Technical Report

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“A numerical analysis of new nitrogen sources of NO_3 and N_2 effecting carbon cycling in the southern Caribbean Sea: a key to CDOC contamination of satellite color signals.”

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Hypotheses:

With funds from this NASA award, we wished to examine the role of nitrogen-fixation in oligotrophic regions, since prior NASA-supported studies by us had suggested that, based on budgets of carbon dioxide removal, nitrate supplies to subtropical regions were insufficient to support primary production, even during coastal upwelling (Walsh, 1996). Although simple N–P-Z [Nutrient-Phytoplankton-Zooplankton] models, with one state variable each to represent the plant and animal communities of the marine biological pump, have a long history and are still used in basin-scale models, they were of little utility in addressing the sources of new production.

In terms of altered climate cycles, moreover, we are now concerned with the future consequences of regional change in other phytoplankton composition: from calcium-clad, DIC-releasing coccolithophores to nitrogen-fixing, DON-secreting diazotrophs; to silica-requiring, usually edible diatoms; to toxic, motile dinoflagellates; and to carbon-cycling picoflagellates at the base of the microbial food web. Prediction of tomorrow's global biogeochemical states, induced by changing dominance of marine phytoplankton thus requires both synoptic, i.e. remotely-sensed, assessment of time series of the abundant functional groups of microalgae and numerical models to understand processes effecting their population fluctuations.

Long-term changes in plankton dynamics of the oceanic North Pacific, with a possible shift to more new production by the colonial nitrogen-fixer *Trichodesmium* as a consequence of global warming, and recent observations there of N_2 uptake by the unicellular *Synechocystis* demand continued revisions of our previous paradigms of marine carbon cycling (Walsh, 1996). Since the N_2 source of "new" nitrogen, used to fuel carbon sequestration, is not associated with a resupply of carbon dioxide, as during upwelling of NO_3 from the deep sea, the former is a "carbon free" supply. Furthermore, within oligotrophic shelf regions, DON release by nitrogen-fixers may lead to red tides of toxic dinoflagellates (Walsh and Steidinger, 2002).

Accordingly, we constructed a series of one-dimensional (Bissett et al., 1999a, b; Walsh et al., 2001: Lenes and Walsh, 2002; Penta et al., 2002) and three-dimensional (Walsh et al. 1999: 2002a, b) models for analysis of C, N, P, Fe, and Si cycling by multiple functional groups of phytoplankton in the Sargasso Sea around Bermuda, in the Caribbean Sea off Venezuela and Barbados, and on the West Florida shelf in the eastern Gulf of Mexico. The phytoplankton community in these models included large and small siliceous diatoms, phosphate-efficient coccolithophores, DOP-using toxic dinoflagellates [*Karenia brevis*], non-toxic dinoflagellates of high palatability, iron-regulated diazotrophs [*Trichodesmium*], sun-adapted chlorophytes, and shade-adapted cryptomonads, prochlorophytes, and cyanophytes [*Synechococcus*].

Results:

1. Models

In our first seasonal study of carbon/nitrogen cycling at the JGOFS time series site in the oligotrophic Sargasso Sea at 32°N (Bissett et al., 1999a), a complex light formulation of the Bermuda model involved spectral decomposition of the radiation field (Bissett et al., 1999b), with depth-dependent and seasonally varying UV-induced photolysis of the phytoplankton community and CDOM (colored dissolved organic matter). This one-dimensional model, forced by a time-dependent surface mixed layer (SML), replicated the observed monthly cycles of nitrate, ammonium, dissolved inorganic carbon, POC/PON, DOC, chlorophylls *a, b, c* , and of the spectral attenuation of light penetration at the BATS site. On an annual basis, a modest sequestration of atmospheric CO_2 was simulated in the Sargasso Sea, similar to the observations around Bermuda.

In the second seasonal analysis of carbon/nitrogen cycling at the Barbados time series site in the oligotrophic eastern Caribbean Sea at ~13°N, 60°W, we added *Trichodesmium*, iron, and phosphorus as state variables of another one-dimensional model (Lenes et al., 2002). Data on dust loadings (Walsh and Steidinger, 2001) and SML depth drove population fluctuations of simulated diazotrophs, which matched observed cell counts of *Trichodesmium* over the upper 50 m of the water column. Our simple model suggested that both P-limitation and Fe-limitation might curtail nitrogen-fixation off Barbados, so we next chose the West Florida shelf (WFS) as a natural laboratory to study these processes.

Coccolithophores are a co-dominant of the nanoplankton component of a total biomass of <0.2 g chl l^{-1}, found at the seaward edge of the oligotrophic WFS, while red tides of *Karenia brevis* amount to >20.0 g chl l^{-1} of net plankton near the coast (Walsh and Steidinger, 2001; Lenes et al.,2001). Accordingly, we added these phosphate-efficient, calcium-clad prymnesiophytes and DOM-utilizing, toxic dinoflagellates to our numerical food web. This third 1-dimensional model was used to study the response of the phytoplankton community to idealized nutrient perturbations of Loop Current intrusions, of estuarine outwellings, and of aeolian supplies of Saharan dust (Walsh et al., 2001; Penta et al., 2002), which again mimicked sparse observations.

Unvalidated three-dimensional biophysical models of any plankton succession are rather ethereal tools at best - at worst, they hide the lack of quantitative understanding behind the voluminous amounts of numerical output, which require equally large amounts of validation data to test model results. We thus began these 3-d analyses with simpler numerical food webs of the Venezuelan (Walsh et al., 1999) and West Florida (Walsh et al., 2002a) shelves, in which first diatoms and then dinoflagellates were the only groups of phytoplankton, culminating with three groups of diatoms, dinoflagellates, and microflagellates in the most recent study (Walsh, 2002b). None of this second set of models contained a diazotroph state variable, because the spatial fields of *in situ* and satellite observations of *Trichodesmium* are just now becoming available as future model constraints - see the last two sections of this report.

Our first coupled 3-d biophysical model considered carbon/nitrogen cycling by phytoplankton, zooplankton, and bacteria within the shelf environs of the Cariaco Basin (Walsh et al., 1999). During spring upwelling, the results of the reduced gravity circulation model matched both AVHRR and hydrographic estimates of surface temperature. The solutions of the embedded simple food web of diatoms, adult calanoid copepods, and ammonifying/nitrifying bacteria approximated within ~91% the mean spring observations of settling fluxes caught by a sediment trap at ~240 m, moored at a time series site in the Basin. The coupled models also estimated within ~89% the average ^{14}C net primary production and mimicked the sparse observations of the spatial fields of nitrate and light penetration during the same time period of February-April.

The WFS eventually provided a richer data set for continued evolution of our models. Here, a second simple ecological model, coupled now to a more complex primitive equation circulation model - the Princeton Ocean Model (POM), was able to replicate the observed alongshore transport of the toxic dinoflagellate *Karenia brevis* on the WFS shelf during a fall red tide in 1979 (Walsh et al., 2002). Initial land fall of these populations at the barrier islands in our model matched coastal data sets as well. The simulated vertical movement of *K. brevis*, in response to light-cued migration and nocturnal mixing, also mimicked these aspects of the fall red tides in 1980 and 1986, suggesting that sunrise populations may provide the strongest surface signal, for detection of red tides by remote sensors aboard aircraft and satellites. However, supplies of Loop Current nutrients and estuarine CDOM were not considered in this study.

In response to observed large-scale upwelled intrusions of nitrate-rich Gulf of Mexico slope water onto the WFS, diatoms won over both the microflagellates and toxic dinoflagellates during May-November 1998. In the absence of light-limitation by CDOM, a more complex biological model of the three phytoplankton groups, slope-water supplies of nitrate and silicate, and selective grazing stress by copepods and protozoans similarly allows the siliceous competitors to prevail within the 3-dimensional flow fields of the POM (Walsh et al., 2002b). However, a large red tide of *K. brevis* formed in the coupled models, when another case of estuarine supplies of CDOM favored growth of the shade-adapted, ungrazed dinoflagellate.

Over a 7-month period of the CDOM-free scenario, the simulated total primary production of the phytoplankton community amounts to a daily maximum of ~1.8 g C m^{-2} day^{-1} along the 40-m isobath of the northern WFS - as observed, with the largest accumulation of biomass on the Florida Middle Ground (FMG) at ~28°10'-28°45'N, 84°-84°25'W. Despite such photosynthesis, the WFS was a net source of CO_2 to the atmosphere during spring and summer and a small sink in the fall. With diatom losses of 90% of their daily carbon fixation to herbivores, the model results supported earlier impressions of a short, diatom-based food web on the FMG, where organic carbon content of the surficial sediments is ten-fold those of the surrounding sea beds.

Farther south, the simulated near-bottom pools of ammonium were highest in summer, where silicon regeneration was minimal, leading to temporary Si-limitation of the diatoms. Termination of these transient pulses of production by diatoms and microflagellates instead resulted from nitrate exhaustion in the model, mimicking ^{15}PON observations in the field - see next section. However, the model failed to replicate the observed red tide in December 1998, tagged with the ^{15} signature of nitrogen fixation. Formation of large harmful algal blooms of >1 ug chl l^{-1} (10^5 cells l^{-1}) in the southern part of the WFS, between Tampa Bay and Charlotte Harbor, must instead depend upon additional aeolian and/or estuarine supplies of nutrients and CDOM sun screen, focused by local upwelling.

2. Field experiments

As part of our NOAA/EPA ECOHAB [Ecology and Oceanography of Harmful Algal Blooms] field study of causative factors of harmful algal blooms, a series of ~175 cruises provided cross-shelf sections past some moored ADCP arrays off Sarasota, FL during March 1998-December 2001. These repeated sections provided the following set of measurements: temperature, salinity, nutrients (NO_3, NO_2, NH_4, PO_4, SiO_4, DOP, DON), O_2, chlorophyll, phaeopigments, PON, POC, POP, and the dominant species of phytoplankton and zooplankton. Some of these data were used in our last simulation analysis (Walsh et al., 2002b).

Additionally, on some of the cruises, optical measurements were made of plankton particles, of their images, of turbidity, and of the spectral dependence of absorption, backscatter, water-leaving radiance, and light attenuation during the ONR HyCODE [Hyperspectral Coastal Ocean Dynamics Experiment] program. Surface seawater samples were collected at discrete optical stations and processed for absorption spectra by total particulates ($a_p(\ )$), detritus ($a_d(\ )$), and CDOM ($a_{CDOM}(\ )$) and for high-performance liquid chromatography (HPLC) of pigments. Remote sensing reflectance spectra were measured at daylight stations to validate atmospherically corrected satellite data. Finally, seawater was pumped continuously from ~2 m through a flow-through system equipped with instruments for measuring temperature, salinity, fluorescence of chlorophyll *a* and CDOM, backscattering at two wavelengths ($b_b(488)$ and $b_b(676)$), and beam attenuation at three (480, 532, and 660 nm).

Farther to the north, other quarterly surveys of the MMS NEGOM [Northeastern Gulf of Mexico] project provided the upstream conditions across 11 other sections during 1998-2000. This third set of observations included underway ADCP, salinity, temperature, chlorophyll and CDOM fluorescence data and discrete observations of light penetration, nutrients (NO_3, NO_2, NH_4, urea, PO_4, SiO_4), O_2, HPLC pigments, CDOM absorption, POC, and PON. Using funds from this NASA grant, we contributed measurements of low levels of dissolved Fe and natural abundances of the ^{15}N of PON to both supplement the above data sets and test our hypotheses.

Unfiltered seawater samples were analyzed for total dissolved iron, using a 10-m pathlength liquid core waveguide to increase the sensitivity of the system, such that a minimum detection limit of 0.1 nmol kg^{-1} was achieved (Lenes et al., 2001). During the ECOHAB field studies, background levels of 0.1-0.5 nmol Fe kg^{-1} were found at the surface during periods of minimal dust delivery in May 2000 and October 1999. In contrast, total dissolved iron concentrations of ~16 nmol Fe kg^{-1} were measured at the West Florida shelf-break after a July 1999 Saharan dust event, identified by AVHRR imagery, ground-based radiometers, air mass analysis, and aerosol samples of dust and non-sea salt nitrate, located at Miami, Dry Tortugas, and St. Petersburg. Wet deposition was monitored at these land sites.

The *Trichodesmium* response following this July dust event was also a 100-fold increment over their background biomass, reaching a surface stock of ~20 colonies l^{-1}. These diazotrophs excrete up to ~50% of their nitrogen-fixation in the form of dissolved organic nitrogen. Consequently, their associated surface summer DON pools were found to be 3-4 fold greater than background stocks of ~5 mol DON kg^{-1}, compared to nitrate stocks of <0.5 mol NO_3 kg^{-1} (Lenes et al., 2001). After bacterial mediation of this diazotrophic source of new nitrogen and appropriate physical conditions, urea and ammonium could then have supported the red tide of >20 g chl l^{-1} of the toxic *K. brevis*, found along the West Florida coast during October 1999.

At that time, red tides of *K. brevis* had positive ^{15}PON values of 4.4 $^{o}/_{oo}$ during October 1999, compared to 3.6-5.1 $^{o}/_{oo}$ in October 2000, and 4.9 $^{o}/_{oo}$ in December 1998 - the expected value of phytoplankton growing within nitrate-stripped waters of the WFS is + 7.5 $^{o}/_{oo}$ (Walsh et al., 2002b). Values of + 3-5 $^{o}/_{oo}$ were found for the 2001 red tide as well. Organic nitrogen released from *Trichodesmium spp*, sea-grasses, mangroves, and even agricultural leachates may all supply an isotopic nitrogen-fixation signal for *K. brevis*, such that specific DON supplies have yet to be identified. Our most recent ^{13}C analyses at USF may rule out the macrophytes, however.

3. Satellite observations

Surface observations, after Saharan dust events tracked by AVHRR imagery, on the WFS in 1999 showed increments of dissolved iron, of *Trichodesmium*, and of DON, as well as depletion of DOP and PO_4 (Lenes et al., 2001), but the spatial juxtaposition of populations of *Trichodesmium* and *K. brevis* had only been inferred from previous helicopter sightings and a few cell counts (Walsh and Steidinger, 2001). Thus, in collaboration with Ken Carder , he introduced a satellite classification technique (Carder et al., 2002) for identifying both *K. brevis* and *Trichodesmium* stocks, based on optical field data of backscattering collected above the WFS - to provide validation data for future models. *Trichodesmium* populations at subsurface depths of 10-15 m were indeed found just offshore of red tides on both the Texas and Florida shelves within MODIS and SeaWiFS images.

The fate of these red tides must await the next set of simulation analyses from our 3-d coupled biophysical models, with addition of: atmospheric and estuarine supplies of nutrients; phosphorus, dissolved organic nitrogen, sediment microflora, labile CDOM, iron, and diazotroph state variables; and of imposed grazing demands of the major groups of herbivores sampled during ECOHAB and HyCODE. Yet, we are pleased that past cases of our 1-d and 3-d models replicated field data on intrusions of nitrate and silicate, regeneration of ammonium, light penetration, phytoplankton partition of primary production, estimated grazing demands, and carbon dioxide emissions in oligotrophic regions of the Sargasso Sea, the Caribbean Sea, and the eastern Gulf of Mexico. Thus far, the NASA support from Grant NAG5-6449 has yielded 11 reviewed publications, two Ph.D. dissertations, and 1 M.S. thesis.

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