^{-1}$ in this case (Table 1) also approximates the mean of 1.8 g C m$^{-2}$ d$^{-1}$ for net photosynthesis found from $^{14}$C measurements during February–April 1996–1997, yielding a fidelity of 89%.

As a result of the nitrate-induced primary production, simulated DIC stocks of ~2070 μmol Σ CO$_2$ kg$^{-1}$ at a depth of 25 m in the model (Figures 8d and 9a) similarly underestimate...
mean DIC observations of $\sim 2130$ μmol $\sum CO_2$ kg$^{-1}$ (with an analytical error of 5–10 μmol $\sum CO_2$ kg$^{-1}$) during February–April 1996–1997 at the same depth of the site (Figure 10b), as near the coast [Avila-Melean, 1976]. A greater model fidelity of 97% results from the large unutilized DIC stocks, of course. More importantly, the underestimate by the remaining simulated DIC stocks of the model is consistent with the prior overestimates of photosynthesis and biomass and suggests that no other "new" nitrogen sources, i.e., nitrogen fixation in addition to nitrate, are required for support of spring carbon fixation.

Under an anthropogenic atmosphere, with a $pCO_2$ of 355 μatm, a simulated spring fugacity of $\sim 325$ μatm (Figure 9) in surface seawater of 23.5°C (Figure 5b) at the CARIACO site suggests that part of the Cariaco Basin may be a significant sink of atmospheric $CO_2$ [Walsh and Dieterle, 1994], yielding an influx of $\sim 79$ mg C m$^{-2}$ d$^{-1}$ forced by the 8 m s$^{-1}$ wind. In the scenario of a constant temperature of 25.4°C, however, the model's surface DIC stock of $2040$ μmol kg$^{-1}$ at the site instead yields a partial pressure of only $\sim 351$ μatm, providing a minimal sink.

Smaller relative changes in DIC stocks alter the sign of CO$_2$ exchange, moreover. For example, the measured surface mean of $\sim 2080$ μmol $\sum CO_2$ kg$^{-1}$ during February–April 1996–1997 at the site (Figure 10b) and the model's temperature of 23.5°C provide a $pCO_2$ of 389 μatm, fostering evasion of carbon from the Cariaco Basin. Higher simulated stocks of DIC near the coast (Figure 8d) and higher temperatures offshore (Figure 5b) also yield fugacities of $>355$ μatm (Figure 9f), such that spring outgassing occurs in these regions of the model. Later in the year, even higher surface temperatures of $>25.5^\circ$C prevail at the site (Figure 10a), such that minimal DIC stocks of $\sim 2055$ μmol kg$^{-1}$ would still provide fugacities of $>375$ μatm, suggesting that Cariaco Basin continues to be a carbon source to the atmosphere on an annual basis.

The larger grazing pressure exerted by the greater biomass of the herbivores in this case consumes 33% of the particulate production by diatoms. Copepod excretion and additional carnivore activity in the baseline scenario leads to 63% of the supply of recycled nitrogen from metazoan release in the model (Table 1) and a "standard" $f$ ratio, i.e., $\{NO_3$ uptake $+ NH_4$ uptake $\}$, of 0.72 at the site, with relict ammonium stocks of $<0.15$ μmol NH$_4$ kg$^{-1}$ left behind in the basin (Figure 9c). Near the coast, higher remaining values of 1 μmol NH$_4$ kg$^{-1}$ of the model (Figure 8f) mimic spring observations on the Venezuelan shelf [Gomes and Chanut, 1993].

The ratio of local nitrification to the sum of biotic and advective supplies of $NO_3$, $r$, in the baseline case of the model is 0.075. A corrected $f$ ratio, i.e., $\{NO_3$ uptake $(1 - r)/[NO_3 + NH_4$ uptake $]$, provides a more realistic index of 0.67 for new production from allochthonous nitrate (Table 1). Within a one-dimensional ocean this ratio would set an upper bound for the particle export from the euphotic zone at the site of $\sim 1340$ mg C m$^{-2}$ d$^{-1}$. 

Figure 9. A vertical section, northwest from the coast past the CARIACO site (plus symbols; see Figure 2 for location), of the model's spring distributions of (a) total CO$_2$ (μmol DIC kg$^{-1}$), (b) nitrate (μmol NO$_3$ kg$^{-1}$), (c) ammonium (μmol NH$_4$ kg$^{-1}$), (d) chlorophyll, (e) net primary production, and (f) $pCO_2$ at the surface and particulate detrital flux at 240 m.
Figure 10. Observed seasonal cycles at the CARIACO site during 1995–1997 of (a) temperature (degree Celsius), (b) total DIC (µmol C L⁻¹), (c) chlorophyll (mg L⁻¹), (d) primary production (µg C m⁻² h⁻¹), and (e) particulate detrital flux and δ¹⁵N.
Table 1. Ecosystem Response to Different Scenarios of Changing Biological Processes of a Diatom-Based Food Web During Variable Upwelling at a Time Series Site in the Cariaco Basin

<table>
<thead>
<tr>
<th>Scenario</th>
<th>Net Photosynthesis</th>
<th>Grazing Loss</th>
<th>Algal DOC</th>
<th>Bacteria [NH₄]⁺</th>
<th>Bacteria [NO₃]⁻</th>
<th>f Ratio</th>
<th>POC Flux</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>g C m⁻² d⁻¹</td>
<td>mg C m⁻² d⁻¹</td>
<td>mg C m⁻² d⁻¹</td>
<td>mol C kg⁻¹</td>
<td>mol C kg⁻¹</td>
<td></td>
<td>mg C m⁻² d⁻¹</td>
</tr>
<tr>
<td>February–April 1996–1997</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mean observations</td>
<td>1.80</td>
<td>33</td>
<td>21</td>
<td>37</td>
<td>8</td>
<td>0.72 [0.67]</td>
<td>80</td>
</tr>
<tr>
<td>Spring baseline</td>
<td>2.01</td>
<td>43</td>
<td>17</td>
<td>37</td>
<td>12</td>
<td>0.62 [0.55]</td>
<td>73</td>
</tr>
<tr>
<td>Half herbivore biomass</td>
<td>1.17</td>
<td>34</td>
<td>21</td>
<td>36</td>
<td>7</td>
<td>0.74 [0.69]</td>
<td>52</td>
</tr>
<tr>
<td>Twofold colored DOC</td>
<td>1.83</td>
<td>99</td>
<td>8</td>
<td>32</td>
<td>21</td>
<td>0.67 [0.53]</td>
<td>67</td>
</tr>
<tr>
<td>August–September 1996–1997</td>
<td>0.96</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>50</td>
</tr>
<tr>
<td>Summer</td>
<td>0.13</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>15</td>
</tr>
</tbody>
</table>

DOC, dissolved organic carbon; POC, particulate organic carbon.

aGross production – respiration – excretion.

bPercentage of net production.

cPercentage of algal DOC release of the total supply from diatoms and copepods.

dPercentage of ammonium recycled by bacteria of the total supply from herbivores, carnivores, and the microbial loop.

ePercentage of nitrate recycled by local nitrifying bacteria of the total supply from advection and nitrification, denoted r.

fStandard ratio of nitrate uptake/total nitrogen assimilation of (NO₃/[NO₃ + NH₄⁺]) and (in brackets) corrected ratio of (NO₃ [1 – r]/[NO₃ + NH₄⁺]).

The upwind slope of boundary conditions, 8 m s⁻¹ wind, spatially varying thermal field, Redfield uptake of nutrients with maximum growth rate of 0.12 hour⁻¹, higher grazing stress, and CDOC (colored DOC) = 45% of DOC.

In terms of such export within our three-dimensional flow field, the mean measured February–April particle flux of 80 mg C m⁻² d⁻¹ caught at ~240 m (Figure 10e) is again similar to the model’s baseline flux of 75 mg C m⁻² d⁻¹ at this depth of the site (Figure 9f), with a fidelity of 91%. We do not attribute the model’s small underestimate to any significant spring N₂ uptake by cyanophytes and thence subsequent additional particle export in the “real world,” since microbial degradation of detritus in the basin’s water column is a greater unknown.

Although the spring influxes and effluxes of carbon and nitrogen to and from a diatom-based food web appear to be “reasonably” represented in our coupled model, the internal cycling of elements by the microbial loop may be poorly formulated. During processing of the other ~37% of recycled nitrogen in the baseline case (Table 1), the simulated mean bacterial biomass was 0.94 μmol C kg⁻¹ within the upper 50 m at the site. In the model the bacteria left behind a total near-surface stock was left behind of only 56.1 μmol DOC kg⁻¹ (0.31 μmol C kg⁻¹ of monomeric DOC, 0.79 μmol C kg⁻¹ of macromolecular DOC, and 55.00 μmol C kg⁻¹ of background DOC.) at depths of 0–25 m.

During February–April 1996 we indeed found a mean bacterial biomass of 0.79 μmol C kg⁻¹ over the upper 0–200 m and a DOC stock of ~62.5 μmol DOC kg⁻¹ at a depth of 200 m. Within the upper 25 m, however, the measured spring DOC stocks were instead a mean of ~76.5 μmol DOC kg⁻¹ in 1996, compared with a similar amount of 64–73 μmol DOC kg⁻¹ found here in surface waters of March 1972 [Karl et al., 1977]. With respect to the fidelity of our model, it is 81% for the bacterial stocks, but only 73% for the amount of total DOC—presumably more of the DOC in the “real world” is refractory, yielding smaller populations of bacteria.

A smaller growth efficiency of the bacteria would reduce their biomass in the model but not necessarily their removal of total DOC, i.e. a greater conversion to CO₂. Without field data on the residence times of monomeric DOC, and macromolecular DOC, however, we did not pursue more bacterial scenarios. Before proceeding to the summer case, in which the fidelity of the model is much less, we instead consider the implications of the DOC mismatch for nonsaprovore trophic levels, which provide additional constraints on parameter values. We thus discuss the spring model’s response to two additional cases in which (1) herbivores release smaller amounts of DOC and (2) greater light-limitation of phytoplankton is effected by larger amounts of CDOM.

3.3.2. Minimal grazing stress. A spring accumulation of only 1.1 μmol DOC₁₂ kg⁻¹ in the surface layers of the baseline case of the model, compared with an observed vertical increment of ~14.0 μmol DOC kg⁻¹ above “background” of deep water values in February–April 1996, suggests that additional sources of DOM are required from both “sloppy” phytoplankton and zooplankton, rather than the inverse situation of smaller release rates of dissolved materials by copepods. If we increase the sloppy grazing of the baseline case to produce more DOC, however, we then have less production of fecal pellets, whose simulated flux already underestimates the observed particle rain at 240 m in the Cariaco Basin.

Not surprisingly, a twofold decrement of zooplankton biomass in the model reduces by 50% the supply of DOC to the bacteria, of ammonium to the phytoplankton, and of herbivore fecal pellets to the aphotic zone. As a consequence, the net photosynthesis declines to 1.2 g C m⁻² d⁻¹ and the particle flux at 240 m is reduced to 52 mg C m⁻² d⁻¹ at the site (Table 1); greater amounts of algal biomass and production are now shifted landward. The bacterial biomass remained the same as that of the baseline case, but the DOC₁₂ stocks of the upper 25 m are each reduced by ~35% in this scenario. A possible solution to our need for more particles and more DOC is greater amounts of refractory DOC₁₂.

3.3.3. Coastal source of CDOM. Possible insight into the amount and palatability of such DOM may be derived from its C/N ratio and color. No measurements of DON are available from the Cariaco Basin, but in the adjacent Gulf of Cariaco, between Cumana and the Araya Peninsula (Figure 1), prior
time series yield February–March maxima of ~8 μmol DON kg⁻¹ [Benitez-Alavez and Okuda, 1985]. Such a composite spring C/N ratio of ~9 for labile surface DOM in the gulf and basin, i.e., increments above the residual pool of deep waters, is an intermediate value between sources of (1) grazing and lysis [Murray, 1995; Brussard et al., 1995] of algal body C/N at the Redfield ratio, and (2) excretion of DOM at ratios of 15 during diatom release of desirable carbohydrates [Bener et al., 1992; Amon and Benner, 1994, 1995; Norman et al., 1995]. But how much of this DOM is colored? C/N ratios of ~16 are unfortunately found for refractory humic matter [Gardner and Stephens, 1978; Vallino et al., 1996].

To evaluate the importance of DOC impact on both the amount of refractory metabolites and light-regulated primary production, one must have some understanding of its time-dependent sources and sinks [Walsh et al., 1992]. We are aware of only 12 time series of the annual cycles of total DOC, obtained within coastal waters over the last 35 years, that have concurrent data on phytoplankton biomass [Hochman et al., 1995]. They indicate that the seasonal peaks of DOC follow those of the phytoplankton at time lags of weeks to months. Our data indicate that maximum DOC stocks of the Cariaco Basin occur in May–June, following the spring bloom as well. Thus noncolored DOC should prevail during February–April, if simple sugars are the major excretory product of phytoplankton [Lancelot, 1986].

Recent ¹⁴C-label studies of a nonaxenic culture of Antarctic diatoms indicate that 44% of the phytoplankton exudates of DOC, left behind by the bacteria, were hydrophobic humic substances [Lara and Thomas, 1995], however. These data are consistent with other observations of both diatom excretion of fluorescent proteins and flavins [Seritti et al., 1994], and earlier culture work suggested release of colored compounds by phytoplankton as well [Fogg, 1966]. To explore these conflicting paradigms, we considered a strongly colored source of CDOC in this case of the model.

A shallower euphotic zone of 55 m was now simulated offshore, but not observed (Figure 7d). As a result of less light at depth in coastal waters, moreover, the model’s net primary production and particle flux at the CARIACO site decreased to 1.8 g C m⁻² d⁻¹ and 67 mg C m⁻² d⁻¹ (Table 1). We thus conclude that smaller amounts of CDOC are a correct description of the inherent optical properties of the site’s light field during spring. Accordingly, we have no basis for suggesting larger pools of the less labile macromolecular DOC₂ in the model. We could, of course, invoke greater mortalities of bacteria to account for larger accumulation of total DOC. However, we must be content with the model’s spring fidelity of 71% for phytoplankton biomass, 73% for total DOC, 81% for bacteria, 89% for primary production, 91% for settling fluxes, and 97% for DIC stocks, until more field data at greater ecological and temporal-spatial resolution are available.

3.3.4. Summer infidelity. With a smaller wind forcing of 6 m s⁻¹ (Figure 3a) and simulated and observed (Figure 3b) surface temperatures of >25°C, the summer case has no upward slope of the bottom boundary conditions, typical of weak upwelling or prior downwelling in August–September (note the relaxation of the 22°C isotherm at the CARIACO site during these months in Figure 10a). In this postbloom scenario, both the larger grazing stress and greater amount of CDOC prevail. This case of our model predicted a net primary production by diatoms of only 0.13 g C m⁻² d⁻¹ (Table 1), compared with 0.96 g C m⁻² d⁻¹ found in August–September 1996–1997 (Figure 10d), i.e., a fidelity of just 14% for simulation of net carbon fixation. Since we do find concurrent nutrient impoverished conditions of <0.02 μmol NO₃ kg⁻¹ over the upper 25 m at the CARIACO site during August–October, other phytoplankton groups, besides nitrate-assimilating diatoms, are clearly responsible for summer–fall photosynthesis in the real world.

In this summer case a grazing removal of 99% of the net production yielded a standard f ratio of 0.67, a corrected one of 0.53 as a result of larger nitrification, a chlorophyll biomass of ~0.1 μg chl L⁻¹ within the upper 25 m, and a detrital flux at 240 m of 15 mg C m⁻² d⁻¹ (Table 1). In contrast, a phytoplankton stock of ~0.3 μg chl L⁻¹ and a detrital flux of 50 mg C m⁻² d⁻¹ were observed during August–September 1996 (Figure 10c) and 1997 (Figure 10e), respectively; i.e., ensuing respective model fidelities were only 33% and 30%. These oligotrophic oceanic conditions of the last case stress the importance of both our imposition of bottom boundary conditions for no prior upwelling and the lack of nitrogen fixers.

4. Discussion

Our coupled biological-physical models of carbon-nitrogen cycling by phytoplankton, zooplankton, and bacteria provide an assessment of the impacts of nitrogen fixation and nitrate supplied by upwelling during spring new production within the shelf environs of the Cariaco Basin. During upwelling in response to a mean wind forcing of 8 m sec⁻¹, the physical model matches AVHRR and hydrographic estimates of surface temperature and sparse measurements of currents. The model’s vertical velocity is ~8 m d⁻¹ near the coast and 3 m d⁻¹ at the CARIACO site, where spring SST of 23°–24°C are predicted and observed during February–April 1996–1997.

The baseline case (Table 1) of a simple spring food web of diatoms, adult copepods, and heterotrophic bacteria appears to underestimate by ~9% the mean settling POC fluxes of 80 mg C m⁻² d⁻¹ caught by a sediment trap at ~240 m in the basin. It also overestimates the average ¹⁴C estimate of total primary production of 1.8 g C m⁻² d⁻¹ at the CARIACO site by ~11% and the chlorophyll biomass of 2.1 μg chl L⁻¹ by 29% during the same time period of February–April. With respect to the microbial loop, we underestimate the bacterial biomass by 19% and underestimate the total DOC stock by 27%. An analysis of the supply rate and optical properties of DOC suggests that greater accumulations of spring DOC may be associated with changes of bacterial predators rather than with the refractory nature of their food.

We conclude that diazotrophs make minimal contribution, if any, to new production during spring in the Cariaco Basin. In their absence, uptake of the upwelled DIC and nitrate in a Redfield ratio allows a weak simulated evasion of CO₂ to the atmosphere, about 19.2 mg C m⁻² d⁻¹ over the whole model’s domain of a spatially varying temperature field. Since the model underestimates the observed DIC time series, however, and thermal impacts on solubility of aqueous CO₂ become more significant in summer, we conclude that the basin is now a small spring sink, and probably a weak annual source as well. At projected greater atmospheric pCO₂ levels of ~370 ppm within the next decade, however, the Cariaco Basin might become a net sink, particularly if neglected nitrogen fixation is a major source of new nitrogen during summer periods.

Further assessment of the nitrogen-carbon economies of the Venezuelan shelf requires (1) representation of Trichodes-
mium as an explicit state variable of a more complex model, (2) a numerical analysis of their role in other seasons of the year, (3) consideration of the time-dependent delivery of possibly limiting atmospheric nutrients, e.g., iron, and (4) addition of picoplankton and protozoan components of the microbial food web as a co-occurring state variables with diatoms and cyanophytes. Explicit time series of DOM components and the optical signatures of the excretory products of these phytoplankton groups are similarly required.

Appendix A

In a right-handed coordinate system with $t$ denoting time, $x$ positive eastward, $y$ positive northward, and $z$ positive upward, the governing equations for the depth-averaged flow for the upper and lower layers, $i = 1, 2$, are

$$
\frac{\partial U_i}{\partial t} = -\frac{\partial U_i}{\partial x} U_i + \frac{\partial V_i}{\partial y} + fV_i - \frac{h_i}{\rho_0} \frac{\partial P_i}{\partial x} + \frac{1}{\rho_0} (\tau'_i - \tau''_i) + S'_i
$$

(A1)

$$
\frac{\partial V_i}{\partial t} = -\frac{\partial U_i}{\partial x} V_i - \frac{\partial V_i}{\partial y} - fU_i - \frac{h_i}{\rho_0} \frac{\partial P_i}{\partial y} + \frac{1}{\rho_0} (\tau'_i - \tau''_i) + S'_i
$$

(A2)

$$
\frac{\partial h_i}{\partial t} = -\frac{\partial U_i}{\partial x} h_i - \frac{\partial V_i}{\partial y} h_i + E_i - \frac{\rho_0 \gamma_T}{\rho c_p} H_i
$$

(A3)

where $u_i$, $v_i$, $U_i$, $V_i$ are the $x$ and $y$ components of velocity, respectively, and $h_i$ is layer thickness. Also, $\rho_i$ is density, $\rho_0$ is a reference density, $\Delta \rho = \rho_2 - \rho_1$, and $f = f_0 + \beta (y - y_0)$ is the Coriolis parameter, $\gamma_T$ is the coefficient of thermal expansion, $c_p$ is the specific heat of seawater at constant pressure and is given in Table A1 along with the other model parameters. The variable $T_i$ in (A5) represents the departure from a reference temperature of 22°C for the respective layers. The heating term $H_i$ is, of course, zero for the second layer.

The pressure gradient terms in (A1) (and similarly in (A2)) for the respective layers are

$$
\frac{\partial P_i}{\partial x} = gh_1 \frac{\partial \rho_i}{\partial x} + \frac{\partial \eta}{\partial x} + \frac{\partial \rho_i}{\partial x} + g \rho_0 \frac{\partial \eta}{\partial x}
$$

$$
\frac{\partial P_2}{\partial x} = gh_1 \frac{\partial \rho_2}{\partial x} + g \rho_0 \frac{\partial \eta}{\partial x} - g \Delta \rho \frac{\partial h_1}{\partial x} + gh_2 \frac{\partial \rho_2}{\partial x} + \frac{\partial \eta}{\partial x}
$$

where $\eta = h_1 + h_2 - D$, is the sea surface elevation and $D$ is the depth of the water column.

The stress terms, $\tau'_i$ in (A1) and (A2) are the $x$ and $y$ components of the surface wind stress, while $\tau''_i$ and $\tau''_i$ are the interior interfacial and bottom stress, respectively. They are given by

$$
\tau'_i = \rho_0 f_x \bar{q} (u_i - u_2), \quad \rho_0 f_x \bar{q} (v_i - v_2)
$$

$$
\tau''_i = \rho_0 \bar{q} \bar{q} (v_i - v_2)
$$

Table A1. Parameter Values of the 8 m s\(^{-1}\) Case of the Physical Model

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$f_0$</td>
<td>$2.56 \times 10^{-5}$ s(^{-1})</td>
</tr>
<tr>
<td>$\beta$</td>
<td>$2.19 \times 10^{-11}$ m(^{-1}) s(^{-1})</td>
</tr>
<tr>
<td>$\gamma_T$</td>
<td>$2.746 \times 10^{-4}$ °C (^{-1})</td>
</tr>
<tr>
<td>$c_p$</td>
<td>$3.6274 \times 10^3$ J kg(^{-1}) °C (^{-1})</td>
</tr>
<tr>
<td>$\rho_0$</td>
<td>1025.0 kg m(^{-3})</td>
</tr>
<tr>
<td>$g$</td>
<td>9.81 m s(^{-2})</td>
</tr>
<tr>
<td>$c_3$</td>
<td>$2.0 \times 10^{-3}$</td>
</tr>
<tr>
<td>$K_x$</td>
<td>300 m s(^{-1})</td>
</tr>
<tr>
<td>$K_{x'}$</td>
<td>$(500/\Delta y_2) \Delta y_2$ m(^2) s(^{-1})</td>
</tr>
<tr>
<td>$K_y$</td>
<td>$2K_x$</td>
</tr>
<tr>
<td>$K_{y'}$</td>
<td>$2K_x$</td>
</tr>
<tr>
<td>$K_\sigma$</td>
<td>$100 \times 10^{-4}$ m(^2) s(^{-1})</td>
</tr>
<tr>
<td>$e_2$</td>
<td>$5.0 \times 10^{-4}$</td>
</tr>
</tbody>
</table>


\(\bar{q} = (q_1 + q_2)/2\) and $q_i = (u_i^2 + v_i^2)^{1/2}$. The entrainment terms in (A1) and (A2) are

$$
[S'_1, S'_2] = [(\rho/\rho_i)Q(u_i - u_2), (\rho/\rho_i)Q(v_i - v_2)]
$$

$$
[S'_2, S'_2] = [-(\rho/\rho_i)Q(u_i - u_2), -(\rho/\rho_i)Q(v_i - v_2)],
$$

and in (A3),

$$
E_1 = Q_1 - Q_2
$$

$$
E_2 = -E_1 = Q_2 - Q_1
$$

where $Q_1$ and $Q_2$ are derived as a function of the bulk Richardson number by Thompson [1974]. They are given by

$$
Q_1 = \rho_0 \phi \bar{u}_i/(g \Delta \rho \bar{h}_1)
$$

$$
Q_2 = \rho_0 \phi \bar{u}_i/(g \Delta \rho \bar{h}_2)
$$

with $u_\phi = \{[(\tau'_x)^2 + (\tau''_x)^2]/\rho_0\}^{1/2}$, $\bar{u}_\phi = \{[(\tau'_y)^2 + (\tau''_y)^2]/\rho_0\}^{1/2}$, and $\phi = 2$ is a constant of proportionality [Thompson, 1974]. We note that when the upper layer thickness becomes less than the minimum allowable value of 10 m, $Q_1$ is calculated using (A3) to restore the upper layer thickness to the minimum value.

The total horizontal velocity at any given depth of the biochemical model is obtained as the sum of the vertically averaged velocity from the appropriate layer of the two-layer model plus the departure from the vertical mean at the specified depth. Thompson [1974] has derived, to lowest order, a set of $z$-dependent equations for the departure of the horizontal velocity components from the vertical mean. These equations can be written for the upper and lower layers, $i = 1, 2$, as

$$
\frac{\partial \bar{u}_i}{\partial z} = \frac{g}{\rho_0} \frac{\partial \rho_i}{\partial y} + K_{\sigma} \frac{\partial \bar{u}_i}{\partial z}
$$

(A6)

$$
-\frac{\partial \bar{v}_i}{\partial z} = \frac{g}{\rho_0} \frac{\partial \rho_i}{\partial x} + K_{\sigma} \frac{\partial \bar{v}_i}{\partial z}
$$

(A7)

where $\bar{u}_i$ and $\bar{v}_i$ are the departures from the respective vertical mean for each layer and $K_{\sigma}$ is a vertical eddy viscosity. Equa-
tions A6 and A7, along with boundary conditions at the surface and the bottom, and a requirement of continuity of velocity at the interior interface, are solved to obtain analytical expressions for the perturbation velocity at any depth within the water column. These expressions are integrated over discrete depths and added to the vertically averaged components from A1 and A2 to obtain the depth-dependent flow field of the biochemical model.

The numerical method is fully explicit. A leapfrog technique is used in time and centered differences in space on a staggered grid arrangement with \( h_i \) and \( p_i \) positioned at the center of the grid cells, with \( U_i, u_i \) at one-half grid increment to the east and west of the cell centers, and with \( V_i, v_i \) at one-half grid increment to the north and south—the so-called "C" stencil [e.g., Batteen and Han, 1981]. The time step was 12 s. We found that application of the weak time filter of Asselin [1972] at every time step, as suggested by Blumberg and Mellor [1983], worked well in preventing decoupling of the solution at odd and even time steps. The occasional use of Euler's backward scheme [Walsh et al., 1989] was no longer necessary.

Steady state solutions were not obtained, although (A3) suggests that such a condition persists when the heating and entrainment terms balance the coastal divergence term. The heating term is small, giving a thermal expansion rate of \(-10^{-2} \text{ m d}^{-1}\). The coastal divergence term [Thompson, 1974] is approximately equal to \( r/(\rho g f) \approx 10 \text{ m d}^{-1} \) for an alongshore wind stress \( r \), of 0.1 N m\(^{-2}\), \( f \) of 2.7 \( \times 10^{-5} \text{ s}^{-1} \), and a Rossby radius of deformation (\( l \)) of 30 km in the 8 m s\(^{-1}\) wind case. The entrainment term, essentially \( Q_l \), is 2 m d\(^{-1}\) for a 10-m-thick upper layer and a 1 kg m\(^{-3}\) density difference across layers, such that a 0.2 kg m\(^{-3}\) density difference would be needed to balance the coastal divergence term. This condition occurs near the Araya Peninsula after about day 5 of the simulation. Because of the model's complicated coastline and bathymetry, however, numerical noise dominates the solution before a steady state over the whole domain is attained.

Appendix B

The state equations for phytoplankton carbon (\( P \)), bacteria (\( B \)), zooplankton pellets (\( Z \)), monomeric DOC (\( \text{DOC}_1 \)), macromolecular DOC (\( \text{DOC}_2 \)), nitrate (\( \text{NO}_3 \)), ammonium (\( \text{NH}_4 \)), and total dissolved inorganic carbon (\( \text{DIC} \)) are

\[
\frac{\partial P}{\partial t} = -\nabla \cdot (VP) + \frac{\partial}{\partial z} K_z \frac{\partial P}{\partial z} - g_P e P + g_{\rho}(1 - \Psi) P - \gamma Z - \alpha_1 P - \frac{\partial w P}{\partial z} \tag{B1}
\]

\[
\frac{\partial B}{\partial t} = -\nabla \cdot (VB) + \frac{\partial}{\partial z} K_z \frac{\partial B}{\partial z} + (g_3 + g_4)(1 - \zeta)B - mB \tag{B2}
\]

\[
\frac{\partial Z_f}{\partial t} = -\nabla \cdot (VZ_f) + \frac{\partial}{\partial z} K_z \frac{\partial Z_f}{\partial z} + a_3 \gamma Z + b_m m B - \alpha_2 Z_f - \frac{\partial w Z_f}{\partial z} \tag{B3}
\]

\[
\frac{\partial \text{DOC}_1}{\partial t} = -\nabla \cdot (V\text{DOC}_1) + \frac{\partial}{\partial z} K_z \frac{\partial \text{DOC}_1}{\partial z} - g_B B + g_p \Psi P + a_1 \gamma Z + \frac{\alpha_1}{\alpha_1 + \alpha_2} (\alpha P + \alpha_2) - X_2 \tag{B4}
\]

\[
\frac{\partial \text{DOC}_2}{\partial t} = -\nabla \cdot (V\text{DOC}_2) + \frac{\partial}{\partial z} K_z \frac{\partial \text{DOC}_2}{\partial z} - g_B B + a_2 \gamma Z + \frac{a_2}{\alpha_1 + \alpha_2} (\alpha P + \alpha_2) - X_2 \tag{B5}
\]

\[
\frac{\partial \text{NO}_3}{\partial t} = -\nabla \cdot (V\text{NO}_3) + \frac{\partial}{\partial z} K_z \frac{\partial \text{NO}_3}{\partial z} - g_1 \frac{P}{R} + X_1 \tag{B6}
\]

\[
\frac{\partial \text{NH}_4}{\partial t} = -\nabla \cdot (V\text{NH}_4) + \frac{\partial}{\partial z} K_z \frac{\partial \text{NH}_4}{\partial z} - g_2 \frac{P}{R} + a_4 \gamma Z + \frac{b_m (g_3 + g_4)}{\gamma R} - X_1 \tag{B7}
\]

\[
\frac{\partial \text{DIC}}{\partial t} = -\nabla \cdot (V\text{DIC}) + \frac{\partial}{\partial z} K_z \frac{\partial \text{DIC}}{\partial z} + g_3(1 - \epsilon)P - g_5 P + a_2 \gamma Z + \frac{b_m (g_3 + g_4)}{\gamma R} \tag{B8a}
\]

where at the surface boundary

\[
z = 0, \quad K_z \frac{\partial \text{DIC}}{\partial z} = \left( \frac{K_m}{h_i} \right) \alpha [(p\text{CO}_2)_0 - (p\text{CO}_2)_{\text{air}}] \tag{B8b}
\]

and the coefficient \( \alpha \) is the solubility of CO\(_2\) in seawater, while \((p\text{CO}_2)_0\) is the partial pressure of CO\(_2\) in the topmost layer of the water column. Both \( \alpha \) and \((p\text{CO}_2)_{\text{air}}\) are calculated following Peng et al. [1987], with \((p\text{CO}_2)_{\text{air}} = 355 \mu\text{atm}\). The piston velocity is \( K_n h_i^{-1} \) from

\[
K_n h_i^{-1} = 1.11 \times 10^{-3} W \tag{B8c}
\]

and \( W \) is the wind speed in meters per second.

The lower boundary conditions specify that the outflux of POM in (B1) and (B3) be returned without delay as an influx of 25% organic and 75% inorganic carbon, with inorganic nitrogen returned in the Redfield ratio as 25% NO\(_3\) and 75% NH\(_4\), and DOC\(_1\)/DOC\(_2\) in the ratio of 33%/67%.

The first terms on the right in (B1)–(B8) are the advective flux divergences, e.g., for phytoplankton,

\[
\nabla \cdot (VP) = \frac{\partial u P}{\partial x} + \frac{\partial v P}{\partial y} + \frac{\partial w P}{\partial z} \tag{B9}
\]

The eddy diffusivity \( K_z \) is calculated following Walsh and Dieterle [1994] with the additional assumptions that the surface mixed layer encompasses the upper layer of the physical model and that the lower layer of the physical model is stably stratified. It is also noted that the background diffusivity in stably stratified water is 0.2 cm\(^2\) s\(^{-1}\) [Martin, 1985], as opposed to 0.1 cm\(^2\) s\(^{-1}\) in Walsh and Dieterle [1994].

The growth terms, \( g_p \) in (B1) and \( g_1 \) and \( g_2 \) in (B1), (B6), and (B7), are given by

\[
g_p = c_i \min \left[ \frac{L(t, z)}{L_s} \exp \left( 1 - \frac{L(t, z)}{L_s} \right), g_N \right] \tag{B10}
\]

\[
g_N = \frac{\text{NO}_3}{(n_1 + \text{NO}_3)} e^{\text{NH}_4} + \frac{\text{NH}_4}{(n_2 + \text{NH}_4)} \tag{B11}
\]

\[
g_1 = \frac{g_p}{g_N} \frac{\text{NO}_3}{(n_1 + \text{NO}_3)} e^{\text{NH}_4} \tag{B12}
\]

\[
g_2 = \frac{g_p}{g_N} \frac{\text{NH}_4}{(n_2 + \text{NH}_4)} \tag{B13}
\]
Table B1. Parameter Values of the Ecological Model

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_1$</td>
<td>fraction of grazed POC converted to monomeric DOC_1 by copepods</td>
<td>0.20</td>
</tr>
<tr>
<td>$a_2$</td>
<td>fraction of grazed POC converted to macromolecular DOC_2 by copepods</td>
<td>0.30</td>
</tr>
<tr>
<td>$a_3$</td>
<td>fraction of grazed POC converted to fecal pellets; 70% assimilation efficiency</td>
<td>0.15</td>
</tr>
<tr>
<td>$a_4$</td>
<td>fraction of grazed POC converted to NH_4 and DIC by copepods</td>
<td>0.35</td>
</tr>
<tr>
<td>$b$</td>
<td>coefficient for the preferential uptake of NH_4 in the phytoplankton growth term</td>
<td>1.5</td>
</tr>
<tr>
<td>$b_1$</td>
<td>fraction of grazed bacteria converted to fecal pellets</td>
<td>0.01</td>
</tr>
<tr>
<td>$b_2$</td>
<td>fraction of grazed bacteria respired, i.e., converted to NH_4 and DIC</td>
<td>0.99</td>
</tr>
<tr>
<td>$c_1$</td>
<td>maximum algal growth rate over photoperiod</td>
<td>0.12 h^{-1}</td>
</tr>
<tr>
<td>$c_2$</td>
<td>maximum bacterial growth rate over 24-hour day</td>
<td>0.066 h^{-1}</td>
</tr>
<tr>
<td>$C/chl$</td>
<td>carbon/chlorophyll ratio for diatoms</td>
<td>50</td>
</tr>
<tr>
<td>DOC_3</td>
<td>DOC, dissolved organic carbon</td>
<td>55.0 \mu mol C kg^{-1} of refractory DOC</td>
</tr>
<tr>
<td>$I_0$</td>
<td>incident PAR</td>
<td>138 W m^{-2}</td>
</tr>
<tr>
<td>$k_w$</td>
<td>attenuation coefficient of PAR for seawater</td>
<td>0.03 m^{-1}</td>
</tr>
<tr>
<td>$k_p$</td>
<td>backscatter coefficient of bacteria</td>
<td>$6.0 \times 10^{-3}$ m^{-1} C m^{2}</td>
</tr>
<tr>
<td>$k_d$</td>
<td>attenuation coefficient of colored DOC (22% and 45% of DOC)</td>
<td>$1.84 \times 10^{-5}$ m^{-1} CDOM m^{2}</td>
</tr>
<tr>
<td>$L_o$</td>
<td>attenuation coefficient of chlorophyll</td>
<td>0.023 mg^{-1} chl m^{2}</td>
</tr>
<tr>
<td>$m$</td>
<td>optimal light intensity for phytoplankton growth</td>
<td>45 W m^{-2}</td>
</tr>
<tr>
<td>$n_1$</td>
<td>Michaelis-Menten half saturation constant for nitrate uptake</td>
<td>0.50 \mu mol N kg^{-1}</td>
</tr>
<tr>
<td>$n_2$</td>
<td>Michaelis-Menten half saturation constant for ammonium uptake</td>
<td>0.50 \mu mol N kg^{-1}</td>
</tr>
<tr>
<td>$n_3$</td>
<td>Michaelis-Menten half saturation constant for DIC uptake</td>
<td>0.83 \mu mol C kg^{-1}</td>
</tr>
<tr>
<td>$n_4$</td>
<td>half saturation constant for phytoplankton grazing losses</td>
<td>0.20 \mu mol C kg^{-1}</td>
</tr>
<tr>
<td>$\rho CO_2 - air$</td>
<td>partial pressure of atmospheric carbon dioxide</td>
<td>355 \mu atm</td>
</tr>
<tr>
<td>$R$</td>
<td>Redfieldian C/N uptake ratio by atoms of 7.0</td>
<td></td>
</tr>
<tr>
<td>$w_f$</td>
<td>fecal pellet settling rate of copepods</td>
<td>100 m day^{-1}</td>
</tr>
<tr>
<td>$X_1$</td>
<td>nitrification rate at low light and minimal NH_4 substrate</td>
<td>0.025 \mu mol N kg^{-1} d^{-1}</td>
</tr>
<tr>
<td>$X_2$</td>
<td>photolytic destruction of refractory DOC_2 to DOC_1</td>
<td>0.020 \mu mol DOC kg^{-1} h^{-1}</td>
</tr>
<tr>
<td>$Z_f$</td>
<td>standing stock of algal grazers</td>
<td>0.83 to 1.67 mmol C kg^{-1}</td>
</tr>
<tr>
<td>$\alpha_1$</td>
<td>phytoplankton lysing rate</td>
<td>0.0075 day^{-1}</td>
</tr>
<tr>
<td>$\alpha_2$</td>
<td>fecal pellet lysing rate</td>
<td>0.132 day^{-1}</td>
</tr>
<tr>
<td>$\epsilon$</td>
<td>fraction of phytoplankton growth that is respired</td>
<td>0.05</td>
</tr>
<tr>
<td>$\gamma_1$</td>
<td>fraction of phytoplankton growth that is excreted as DOC_1</td>
<td>0.04</td>
</tr>
<tr>
<td>$\xi$</td>
<td>maximum grazing rate of zooplankton, i.e. percent of body weight</td>
<td>1.0 day^{-1}</td>
</tr>
<tr>
<td>$\omega$</td>
<td>fraction of bacterial growth that is respired</td>
<td>0.50</td>
</tr>
<tr>
<td>$\psi$</td>
<td>fraction of bacterial growth that is excreted as DOC_2</td>
<td>0.04</td>
</tr>
<tr>
<td>$\phi_0$</td>
<td>photoperiod</td>
<td>12.25 hour</td>
</tr>
</tbody>
</table>

POC, particulate organic carbon; DOC, dissolved organic carbon, DIC, dissolved inorganic carbon; PAR, photosynthetically available radiation; CDOC, colored DOC.

where $b$ is 1.5 for the preferential uptake of ammonium.

With $t$ denoting time of day and $s$ denoting the time of sunrise, the light field $L(t,z)$ is calculated as a function of time of day assuming a sinusoidal distribution over the photoperiod by

$$L(t,z) = I_m \sin \left[ \pi \frac{(t-s)}{\omega} \right] e^{-kt} \tag{B14}$$

where $I_m$ is the amount of DOC, that is colored and $I_p$ is the daily mean PAR of 138 W m^{-2}, estimated from climatological data [Whitlock et al., 1995].

The grazing stress $\gamma Z$ in (B1) is calculated from

$$\gamma Z = \gamma Z_s \frac{P}{(n_4 + P)} \tag{B17}$$

where $\gamma$ is the ingestion rate and $Z_s$ is the zooplankton standing stock, assumed to be uniformly distributed over the upper 100 m of the water column.

Finally, the bacteria growth terms $g_3$ and $g_4$ in (B2), (B4), and (B5) are

$$g_3 = [c_3] \frac{DOC_1}{(n_4 + DOC_1)} \tag{B18}$$

$$g_4 = [c_4] [0.4] \frac{DOC_2}{(n_4 + DOC_2)} \tag{B19}$$

where the half-saturation, $n_3$, for uptake of DOC is 0.83 \mu mol kg^{-1} (Table B1).

Standard methods [O'Brien, 1986] are used for numerical solution of the model equations (B1)-(B8), using forward in time finite differences, with a time step of 600 s. The vertical diffusion terms are solved using centered differences, and upstream differencing is used for the advective terms. Inherent in the upstream numerical technique is relatively large artificial numerical diffusion, with implied diffusivities as large as 10^7 cm^2 s^{-1}, similar to that of $K$ of the circulation model (Table A1). Thus the computed steady state distributions of the ecological model tend to be quite smooth spatially. However, the
scheme always gives positive solutions, is transportive, has relatively small phase errors, and is easily implemented.

Acknowledgments. This research was supported by NSF grants OCE-9216626 to F.M.K. and J.J.W., OCE-9415790 to M.I.S. and G.T.T., and OCE-9401537 to R.T. as part of the CARIACO project. Additional funds were provided by NASA grants NAG5-6449 to J.J.W. and NAG5-6448 to F.M.K. and by the Venezuelan CONICIT to R.I.V. and R.A.

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