

Dispersal of the Suwannee River plume over the West Florida shelf: Simulation and observation of the optical and biochemical consequences of a flushing event

Jason K. Jolliff, John J. Walsh, Ruoying He, Robert Weisberg, Antoya Stovall-Leonard, Paula G. Coble, Robyn Conmy, Cynthia Heil, Bisman Nababan, Haiying Zhang, Chuanmin Hu, and Frank E. Muller-Karger

College of Marine Science, University of South Florida, St. Petersburg, Florida, USA

Received 21 January 2003; accepted 14 May 2003; published 11 July 2003.

[1] We have combined a circulation model with one of colored dissolved organic matter (CDOM) photolysis to describe the fate of terrestrial CDOM on the West Florida shelf (WFS). Our results for summer 1998 suggest that a near shore plume of CDOM became entrained in a coastal jet extending south from the Suwannee River (Big Bend) region of the WFS towards the Florida Keys—a feature also evident in satellite ocean color imagery. The coupled models suggest that photochemical losses of CDOM were significant, but provided only a minimal nitrogen source for phytoplankton growth on the WFS. **INDEX TERMS:** 4219 Oceanography: General: Continental shelf processes; 4852 Oceanography: Biological and Chemical: Photochemistry; 4255 Oceanography: General: Numerical modeling; 4847 Oceanography: Biological and Chemical: Optics. **Citation:** Jolliff, J. K., et al., Dispersal of the Suwannee River plume over the West Florida shelf: Simulation and observation of the optical and biochemical consequences of a flushing event, *Geophys. Res. Lett.*, 30(13), 1709, doi:10.1029/2003GL016964, 2003.

1. Introduction

[2] On the west coast of Florida, ~25 river and estuary systems discharge terrestrially derived colored dissolved organic matter (CDOM) to the shelf. Eastward advection of colored effluent from rivers west of the Apalachicola River has also been observed [Muller-Karger et al., 1991; Del Castillo et al., 2001]. Accordingly, Gilbes et al. [1996] attempted to correlate the radiance signal remotely sensed by the Coastal Zone Color Scanner, a signal often contaminated in coastal regions by CDOM [Hochman et al., 1995], with river discharge data. Over the WFS, however, no obvious correlation between river discharge and ocean color variability could be inferred without further consideration of the time-dependent variability of the sinks and dispersal mechanisms of terrestrial CDOM discharged into the coastal ocean.

[3] We have analyzed these processes with a coupled physical-photochemical model of the dispersal and photolysis of terrestrial CDOM on the WFS from the perspective of possible CDOM sources of new nitrogen for algal growth. We have compared our model results with sea-viewing wide field-of-view (SeaWiFS) satellite imagery, *in situ* bio-optical measurements, and laboratory studies of phytoplankton

uptake of terrestrial CDOM (i.e., humic and fulvic acids). We infer from our time-dependent simulations that a significant optical feature of June 1998, a plume of ocean color extending south from the Florida peninsula to the Florida Keys, was due to the entrainment of Suwannee River effluent in the surface Ekman layer during upwelling favorable wind events. Our model results provide an estimate of the optical and photochemical processes that occurred within the Suwannee River plume during this time period. The additional consistency between our modeled photochemical yield of nitrogen and our culture work suggests that CDOM provides, at most, ~5% of the daily nitrogen demand for phytoplankton growth.

2. Methods

2.1. Physical and Photochemical Models

[4] A regional adaptation of a primitive equation ocean model [Blumberg and Mellor, 1987], forced by the National Center for Environmental Prediction's reanalysis wind product, surface heat flux fields, and lateral inputs of buoyancy at the coast [He and Weisberg, 2002, 2003; Weisberg and He, 2003], provided daily flow fields (u , v , ω) and the vertical mixing coefficient (K_z) over an orthogonal, curvilinear grid (Figure 1) for the solution of:

$$\frac{\partial \text{CDOM}}{\partial t} = -u \frac{\partial \text{CDOM}}{\partial x} - v \frac{\partial \text{CDOM}}{\partial y} - \omega \frac{\partial \text{CDOM}}{\partial z} + \frac{\partial}{\partial z} K_z \frac{\partial \text{CDOM}}{\partial z} - \text{photCDOM} \quad (1)$$

where the carbon and nitrogen components of terrestrial CDOM were a constant CDOC/CDON ratio of 40 [Ertel et al., 1986].

[5] A photolysis submodel served as the last term in equation (1), following the equations of Zepp and Cline [1977]. Spectral (290–400 nm) incident ultraviolet (UV) radiation was simulated as a function of stratospheric ozone layer thickness, location, day-of-year, and time-of-day [Baker et al., 1980; Green et al., 1980]. A spectrally neutral reduction factor of 15% was used to account for clouds. Water column scattering in the UV wavelengths was ignored, simplifying the solution for the depth attenuation of downwelling UV irradiance to an iterative solution of the Lambert-Beer law. Spectral quantum yield values for the production of dissolved inorganic carbon, biologically labile photoproducts, and refractory bleached organic carbon were

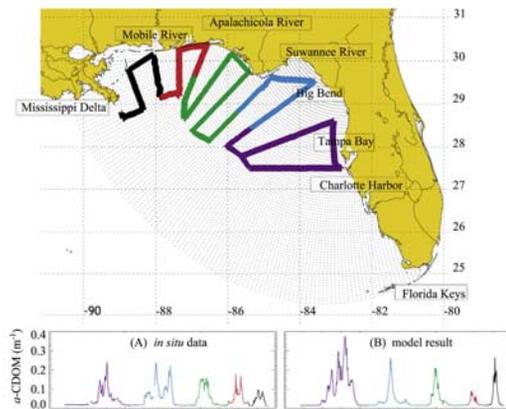


Figure 1. The model domain (black dots) and the cruise track for NEGOM 4, 12–25 November 98, is overlaid in colors corresponding to (a) the along track underway CDOM absorption measurements at 443 nm (calibrated from underway fluorescence measurements using discrete station CDOM absorption/fluorescence relationships, [Hu *et al.*, 2003]) and (b) the corresponding model results for surface CDOM absorption at 443 nm.

obtained from the literature [Amon and Benner, 1996; Miller and Moran, 1997; Miller *et al.*, 2002b].

2.2. Boundary Conditions and Validation Data

[6] A freshwater CDOM boundary condition for simulated year 1998 was established for 32 rivers encompassed by the model domain from (a) U.S.G.S. streamflow data ($\text{m}^3 \text{s}^{-1}$) and (b) spectrophotometric CDOM absorption measurements (m^{-1}) both collected by us and supplemented with literature values [Zepp and Schlotzhauer, 1981; Clark *et al.*, 2002; Miller *et al.*, 2002a]. These 32 CDOM absorption measurements at zero salinity were then divided by a mean mass specific absorption (at 443 nm) for CDOM of $6.4 \text{ m}^2 \text{ mol}^{-1}$ [Zepp and Schlotzhauer, 1981] and multiplied by (a) to determine the mass flux (mol s^{-1}) of CDOM along the coasts. This flux was superimposed upon a constant background marine CDOM signal (0.015 m^{-1} at 443 nm).

[7] Other *in situ* CDOM absorption data over the north-eastern Gulf of Mexico during November 1998 (Figure 1) provided validation data [Hu *et al.*, 2003]. Uptake rates of terrestrial CDOM (the nitrogen content of humic and fulvic acids from the Suwannee and Peace Rivers) obtained from laboratory cultures of diatoms, cyanophytes, chlorophytes, and the toxic dinoflagellate *Karenia brevis* provided a comparison for our model calculated photoproduction rates of labile nitrogen species, i.e. the photoproduction of inorganic nitrogen and biologically labile photoproducts from refractory humic substances. Finally, SeaWiFS observations processed with the OC4 algorithm [O'Reilly *et al.*, 1998] provided a qualitative comparison between our model calculated surface distribution of CDOM and regional patterns of ocean color.

3. Results

3.1. Northwest WFS

[8] The model results for 22 November 1998 (Figure 1b) mimic the *in situ* surface CDOM absorption measurements

(Figure 1a). The overall magnitude (maximum values $\sim 0.2\text{--}0.4 \text{ m}^{-1}$ at 443 nm) and position of the modeled peaks agree well with the observations. The model underestimates the CDOM absorption peaks between the Mobile and Apalachicola Rivers (red region of Figure 1). This discrepancy may be due to the sensitivity of the model to spectral quantum yield values assigned, as discussed below.

3.2. Suwannee River Plume

[9] The summer 1998 model result depicts a plume of CDOM extending south from the Big Bend region towards the Florida Keys (Figure 2). We provide a supplementary animation of the model result¹ that shows the southward advection of this CDOM plume during June 1998. A similar pattern is seen in SeaWiFS ocean color imagery. A time series of normalized SeaWiFS chlorophyll-*a* values and the normalized modeled surface CDOM absorption values peak at 27.7°N , 83.2°W on 5–7 June, peak again at 27.0°N , 83.0°W on 15–17 June, and subsequently peak again 80 km further south (Figure 2). Thus, the model suggests that some of the variability observed in SeaWiFS ocean color at these locations is due to terrestrial CDOM. Furthermore, analysis of the 32 modeled river sources, performed by removing different river effluents in other simulation runs, confirms that the source of the modeled terrestrial CDOM at these locations was the Suwannee River.

[10] In the model and composite SeaWiFS imagery, a plume of color traverses the length of the WFS from the Big Bend region south towards Charlotte Harbor, and is then flushed off-shelf past the Florida Keys. The modeled optical consequences of the Suwannee River plume's $\sim 400 \text{ km}$ southward journey to the Florida Keys—a flushing event—are shown in Figure 3. The increased CDOM absorption values found within the plume (Figure 3a) significantly attenuate UV-B irradiance ($280\text{--}320 \text{ nm}$), a spectral range potentially harmful to the biota (Figure 3b). Downwelling UV-B irradiance within the path of the plume at 27.0°N is $150 \mu\text{W cm}^{-2}$ the first week of June, and then reduced by 70% two weeks later as the Suwannee River plume is advected through that location (Figure 3b).

[11] The biochemical consequences of the Suwannee River plume's southward dispersal are assessed by calculating the maximum amount of nitrogen potentially made available to phytoplankton via photochemical CDOM degradation. The maximum photochemical yield of inorganic nitrogen [Bushaw *et al.*, 1996], as well as labile organic nitrogen from biologically labile photoproducts [Miller *et al.*, 2002b], is $\sim 250 \mu\text{mol N m}^{-2} \text{ d}^{-1}$ near the mouth of the Suwannee River and $\sim 150\text{--}200 \mu\text{mol N m}^{-2} \text{ d}^{-1}$ within the plume as it is advected south (Figure 3c). Sensitivity analysis shows this photochemical N yield not to be significantly impacted by the probable range of CDOM mass specific absorptions we calculated from our river CDOM absorption and DOC concentration observations ($\sim 3\text{--}12 \text{ m}^2 \text{ mol}^{-1}$ at 443 nm for a CDOM/DOC ratio of 1.0–0.15). In contrast, halving and doubling the spectral

¹ Auxiliary material may be found at <ftp://ftp.agu.org/apend/gl/2003GL016964>.

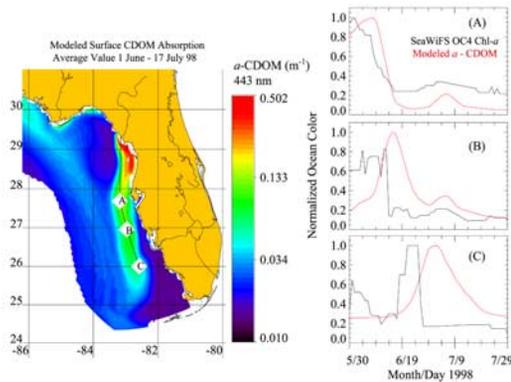


Figure 2. The average surface CDOM absorption over the WFS for the period 1 June 98–17 July 98 shows the southward dispersal of the Suwannee River plume. At right, a time series (5 May 98–29 July 98) for locations along a transect through the river plume shows the variability in the modeled surface CDOM normalized by the highest value modeled for that location during the time period (red). Similarly, 7-day composite SeaWiFS chlorophyll-*a* values for the corresponding pixel locations are presented (black) as values normalized by the highest value observed during that time period. Values were interpolated when cloud cover obscured retrieval.

quantum yield values we obtained from the literature halves and doubles the maximum photochemical nitrogen yield near the Suwannee River’s mouth ($125\text{--}500\ \mu\text{mol N m}^{-2}\ \text{d}^{-1}$; Figure 3c). Nevertheless, the spectral quantum yield values used for this study were some of the highest reported in the literature [Miller *et al.*, 2002b], such that we regard the maximum photochemical nitrogen yield from the baseline model run as a reasonable estimate.

4. Discussion

4.1. Physical Setting

[12] Persistent southward and offshore currents characterized the surface flow of the WFS in summer 1998 as a consequence of upwelling favorable wind events, the seasonal succession of the baroclinic circulation, and remote Loop Current influence [Weisberg and He, 2003]. The coupled models suggest that the Suwannee River plume became entrained in the surface Ekman layer due to a combination of upwelling favorable wind events and strong thermal stratification. The river plume’s trajectory within this frictional boundary layer was then significantly modified by the WFS geometry.

[13] In the north, the convex curvature of the Big Bend coastline and the southeast/northwest orientation of isobaths further offshore set up an area of convergent southward flow east of Tampa Bay. In the south, the partial closure of the southern boundary by the Florida Keys set up an adverse pressure gradient, causing the surface flow to diverge from the coast in the vicinity of Charlotte Harbor [Weisberg *et al.*, 2000]. As a consequence, previous surface drifters tended to avoid the Florida Bay region southeast of Charlotte Harbor, the Forbidden Zone [Yang *et al.*, 1999]. Similarly, the decaying CDOM in our simulation (Figure 2) followed the surface flow fields as they diverged from the coast near

Charlotte Harbor, and was subsequently flushed off-shelf past the Florida Keys.

4.2. Photochemical Yield

[14] Our simulated photochemical rates indicated that 58.5% of the CDOM added from the coastline was ultimately lost to photolysis on the WFS. This finding is consistent with the assertion of Hedges *et al.* [1997] that at least 50% of terrestrial dissolved organic matter discharged to the continental margins must be completely remineralized before export to the open ocean. The maximum nitrogen yield resulting from this photochemical carbon sink, a potential source of nitrogen for phytoplankton growth, is $\sim 250\ \mu\text{mol N m}^{-2}\ \text{d}^{-1}$, while the maximum reported primary production in the Big Bend region is $\sim 0.44\ \text{gC m}^{-2}\ \text{d}^{-1}$ [Lohrenz *et al.*, 1999]. This suggests that photochemical nitrogen yield can, at most, support $\sim 5\%$ of the nitrogen demand of primary production.

[15] This model finding is supported by our continuing culture work with *K. brevis*, which consumed 100-fold more humic and fulvic acids—on a per cell basis—than the diatoms of similar size. Yet, a red tide of $10\ \mu\text{g chl l}^{-1}$ (1×10^6 cells l^{-1}) would have a maximum nitrogen uptake rate of only $0.034\ \mu\text{M N d}^{-1}$ from humic substances (i.e., 3.5% of their daily nitrogen demand). Our simulated maximal photolysis yield of $0.05\ \mu\text{M N d}^{-1}$ within the upper 5 meters of the Suwannee River plume suggests that only the nitrogen in humic substances that undergoes photochemical change is made available to *K. brevis*.

[16] Thus, photolysis of terrestrial CDOM (composed largely of humic substances), while important in determining its shelf-wide distribution and optical impact, falls far short of the nitrogen requirements of *K. brevis*, let alone those of

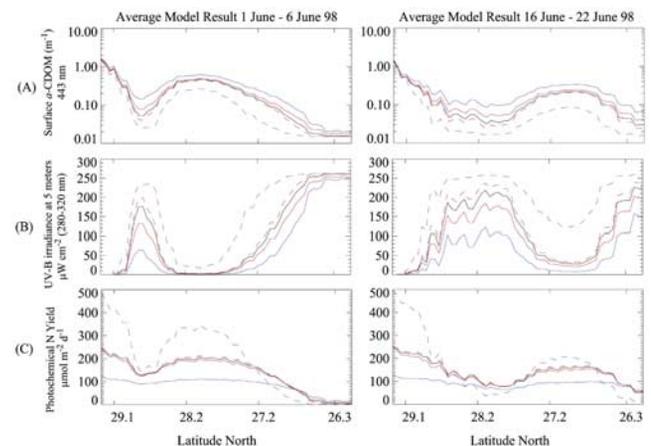


Figure 3. Model results along the transect shown in Figure 2 are given as a 7-day average for 1 June–7 June 98 (Left) and 16 June–22 June 98 (Right). Surface CDOM absorption at 443 nm (a), the 1600 UTC downwelling UV-B irradiance (280–320 nm) at 5 meters below the surface (b), and the depth integrated photochemical yield of labile nitrogen (c) are shown for the base model run (solid black line), half the spectral quantum yield values (solid blue line), double the spectral quantum yield values (dashed blue line), half the 443 nm CDOM mass specific absorption ($3.18\ \text{m}^2\ \text{mol}^{-1}$; solid red line), and twice the mass specific absorption ($12.72\ \text{m}^2\ \text{mol}^{-1}$; dashed red line).

diatoms, chlorophytes, and cyanophytes. Since slope water intrusions are also not a sufficient nitrogen source for *K. brevis* populations [Walsh et al., 2003], nitrogen fixation [Walsh and Steidinger, 2001] continues to be invoked as the trigger mechanism for the onset of WFS red tides.

[17] **Acknowledgments.** This research was funded by the Office of Naval Research N00014-99-1-0212, N00014-96-1-5024, N00014-98-1-0158, N0014-01-1-0041, NASA NAG5-10738, ECOHAB EPA R82792-01-0, and NSF OCE #0095970. We thank Doug Biggs for his assistance with the collection of underway NEGOM data. NEGOM fieldwork was funded by the Minerals Management Service (MMS) through contract No. 1435-01-97-CT-30851 as part of the Northeastern Gulf of Mexico Physical Oceanography Program: Chemical Oceanography and Hydrography Study.

References

- Amon, R. M. W., and R. Benner, Photochemical and microbial consumption of dissolved organic carbon and dissolved oxygen in the Amazon River system, *Geochim. Cosmochim. Acta*, 60(10), 1783–1792, 1996.
- Baker, K., R. Smith, and A. E. S. Green, Middle ultraviolet radiation reaching the ocean surface, *J. Photochem. and Photobiol. B: Biol.*, 32, 367–374, 1980.
- Blumberg, A. F., and G. L. Mellor, A description of a three-dimensional coastal ocean circulation model, in *Three-Dimensional Coastal Ocean Models*, edited by N. Heaps, 208–233, AGU, Washington, D.C., 1987.
- Bushaw, K. L., R. G. Zepp, M. A. Tarr, D. Schultz-Lander, R. A. Bourbonniere, R. Hodson, W. L. Miller, D. A. Bronk, and M. A. Moran, Photochemical release of biologically available nitrogen from dissolved organic matter, *Nature*, 381, 404–407, 1996.
- Clark, C. D., J. Jimenez-Morias, J. Jones II, E. Zanardi-Lombardo, C. A. Moore, and R. D. Zika, A time-resolved fluorescence study of dissolved organic matter in a riverine to marine transition zone, *Mar. Chem.*, 78, 121–135, 2002.
- Del Castillo, C. E., P. G. Coble, R. N. Conmy, F. E. Muller-Karger, L. Vanderbloemen, and G. A. Vargo, Multispectral in situ measurements of organic matter and chlorophyll fluorescence in seawater: Documenting the intrusion of the Mississippi River plume in the West Florida Shelf, *Limnol. and Oceanogr.*, 46(7), 1836–1843, 2001.
- Ertel, J. R., J. I. Hedges, A. H. Devol, J. E. Richey, and M. Ribeiro, Dissolved humic substances in the Amazon river system, *Limnol. and Oceanogr.*, 31(739–754), 1986.
- Gilbes, F., C. Tomas, J. J. Walsh, and F. E. Muller-Karger, An episodic chlorophyll plume on the West Florida Shelf, *Cont. Shelf Res.*, 16(9), 1201–1224, 1996.
- Green, A. E. S., K. R. Cross, and L. A. Smith, Improved analytic characterization of ultraviolet skylight, *Photochem. Photobiol.*, 31, 59–65, 1980.
- He, R., and R. H. Weisberg, West Florida shelf circulation and temperature budget for the 1999 spring transition, *Cont. Shelf Res.*, 22(5), 719–748, 2002.
- He, R., and R. H. Weisberg, West Florida shelf circulation and temperature budget for the 1998 fall transition, *Cont. Shelf Res.*, 23(8), 777–800, 2003.
- Hedges, J. I., R. G. Keil, and R. Benner, What happens to terrestrial organic matter in the ocean?, *Org. Geochem.*, 27(5/6), 195–212, 1997.
- Hochman, H. T., J. J. Walsh, K. L. Carder, A. Sourmia, and F. E. Muller-Karger, Analysis of ocean color components within stratified and well-mixed waters of the English Channel, *J. Geophys. Res.*, 100(C6), 10,777–10,787, 1995.
- Hu, C., F. E. Muller-Karger, D. C. Biggs, K. L. Carder, B. Nababan, D. Nadeau, and L. Vanderbloemen, Comparison of ship and satellite bio-optical measurements on the continental margin of the NE Gulf of Mexico, *Intl. J. Remote Sens.*, in press, 2003.
- Lohrenz, S. E., D. A. Wiesenburg, R. A. Arnone, and X. Chen, What controls Primary Production in the Gulf of Mexico?, in *The Gulf of Mexico Large Marine Ecosystem: Assessment, Sustainability, and Management*, edited by H. Kumpf, K. A. Steidinger, and K. Sherman, Blackwell Science, 151–170, 1999.
- Miller, W. L., and M. A. Moran, Interaction of photochemical and microbial processes in the degradation of refractory dissolved organic matter from a coastal marine environment, *Limnol. and Oceanogr.*, 42, 1317–1324, 1997.
- Miller, R. L., M. Belz, C. Del Castillo, and R. Trzaska, Determining CDOM absorption spectra in diverse coastal environments using a multiple path-length, liquid core waveguide system, *Cont. Shelf Res.*, 22, 1301–1310, 2002a.
- Miller, W. L., M. A. Moran, W. M. Sheldon, R. G. Zepp, and S. Opsahl, Determination of apparent quantum yield spectra for the formation of biologically labile photoproducts, *Limnol. and Oceanogr.*, 47(2), 343–352, 2002b.
- Muller-Karger, F. E., J. J. Walsh, R. H. Evans, and M. B. Myers, On the seasonal phytoplankton concentration and sea surface temperature cycles of the Gulf of Mexico as determined by satellites, *J. Geophys. Res.*, 96(C7), 12,645–12,665, 1991.
- O'Reilly, J. E., S. Maritorea, B. G. Mitchell, D. A. Siegal, K. L. Carder, S. A. Garver, M. Kahru, and C. McClain, Ocean color algorithms for SeaWiFS, *J. Geophys. Res.*, 103(C11), 24,937–24,953, 1998.
- Walsh, J. J., and K. A. Steidinger, Saharan dust and Florida red tides: The cyanophyte connection, *J. Geophys. Res.*, 106(C6), 11,597–11,612, 2001.
- Walsh, J. J., R. H. Weisberg, D. A. Dieterle, R. He, B. P. Darrow, J. K. Jolliff, K. M. Lester, G. A. Vargo, G. J. Kirkpatrick, K. A. Fanning, T. T. Sutton, A. E. Jochens, D. C. Biggs, B. Nababan, C. Hu, and F. E. Muller-Karger, The phytoplankton response to intrusions of slope water on the West Florida shelf: Models and observations, *J. Geophys. Res.*, in press, 2003.
- Weisberg, R. H., B. D. Black, and Z. Li, Upwelling case study on Florida's West Coast, *J. Geophys. Res.*, 104, 11,459–11,469, 2000.
- Weisberg, R. H., and R. He, Local and deep-ocean forcing contributions to anomalous water properties on the West Florida Shelf, *J. Geophys. Res.*, in press, 2003.
- Yang, H., R. H. Weisberg, P. P. Niiler, W. Sturges, and W. Johnson, Lagrangian circulation and forbidden zone on the West Florida Shelf, *Cont. Shelf Res.*, 19, 1221–1245, 1999.
- Zepp, R. G., and D. M. Cline, Rates of direct photolysis in the aquatic environment, *Environ. Sci. Technol.*, 11(4), 359–366, 1977.
- Zepp, R. G., and P. F. Schlotzhauer, Comparison of photochemical behavior of various humic substances in water: Spectroscopic properties of humic substances, *Chemosphere*, 10, 479–486, 1981.

J. K. Jolliff, J. J. Walsh, R. He, R. Weisberg, A. Stovall-Leonard, P. G. Coble, R. Conmy, C. Heil, B. Nababan, H. Zhang, C. Hu, and F. E. Muller-Karger, College of Marine Science, University of South Florida, St. Petersburg, Florida, USA. (jolliff@seas.marine.usf.edu)