

The Ecological Cycling of Colored Dissolved Organic Matter

W. Paul Bissett
Florida Environmental Research Institute
4807 Bayshore Blvd.
Suite 101
Tampa, FL 33611
phone: (813) 837-3374 x102 fax: (813) 902-9758 email: pbissett@flenvironmental.org

Award Number: N00014-00-1-0411
<http://www.flenvironmental.org>

LONG-TERM GOALS

The prediction of water-leaving radiance in coastal waters is strongly dependent on a quantitative prediction of the depth-dependent distribution of Colored Dissolved Organic Matter [CDOM] in the water column. The goal of this project is to support and synthesize laboratory and field experiments conducted by the ONR Environmental Optics Program. Our part of this larger project is to develop a quantitative understanding of the physical, chemical, optical, and biological interactions impacting CDOM cycling, and to codify this understanding into a numerical simulation, EcoSim 2.0.

OBJECTIVES

- 1) Provide satellite image analysis and meteorological support for ONR CDOM cruises.
- 2) Provide quantitative data synthesis support for chemical, biological, and physical interactions of CDOM data.
- 3) Develop ecological equations for CDOM cycling in the coastal marine environment.

APPROACH

We hypothesize that CDOM cycling is a deterministic process, one that can be explained by physical, chemical, and biological interactions. Furthermore, coupling experimental data with environmental modeling will lead to the development of a set of ecological equations that will resolve the sources and sinks of CDOM, and the impacts on water column IOPs and AOPs. A previous one-dimensional numerical simulation of the bio-optical properties of the Sargasso Sea (Ecological Simulation 1.0 (EcoSim 1.0) Bissett et al., 1999a; Bissett et al., 1999b) suggested that the cycling of CDOM could be mathematically described and validated. In this case, the EcoSim 1.0 results were validated against the multi-year bio-optical time series program operating at the Bermuda Atlantic Time-series Station (BATS Siegel and Michaels, 1996; Siegel et al., 1995). In particular, simulated CDOM did not co-vary with the particulate organic absorption or the chlorophyll a concentration, as was previously assumed in these oligotrophic environments (Gordon and Morel, 1983; Smith and Baker, 1981).

Separation of the CDOM signal from the particulate signal in oligotrophic regions is important for understanding the propagation of light to depth, and its impact on water-leaving radiance signals used

Report Documentation Page				Form Approved OMB No. 0704-0188	
Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.					
1. REPORT DATE 30 SEP 2001		2. REPORT TYPE		3. DATES COVERED 00-00-2001 to 00-00-2001	
4. TITLE AND SUBTITLE The Ecological Cycling of Colored Dissolved Organic Matter				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S)				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Florida Environmental Research Institute,,4807 Bayshore Blvd.,Suite 101,,Tampa,,FL, 33611				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT The prediction of water-leaving radiance in coastal waters is strongly dependent on a quantitative prediction of the depth-dependent distribution of Colored Dissolved Organic Matter [CDOM] in the water column. The goal of this project is to support and synthesize laboratory and field experiments conducted by the ONR Environmental Optics Program. Our part of this larger project is to develop a quantitative understanding of the physical, chemical, optical, and biological interactions impacting CDOM cycling, and to codify this understanding into a numerical simulation, EcoSim 2.0.					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT Same as Report (SAR)	18. NUMBER OF PAGES 9	19a. NAME OF RESPONSIBLE PERSON
a REPORT unclassified	b ABSTRACT unclassified	c THIS PAGE unclassified			

in satellite oceanography. These regions cover approximately 80% of the world's oceans. However, the CDOM signal can be 1-3 orders of magnitude higher on coastal shelves and near-shore regions. These higher signals result in part from the higher primary productivity found in coastal regions, but also result from the loading of CDOM from the outflows of rivers and estuaries. Prediction of in-water Inherent Optical Properties [IOPs] and the resultant water-leaving radiance [L_w] would require that we accurately address the ecological cycling of CDOM, i.e. the chemical, photochemical, biological, and physical sources and sinks of CDOM in the near-shore region.

WORK COMPLETED

Mississippi Cruise

To support planning for the CDOM cruise on the R/V Pelican of April 5th-11th, we began data collection on March 28th. Sources for the data included the processed SeaWiFS and AVHRR imagery from NRL-Stennis Code 7240 (<http://www7240.nrlssc.navy.mil/>), COAMPS 27 km current and forecast FNMOC (<http://152.80.49.205/PUBLIC/>), NCAR Research Application Program (<http://www.rap.ucar.edu/weather/>), NOAA National Weather Service (<http://www.srh.noaa.gov/lix/>), and the Colorado Center for Astrodynamics Research Gulf of Mexico Near Real-Time Altimeter Data Geostrophic Velocity Viewer (http://www-ccar.colorado.edu/~realtime/gom-real-time_vel/). In reviewing the SeaWiFS and AVHRR imagery on the 28th, we noticed some interesting SST and color anomalies with definitive edges around the Mississippi Delta region that suggested some far-field physical forcing may be impacting the plume area during the course of the experiment. Thus, we proceeded to analyze data from the beginning of March in order to forecast possible directions of the Mississippi plume over the cruise period.

A synthesis of the satellite and weather forecast data was collected each day into PowerPoint files following the 28th until the end of the cruise on April 11th. Each day these syntheses were placed on the UMB FTP server for access by the R/V Pelican scientific personnel and other interested parties. These syntheses are also currently available on request from FERI.

EcoSim 2.0

During this period we completed a re-analysis of the color cycling equations for wavelengths less than 440 nm EcoSim 1.0. These equations were built from disparate data sets of DOM and CDOM creation and destruction and used to simulate the cycling of color in the Sargasso Sea. A critical error in this simulation was the extreme loss of absorption at shorter wavelengths (<440 nm). This loss was thought to result from a number of possible errors in the quantitative description of color cycling relating to –1) indirect creation of color by phytoplankton and bacteria lysis and grazing; 2) direct creation of color bacteria excretion, 3) destruction of color via heterotrophic utilization of CDOM for energy requirements, 4) destruction of color via photolysis of CDOM to colorless DOM, 5) destruction of color via photolysis of CDOM to DIC.

Each of the above factors was critically analyzed during the period with a new set of equations and parameters derived for the CDOM and color detritus cycling. These new equations were included into a larger simulation analysis of the West Florida Shelf (WFS) during the fall of 1998. In this simulation work, we were attempting to hindcast color and red tide dynamics observed during an EPA/NOAA/ONR/State of Florida funded field campaign (ECOHAB). Multiple simulations were run in order to test the CDOM equations and their sensitivity to parameter settings.

RESULTS

Mississippi Cruise

Figure 1 shows the CCAR geostrophic flow calculations from March 28th. A warm core ring/loop current excursion is clearly evident to the south of the delta. The strong eastward current to the south of the delta held for the entire cruise period. However, the plume appears to be more responsive to surface winds than to offshore flows. The surface winds from the east-southeast were driven by a low-pressure center to the north, and a high-pressure center just to the east, which for the most part kept the plume flowing to the west-southwest (Figure 2 and 3).

We also found that the SeaWiFS backscattering algorithm at 555 nm developed by B. Arnone of NRL-Stennis was a useful indicator of surface plume dynamics near the mouth of the Mississippi (Figure 3). In some cases this is a more useful algorithm than those focused on other SeaWiFS bands. This may appear to be somewhat of a paradox, given that the CDOM does not absorb as much light at 555 nm as it does at 412 nm. However, the Mississippi River also has a high suspended solid load, which produces a high L_w signal at 555 nm, making it possible to readily distinguish the plume waters from background Gulf of Mexico waters. The higher absorption of light at 412 nm may cause signal-to-noise difficulties for CDOM retrieval algorithms. In addition, there may be calibration problems with the 412 nm channel (per. comm. B. Arnone). For this river plume under these conditions, it may be that plume dynamics can best be discerned remotely via backscattering calculations versus absorption calculations.

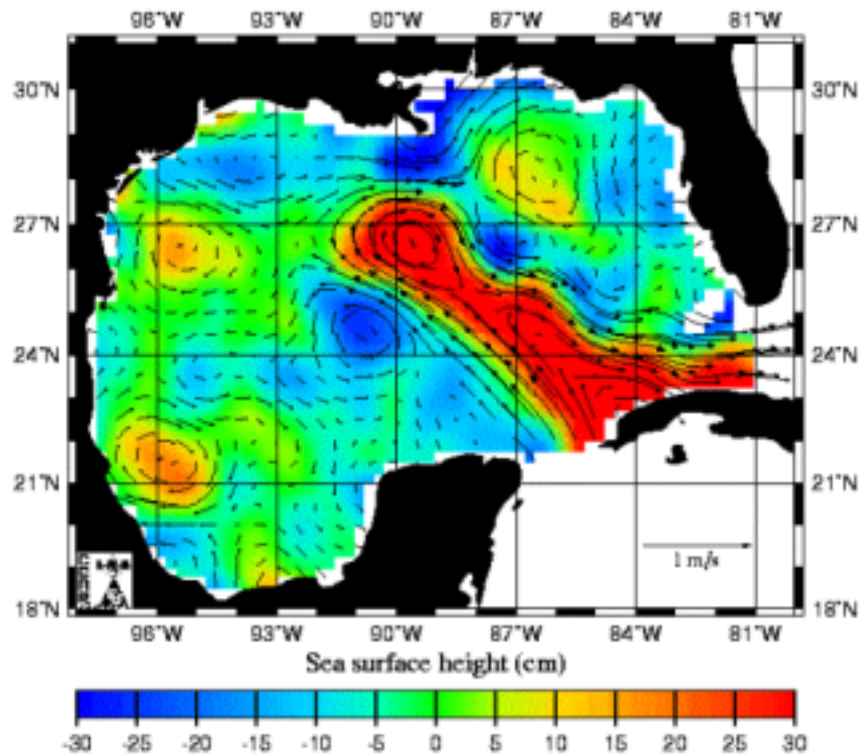


Figure 1. TOPEX/ERS2 analysis of sea surface height and calculated geostrophic flow on March 28, 2001.

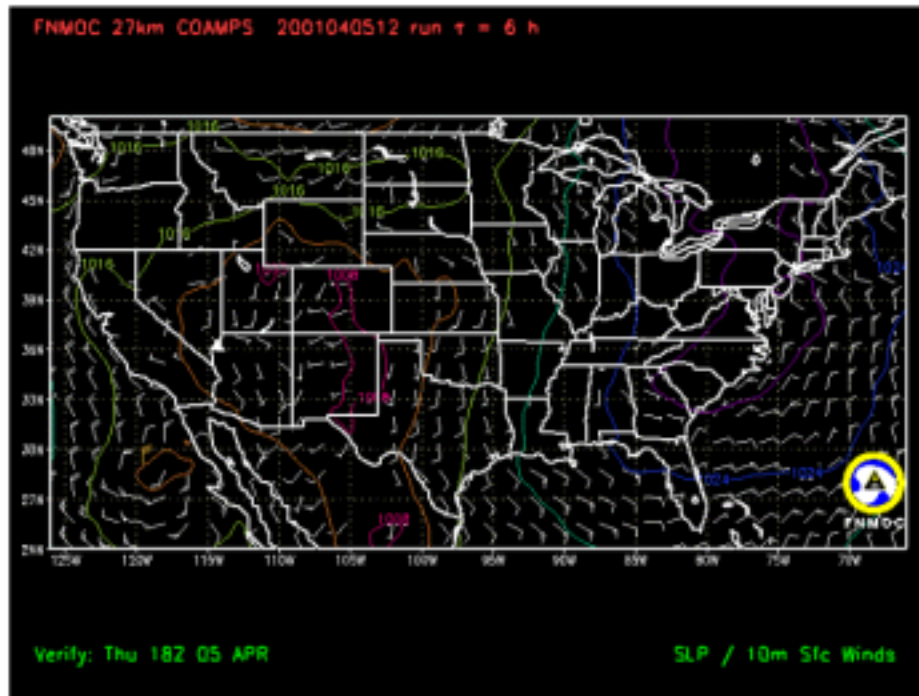


Figure 2. FNMOC COAMPS 27 km resolution surface wind forecast for April 5, 2001. Winds around the Mississippi Delta are from the east-southeast.

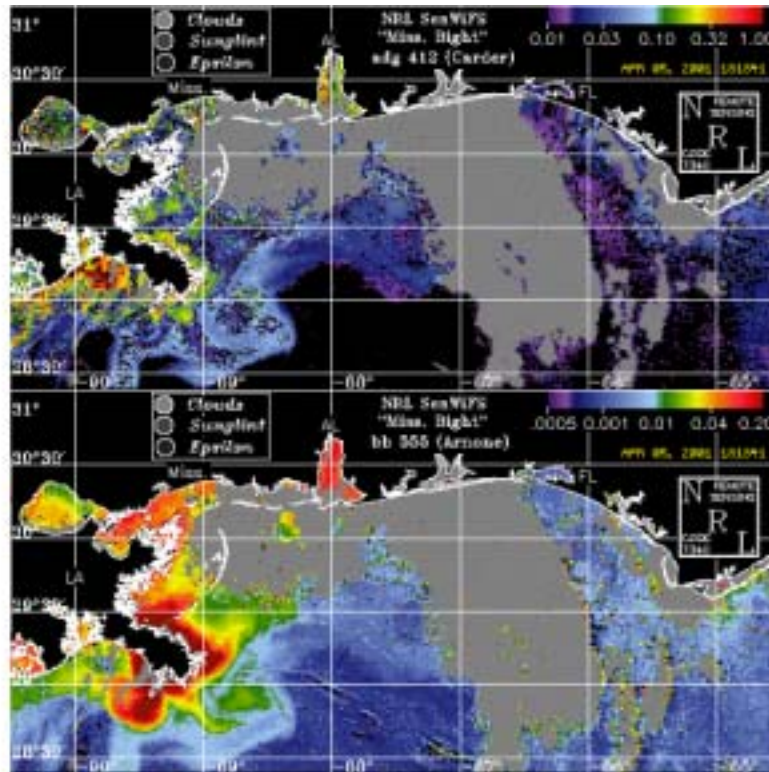


Figure 3. NRL SeaWiFS data products for the Mississippi Bight on April 5, 2001. Upper figure is $a_{dg}(412)$ calculated using K. Carder (USF) algorithm. Lower figure is the $b_b(555)$ calculated using B. Arnone (NRL) algorithm.

Re-analysis of the indirect production of color by phytoplankton and bacteria led to a significantly reduced value of the fraction of CDOM released from lysis and grazing. The fraction of carbon was released as CDOM was reduced from 5.5 to 3.23% during these processes. The value was calculated during a reconstruction of the labile and recalcitrant specific absorption (Bissett et al., 1999a) using the specific absorption of pure water (Pope and Fry, 1997) and the assumption of net non-use of color for bacterial heterotrophic growth (Moran et al., 2000; Vodacek et al., 1997). This change led to a significant increase in the quantity (~300% increase) and total absorption of light by labile CDOM. Prior to this change heterotrophic bacteria had consumed almost all of the labile CDOM production, because in oligotrophic waters they are typically energy (labile DOM) limited (Bissett et al., 1999b).

The other significant change was a decrease in the rates of photolysis. The initial rates (Bissett et al., 1999a) were found to have been derived with experimental data that was not appropriate for the type of calculations we were attempting. In one study, it appeared that there were biological contaminants in the photolysis experiment. In another, the decay rate was calculated over the entire time integral (>8 hours). While this was accurate for that time integral, the EcoSim calculations use a much smaller delta t (<300 seconds), and as a result our estimated decay rate was much too fast for our method of calculation, i.e., we used a linearly calculated time decay in an exponential type equation. Our photolysis decay rates for DIC and colorless DOC were thus reduced (at 410 nm) from 0.62 and 0.59 $\mu\text{M m hr}^{-1}$, respectively, to 0.0193 and 0.0034 $\mu\text{M m hr}^{-1}$. This change also resulted in a significant increase in the accumulation of CDOM (~70%) and an increase in the total absorption by CDOM.

These new terms were placed into our 2-D simulations of the West Florida Shelf for 1998 (see progress report for N00014-98-1-0844). In these numerical experiments we were simulating the impacts of estuarine discharges of 33 psu waters onto the shelf waters of 36 psu. Figure 4 shows the total absorption for these at 412 nm. These compare quite well with the AC-9 derived total absorption at 412 nm versus salinity gradients (Figure 5) collected during the ECOHAB Process cruises (per. comm. G. Kirkpatrick, Mote Marine Laboratory and O. Schofield, Rutgers University)

IMPACT/APPLICATIONS

To forecast the clarity of the water column over both short- and long-term time horizons requires an accurate quantification of the ecological cycling of CDOM. Incorporation of a validated set of CDOM equations into a larger three-dimensional ecological simulation will increase the veracity of the predictions of Inherent and Apparent Optical Properties [IOPs and AOPs], and help achieve the goal of forecasting optical properties as a function of the biological, chemical, and physical forcing.

RELATED PROJECTS

- 1) Robert Chen (UMB) was chief scientist on the ONR-funded CDOM cruise, and collects the spatial distribution of CDOM, as well as a suite of other environmental variables with the ECOShuttle.
- 2) Mary Ann Moran (U of Georgia) and Richard Zepp (EPA) are conducting laboratory and field measurements on the photolysis of CDOM, as well as the bacterial utilization of in situ and photodegraded CDOM.

3) William Miller (Dalhousie, CA) is conducting experiments on the photolysis of CDOM as a function of the spectral distribution of irradiance.

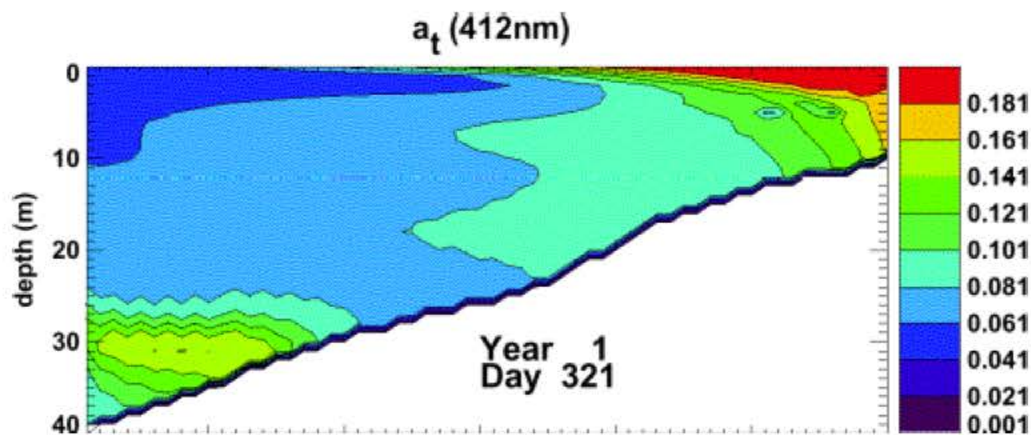


Figure 4. Simulated $a_t(412)$ from 2-D West Florida Shelf EcoSim 2.0 simulation during fall 1998. Cross shelf contours show impacts of low salinity waters (33 psu) on total absorption resulting from CDOM influxes at shoreward boundary.

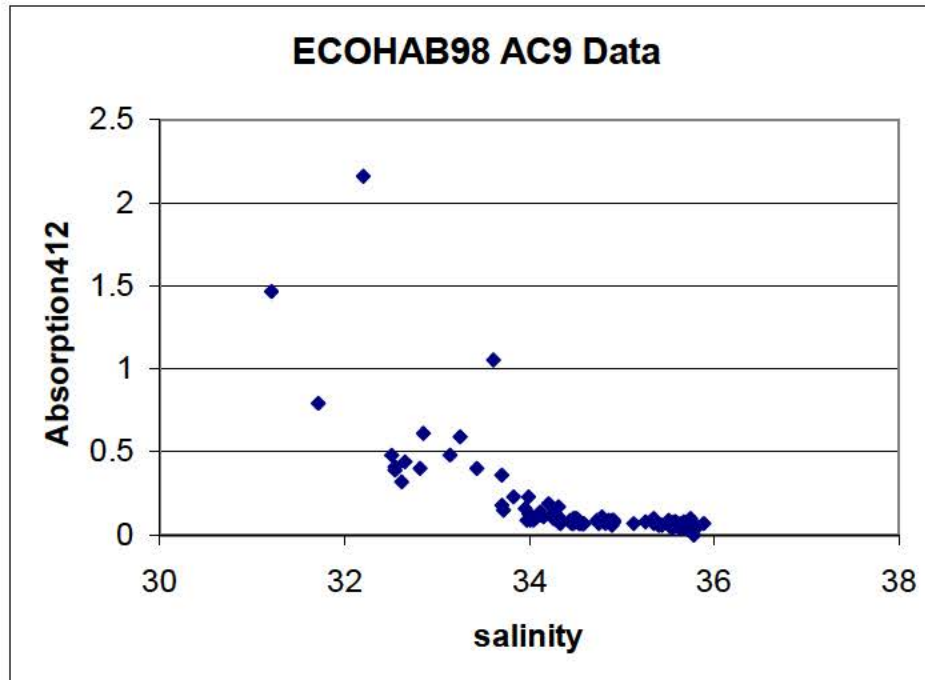


Figure 5. ECOHAB Process Cruise Data from 1998 showing salinity versus absorption relationship from AC-9 measurements at 412 nm.

REFERENCES

- Bissett, W.P., Carder, K.L., Walsh, J.J. and Dieterle, D.A., 1999a. Carbon cycling in the upper waters of the Sargasso Sea: II. Numerical simulation of apparent and inherent optical properties. *Deep-Sea Research I*, 46(2): 271-317.
- Bissett, W.P., Walsh, J.J., Dieterle, D.A. and Carder, K.L., 1999b. Carbon cycling in the upper waters of the Sargasso Sea: I. Numerical simulation of differential carbon and nitrogen fluxes. *Deep-Sea Research I*, 46(2): 205-269.
- Gordon, H.R. and Morel, A., 1983. Remote assessment of ocean color for interpretation of satellite visible imagery, A review. Springer-Verlag, New York, 114 pp.
- Moran, M.A., Sheldon, W.M. and Zepp, R.G., 2000. Carbon loss and optical property changes during long-term photochemical and biological degradation of estuarine dissolved organic matter. *Limnology and Oceanography*, 45(6): 1254-1264.
- Pope, R.M. and Fry, E.S., 1997. Absorption spectrum (380-700nm) of pure water. II. Integrating cavity measurements. *Applied Optics*, 36(33): 8710-8723.
- Siegel, D.A. and Michaels, A.F., 1996. Quantification of non-algal light attenuation in the Sargasso Sea: Implications for biogeochemistry and remote sensing. *Deep Sea Research II*, 43(2-3): 321-345.
- Siegel, D.A., Michaels, A.F., Sorensen, J.C., Brien, M.C.O. and Hammer, M.A., 1995. Seasonal variability of light availability and utilization in the Sargasso Sea. *Journal of Geophysical Research*, 100(C5): 8695-8713.
- Smith, R.C. and Baker, K.S., 1981. Optical properties of the clearest natural waters (200-800nm). *Applied Optics*, 20(20): 177-184.
- Vodacek, A., Blough, N.V., DeGrandpre, M.D., Peltzer, E.T. and Nelson, R.K., 1997. Seasonal variation of CDOM and DOC in the Middle Atlantic Bight: Terrestrial inputs and photooxidation. *Limnology and Oceanography*, 42(4): 674-686.

PUBLICATIONS

- Schofield, O., Arnone, R., Bissett, W. P., Crowley, M., Moline, M. A., Glenn, S. (2001) Cyclops is dead: Tapping the international constellation of ocean color satellites. *Backscatter* (submitted)
- Schofield, O., Bergmann, T., Kohut, J., Glenn, S. M., Pegau, W. S., Boss, E., Davis, C., Synder, W., Bowles, J., Kappus, M., Arnone, B., Weidemann, A. Bissett, W. P., Moline, M. A., Heine, E. L., Case, J., Herren, C. (2001) Adaptive sampling of a "Red River" in the coastal waters using a coastal ocean observatory. *EOS* (submitted)
- Bissett, W. P., Schofield, O., Glenn, S., Cullen, J. J., Miller, W. L., Plueddemann, A. J., Mobley, C. D., (2001) Resolving the impacts and feedbacks of ocean optics on upper ocean ecology. *Oceanography*, 14:(in press).

- Schofield, O., Bergmann, T., Bissett, W.P., Grassle, F., Haidvogel, D., Kohut, J., Moline, M., Glenn, S. (2001). The Long Term Ecosystem Observatory: An integrated coastal observatory. *Journal of Oceanic Engineering*, (in press).
- Walsh, J.J., B. Penta, D.A. Dieterle, and W. P. Bissett. (2001) Predictive ecological modeling of harmful algal blooms. *Human Ecological Risk Assessment*, (in press).
- Walsh, J.J., Haddad, K.D., Dieterle, D.A., Weisberg, R.H., Li, Z., Yang, H., Muller-Karger, F.E., Heil, C.A., and Bissett, W.P., (2001). A numerical analysis of landfall of the 1979 red tide of *Karenia brevis* along the west coast of Florida. *Continental Shelf Research*, (in press).
- Bissett, W.P., Schofield, O., Mobley, C., Crowley, M.F., and Moline, M.A. (2000). In "Methods in Microbiology, Volume 30: Marine Microbiology" (J.H. Paul, ed), Optical Remote Sensing Techniques in Biological Oceanography. Academic Press, London. 519-540.
- Schofield, O., Grzymiski, J., Bissett, W.P., Kirkpatrick, G., Millie, D.F., Moline, M., and Roesler, C.S. (1999). Optical monitoring and forecasting systems for harmful algal blooms: possibility or pipe dream? *Journal of Phycology*, 35, 1477-1496.
- Walsh, J.J., Dieterle, D.A., Muller-Karger, F.E., Bohrer, R., Bissett, W.P., Varela, R.J., Aparicio, R., Diaz, R., Thunell, R., Taylor, G.T., Scranton, M.I., Fanning, K.A., and Peltzer, E.T. (1999). Simulation of carbon-nitrogen cycling during spring upwelling in the Cariaco Basin. *Journal of Geophysical Research* 104, 7807-7825.
- Bissett, W. P., J. J. Walsh, D. A. Dieterle and K. L. Carder (1999) Carbon cycling in the upper waters of the Sargasso Sea: I. Numerical simulation of differential carbon and nitrogen fluxes. *Deep-Sea Research*, 46(2):205-269.
- Bissett, W. P., K. L. Carder, J. J. Walsh and D. A. Dieterle (1999) Carbon cycling in the upper waters of the Sargasso Sea: II. Numerical simulation of apparent and inherent optical properties. *Deep-Sea Research*, 46(2):271-317.
- Bissett, W. P., J. S. Patch, K. L. Carder and Z. Lee (1997) Pigment packaging and chlorophyll a-specific absorption in high-light oceanic waters. *Limnology and Oceanography*, 42(5): 961-968.