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Influence of extreme storm events on West Florida Shelf CDOM distributions

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[1] Colored Dissolved Organic Matter (CDOM) distribution and signatures provide vital information about the amount and composition of organic material in aquatic environments. This information is critical for deciphering the sources and biogeochemical pathways of organic carbon, and thus vital to the understanding of carbon cycling and budgets. Waters of the West Florida Shelf are heavily influenced by many river systems on Florida’s Gulf Coast that, to the first order, control CDOM distributions on the shelf. Three storm events during 2004 and 2005 (Hurricane Charley, Hurricane Wilma, and a Winter Storm) profoundly altered the typical distribution of CDOM fluorescence and absorption properties on the Southern West Florida Shelf. Seasonal surveys revealed that changes in the underwater light field as a result of major hurricanes and resuspension events are linked closely with a number of factors prior to a storm’s passing such as the presence of persistent blooms, rainfall and discharge. Additionally, storm track and wind direction were found to play a significant role in CDOM signatures.


1. Introduction
1.1. Background and Relevance

[2] Dissolved Organic Matter (DOM) in seawater is the largest reactive reservoir of carbon on earth. Contained within it is the photochemically active fraction, CDOM, which has a multitude of sources and undergoes a variety of chemical, biological and physical processes in estuaries and ocean waters [Cabaniss and Shuman, 1987; Donard et al., 1989; Cauwet et al., 1990; Coble et al., 1990; Blough et al., 1997, 2007]. CDOM mediates the sunlight-induced reactions of nonliving systems and also influences biological productivity, affecting primary productivity by determining the quality and quantity of sunlight available for photosynthesis, providing UV shading and nutrients to marine biota, influencing metal binding, materials transport and overall water quality [Aiken, 2002; Blough and Del Vecchio, 2002; Coble, 2007]. As a result many studies have been dedicated to understanding the source, cycling and fate of organic carbon in aquatic environments.

[3] CDOM has distinctive optical properties that may be used to distinguish possible sources, as well as to determine the composition of the material. The major source to coastal waters is from river runoff of humic substances from soils which dominates DOM composition in nearshore waters [Duursma, 1974; Laane, 1981; Berger et al., 1984; Hayase et al., 1987]. Away from the coast, however, CDOM is of marine origin from biological processes such as autotrophic productivity, zooplankton feeding and bacterial interactions [Yentsch and Reichert, 1961; Traganza, 1969; Carlsson and Mayer, 1983; Chen, 1992; Coble, 1996].

[4] In coastal environments, there are many ways in which CDOM measurements are critical for computing ocean carbon fluxes and budgets. First, it is conservative with respect to salinity [Cabaniss and Shuman, 1987] and can be used to track water masses and carbon sources [Del Castillo et al., 1999, 2001; Kowalczyk et al., 2003; Stedmon et al., 2003; Chen et al., 2004; Conny et al., 2004b; Nelson et al., 2007]. Second, color is routinely measured by monitoring and management agencies, is a measure of ecosystem health [McPherson and Miller, 1987; Dixon and Kirkpatrick, 1999; Corbett and Hale, 2006] and fluorescence intensity has been shown to be a proxy for Dissolved Organic Carbon (DOC) in some regions [Ferrari et al., 1996; Vodacek et al., 1997; Del Castillo et al., 1999; Baker and Spencer, 2004; Del Castillo, 2005]. Third, recent studies have also established links between freshwater DOM concentrations and biogeochemistry with Land Use/Land Cover (LULC) [Jaffé et al., 2008], climatology, and hydrology [Williamson and Zagarese, 2003] patterns. Fourth, interference by CDOM with remotely sensed ocean color measurements make it challenging to retrieve accurate chlorophyll a (CHL) concentrations in the world’s oceans [Carter et al., 1989; Muller-Karger et al., 1989; Hu et al., 2003; Del Castillo, 2005] and its measurement is essential for improved primary productivity estimates. Furthermore, this material is the only component of DOM that can be measured with in situ and remote optical sensors. This has

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significant implications, because establishing regional relationships between DOC and CDOM allows for making estimates of the larger organic carbon pool, based on a smaller, easier to measure component. Additionally, because CDOM appears to have longer residence times than timescales of most estuarine and coastal mixing processes, it represents a significant portion of DOM that is exported to the open ocean [Chen and Gardner, 2004].

Using CDOM as a tracer of circulation in coastal and open ocean environments is especially important in regions with complex mixing of marine and terrestrial organic material, where strong gradients exist in chemical and optical properties of CDOM [Del Castillo, 2005]. This is the case on the West Florida Shelf (WFS), where the dominant terrestrial CDOM from the many rivers on the eastern margin of the Gulf of Mexico mixes with the CDOM of marine origin. The distinctive optical properties of each source are altered as a function of mixing on the shelf. Linking the primary factors that determine the distribution of CDOM on river-dominated margins (seasonal currents, precipitation, river discharge, winds, storms, etc.) with the optical properties provides a powerful tool for untangling the ambiguities regarding the cycling and fate of organic material in the ocean. This in turn could make possible predictive capabilities of DOM concentrations in coastal environments.

Presented in this paper are the spatial distributions of CDOM in the southern portion of the West Florida Shelf (WFS) between Tampa Bay and Florida Bay over a three year period. Seasonal differences were observed using discrete and in situ sampling techniques to generate spatial maps. Differences in the optical properties of CDOM were used to infer differences in the source and composition of organic material. Results from this study advance the understanding of CDOM in coastal environments by (1) providing valuable field measurements of optical water quality parameters for ocean color bio-optical algorithms designed to retrieve more accurate regional estimates of seasonal primary productivity, (2) assessing variability in the distribution and sources of CDOM in shelf environments during periods of high and low river discharge, and (3) demonstrating the manner in which CDOM is affected by local forcing of winds, currents, storms, discharge.

1.2. Geographic Setting

The West Florida Shelf (WFS) is located in the eastern portion of the Gulf of Mexico (Figure 1). It is marked by a large shelf width as a result of the gentle sloping of the inner shelf. The shallow nature of the shelf means that the coastal water column can be well mixed and that benthic communities reside within the euphotic zone. The WFS is a river-dominated environment, where freshwater enters from various river sources along the northern and eastern margins of the Gulf. Seasonality of riverine discharge, where rivers to the north peak in spring and summer, and rivers to the south peak only in summer [Cross, 1974; Solis and Powell, 1999], gives rise to temporal and spatial differences in the contribution of freshwater and materials throughout the year on the shelf. In addition, unique environments of the headwaters, including rivers...
that are controlled by dams or gates (Hillsborough, Caloosahatchee) or ones that are swamp-fed (Suwannee, Shark) or ones that traverse agricultural lands (Manatee, Peace) result in compositional differences among rivers and influence the amount and composition of CDOM making it to the WFS [Boehme, 2000; Conmy, 2008].

[8] Once on the shelf, materials originating from freshwater environments are mixed with those from marine waters. This intense mixing makes identification of specific freshwater end-members in this region difficult at salinities above 25 [Conmy, 2008]. Seasonal patterns in winds and currents then impact the distribution of organic material in these coastal waters, where dominant forcing is to the south from October–April and to the north in summer months [Weisberg et al., 2005]. Additionally, intermittent weather phenomena, such as hurricanes, tropical storms and winter storm events, also influence the distribution of substances in shelf waters. This can result in the resuspension of sediments and dissolved material into the water column which influences water clarity. Additionally, distributions of productivity-critical substances such as nutrients, metals, organics and particles are also affected by weather phenomena. It is these distributions that are key in determining if, what type, and where phytoplankton blooms occur on the shelf. This is particularly important on the WFS, where Karenia brevis, a toxic dinoflagellate, blooms nearly annually (late fall to winter) causing red tides that affect the coastal ecosystem. Two of the field experiments (December 2004 and November 2005) detailed in this paper were conducted during times of Harmful Algal Blooms (HABs) of K. brevis. The active 2004 hurricane season has been proposed as a contributing factor to the persistent blooms that initiated in fall 2004 [Hu et al., 2006]. The bloom moved south from the Charlotte Harbor region in October to the Florida Bay and Keys region, where high cell concentrations were observed in November 2004. In January 2005, high counts were also observed 30 miles offshore of Florida’s west coast. In April–May 2005, field measurements showed diminished cell concentrations, satellite imagery using a K. brevis classification criteria [Cannizzaro et al., 2008] showed the bloom moved north and was never sampled. The bloom reappeared between Tampa Bay and Charlotte Harbor in July–August 2005 and cell concentrations continued to increase through November 2005. The bloom finally diminished in December 2005.

2. Methodology
2.1. Sample Collection
[9] Discrete water samples were collected during seasonal field experiments on the Shelf as part of the Florida Bay Circulation and Exchange Study (NOAA/AOML) and the Florida Red Tide Program (Florida Fish and Wildlife Conservation Commission) on board the R/V F. G. Walton Smith and the R/V Suncoaster, respectively. Surveys were conducted during December 2003, August 2004, December 2004, April 2005, August 2005 and November 2005. Surface and subsurface samples (down to water depths of 26.5 m) were collected via Niskin bottles for all field experiments. During the Florida Bay Circulation and Exchange Study, whole water was collected in amber glass bottles and filtered through precombusted GF/F filters (up to 24 h at 450°C) on board using glass filtration apparatus and a pump. During the Florida Red Tide Program cruises, water was gravity filtered through precombusted GF/F filters mounted in stainless steel in-line filtration apparatus. Procedural blanks performed with both filtration methods show good agreement and have fluorescence intensities that are insignificant to that WFS CDOM samples (R. N. Conmy, unpublished data). All filtered water was then stored frozen in precombusted, amber glass bottles until slowly thawed for absorption and fluorescence analyses. To verify that the freezing process did not result in any loss of chromophores, absorption spectra were collected prior to and after freezing to assure no change in spectral properties [Conmy, 2008].

2.2. Absorbance Spectroscopy
[10] Absorbance spectra were obtained using a Hitachi U-3300 dual-beam spectrophotometer with matching one and ten centimeter quartz cells. Measurements were made at 1 nm intervals between 200 and 750 nm with Milli-Q deionized water in the reference cell. Samples were scanned three times and then averaged to reduce noise and yield a more robust spectrum. Data were corrected for scattering and baseline fluctuations by subtraction from each wavelength, the measured absorption at 700 nm [Bricaud et al., 1981]. Absorbance values were converted to absorption coefficients using the following equation,

\[ a(\lambda) = \frac{2.303A(\lambda)}{r}, \]

where \( A \) is the absorbance (Log \( I_o/I \)) and \( r \) is the path length in meters. Spectral slopes were then calculated for a variety of wavelength ranges between 250 and 440 nm using linear least squares regression.

2.3. Fluorescence Spectroscopy
[11] High-resolution fluorescence spectroscopy was performed on the discrete samples according to the method of Coble [1996] using a Horiba Jobin Yvon Inc. Fluoromax II spectrofluorometer with a 150 Watt xenon lamp and single excitation and emission monochromators. Samples with absorbance values above 0.02 at 300 nm using a 1 cm cell were diluted with milliQ water prior to fluorescence analysis to avoid self-shading of the material [Green and Blough, 1994]. Samples were analyzed in ratio mode with 5 nm bandwidths for excitation and emission. Forty-eight emission scans were collected at excitation wavelengths five nanometers apart between 220 and 455 nm. Emission wavelengths spanned between 250 and 700 nm, with data collected every 2 nm over an interval of 0.5 s [Coble, 1996]. Three-dimensional excitation-emission matrices (EEMs) were generated by conjoining the individual spectra. The EEMs were normalized to a fixed value for Raman scatter at Ex/Em = 275/303 nm based on a single emission scan from the Milli-Q water daily blank and then corrected for scatter at all wavelengths by subtracting a Milli-Q EEM (determined weekly). This procedure has been found to improve removal of first and second-order Raman scattering peaks. Blank-subtracted EEMs were corrected for instrument configuration using both emission and excitation correction factors [Coble et al., 1993]. Excitation correction factors were determined every two weeks using a fresh solution of
saturated Rhodamine in ethylene glycol (0.8 g/100 mL). Emission correction factors were provided by the manufacturer. Finally, corrected fluorescence intensities were converted to units of quinine sulfate equivalents (QSE) in ppb using the fluorescence of a dilution series of quinine sulfate dihydrate in 0.05 M sulfuric acid at Ex/Em = 350/450 nm [Velapoldi and Mielenz, 1980], where 1 QSE = 1 ppb quinine sulfate dihydrate. All processing was conducted using Galactic Industries’ Grams 32 software.

2.4. High-Resolution Spatial Mapping

[12] Continuous, underway mapping of organic matter fluorescence in surface waters was performed using a SAFIre (Spectral Absorption and Fluorescence Instrument manufactured by WET Labs). Fluorescence output was stored with salinity and temperature (Seabird Electronics SBE-45 thermosalinograph) and GPS information (Garmin, Inc.) using a WET Labs Data Handler (DH-4). Data streams were merged and processed using the WAP (WET Labs Archive Processing) program which extracted time-stamped raw data from archived files and applied calibration coefficients for all instruments. A Matlab binning routine was used on extracted data to yield data points every 0.3 km. Spatial maps of underway data were generated by kriging and blanking methods in Surfer mapping software, version 8.1. Underway data were unfiltered and represent COM (Colored Organic Matter). The SAFIre measures fluorescence at six excitation and sixteen emission wavelengths, configured for optimum organic matter detection (excitation range: 228–436 nm and emission range: 228–687 nm). Presented in this study is the value at Ex/Em = 313/430 nm. Discrete filtered seawater samples were used to intercalibrate the SAFIre to the benchtop fluorometer [Conmy et al., 2004a].

2.5. Satellite Data

[13] Level-1A MODIS (Moderate Resolution Imaging Spectroradiometer)—Aqua data were retrieved from the NASA Goddard Space Flight Center (GSFC) website (http://oceancolor.gsfc.nasa.gov) and processed to Level-2 using SeaDAS (version 5.0) software. Chlorophyll-α concentrations (CHL) and CDOM absorption coefficients at 443 nm were estimated using the Carder et al. [1989] semianalytical algorithm which can differentiate between phytoplankton and CDOM absorption. Percent differences between field and MODIS measurements of CDOM absorption at 355 nm have been reported within 19% for the Mid Atlantic Bight using a regionally tuned empirical algorithm [Mannino et al., 2008]. Specific for the WFS, percent differences were found to be within 20% for three-quarters of samples collected in August 2002, May 2003 and November 2005. For this data set, range of percent difference was found to be 0.4–37%, where satellites provided overestimation in most cases (R. N. Conmy, unpublished data). Fluorescence line height (FLH) data were calculated according to Abbott and Letelier [1999], where FLH is based on calibrated, normalized water-leaving radiances. This height is the intensity of upwelled radiation at 678 nm above the baseline created from 667 and 748 nm. Overestimations associated with FLH are attributed to the presence of suspended particles and differences in chlorophyll-α fluorescence efficiency of plankton. Water-leaving radiances in three MODIS bands (551, 488, and 443 nm) were used to derive composite enhanced Red-Green-Blue (ERGB) images. All images were stretched to the same scale in accordance with code from C. Hu and the USF Institute of Marine Remote Sensing. Atmospheric effects have been removed from imagery. All processing was conducted by the USF Optical Oceanography Laboratory.

3. Results and Discussion

[14] The coastal waters of the West Florida Shelf are heavily influenced by the multiple rivers from the Pan Handle in the north to the Everglades system in the south. As a result, the CDOM pool on the shelf is mainly due to the mixing of fresh water and seawater. For the field experiments on the shelf between 2003 and 2005, this mixing line, essentially the relationship between CDOM fluorescence and salinity, was found to be relatively constant, with a slope of $\sim-4$ for discrete samples (Figure 2). Separating data by the amount of river discharge, denoted here as high-flow and low-flow conditions (relates to classifications and values in Figure 3), showed no distinct difference in the mixing line, therefore the regression reported in Figure 2 is for both conditions. This inverse relationship was found for all samples with salinities less than 36, where fluorescence intensities ranged between 1.4–44 QSE and 1.2–55 QSE for the high-flow and low-flow seasons, respectively. Additionally, for both high-flow and low-flow conditions, positive correlations between fluorescence and DOC concentrations were found, where the former demonstrated higher fluorescence intensity per unit of DOC [Conmy, 2008]. Regressions were calculated as $y = 0.1606 \times -15.591$, $r^2 = 0.646$ and $y = 0.0765 \times -4.566$, $r^2 = 0.627$ for the high-flow and low-flow conditions, respectively, where fluorescence intensity is the dependent variable. Variability in fluorescence intensity may be attributed to differences in CDOM concentration within various riverine source waters. Deviations above the mixing line at salinities less than 33 occurred for stations near the Caloosahatchee River, Cape Romano and northern Everglades drainage system. Conversely, deviations below result from stations near Charlotte Harbor and Tampa Bay. As was reported by Conmy [2008], mixing lines from regional rivers converge between salinities of 25 and 30, where freshwater CDOM is thoroughly mixed together (and also with seawater) making it difficult to identify particular river sources away from the coast on the West Florida Shelf.

[15] Above salinity of 36, however, the trend reverses and CDOM was found to vary proportionately with salinity for a subset of samples taken during August 2005 near Florida Bay. This positive correlation has been previously observed on the southern portions of the shelf [Coble et al., 2004; E. C. Milbrandt et al., Novel mechanism for formation of high-CDOM, high-salinity water, submitted to Limnology and Oceanography, 2009]. Cited as the source are productive, shallow, sandy sediments that release organic material to the water column. Coincident evaporative processes result in higher-salinity waters that in turn entrain this newly produced organic matter (Milbrandt et al., submitted manuscript, 2009). During the summer months in South Florida, high amounts of sunlight and elevated nutrient delivery to the coast via rivers allow for increased biological production.
**Figure 2.** CDOM fluorescence at Ex/Em 300/430 nm for seasonal cruises on the West Florida Shelf. Both dry and wet seasons fall on the same mixing line, with the exception of hypersaline waters during August 2005.

**Figure 3.** Peace River discharge data from the Bartow Station (source: USGS and CH National Estuary Program, http://www.chnep.org). Bold lines represent dates of the WFS field experiments, and dark circles illustrate dates of storms. Embedded table contains the experiment dates along with USGS and CHNEP discharge and flow classifications. Flows represent monthly averages for the Peace River that supplies Charlotte Harbor. Data and river flow classification correspond to flow condition nomenclature in Figure 2. Note that “normal” during the dry season months translates to low flow and conversely, wet season translates to high flow.
in shallow, benthic environments. This and the fact that no large-scale storms occurred during August 2005 gave rise to the observation of the high-CDOM, high-salinity water mass during that experiment.

[16] Related to the fluorescence intensity is the absorption coefficient of CDOM. Strong correlations, independent of depth, location, or season were found between fluorescence and absorption coefficients over a range of 280 and 440 nm [Conmy, 2008]. Shown in Figure 4 are the relationships for 312 and 440 nm, the latter for relating to satellite derived CDOM. The ability to derive absorption from fluorescence measurements is of great interest to coastal zone researchers, as the latter are easier to obtain from field sensors, robust and can be used for validation of satellite measurements. This demonstrates promise for deriving CDOM absorption values from fluorescence measurements, as the relationship is robust regardless of concentration or distribution.

3.1. Spatial Distribution of COM Fluorescence

[17] Given that CDOM in this region, to the first order, is controlled by freshwater runoff, high concentrations are observed during the South Florida rainy season (summer months) and lower concentrations during times of little rainfall (winter months). This is shown with the FDOM and salinity spatial maps in Figures 5 and 6. It is important to note that due to the shallow nature of the shelf and the close proximity to shore of the field experiments, there tended to be no vertical structure throughout the water column. Of the approximately 200 stations sampled, only 24 profiles exhibited a two layer water mass. For each of the field experiments, stations that exhibited stratification were found between the 10 and 26.5 m isobaths. Of all the field experiments, August 2005 had the largest proportion of stratified stations most likely due to the absence of any large-scale storms and due to the increased fresh water delivery to the shelf. Given this low percentage, and that the waters in this region of the shelf are mostly well mixed, it is a reasonable supposition that when looking at the spatial maps, the patterns observed in the surface waters would be representative of the entire water column for ~90% of sample stations. Also of note is the disparity between maximum fluorescence intensity of discrete samples (Figure 2) versus in situ measurements (Figure 5). Explanation for this difference lay with saturation and self-shading of the SAFire signal at lower concentrations than the discrete samples. In nearshore environments, this results in high-resolution data with lower intensities. For the purposes of this study, elaboration on concentrations is reserved for discrete samples and the high-resolution data is merely to establish trends in fluorescence intensities.

[18] Lowest WFS FDOM values were observed during April 2005, where concentrations were all below 10 QSE. This corresponds with the low discharge as recorded by the Peace River gauge (Figure 3). Similarly, December 2003 had the lowest flow conditions for the Bartow station, and concentrations over much of the shelf were below 12 QSE. Higher concentrations were observed in the southernmost sections of the cruise track, near Florida Bay, which also corresponded to a decrease in salinity (Figure 6). Although dry conditions dominated the region, the Everglades experienced some isolated rain events during this month. Localized precipitation patterns and hydrology of South Florida differs from the West Central portion, therefore the influence of the rivers differs regionally [Conmy, 2008]. In contrast, the Peace River exhibited higher discharge during August 2005, and higher COM concentrations were observed on the shelf. During this experiment a hypersaline CDOM signature was observed, just to the west of Florida Bay. The samples from this water mass appear in Figure 2 above salinity 36, where a positive correlation between salinity and CDOM was observed. This is also shown in

Figure 4. Relationship of CDOM fluorescence to absorption at 312 and 440 nm for all cruises on the West Florida Shelf.

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Figure 5. COM spatial distributions on the West Florida Shelf collected with the WetLabs Inc. SAFire. Measurements obtained using continuous flow-through system of unfiltered surface waters. The months of August 2004, December 2004, and November 2005 were marked by Hurricane Charley, a winter storm event, and Hurricane Wilma, respectively. Ship tracks are shown in black. December 2004 and November 2005 contours are overlain with *Karenia brevis* cell counts collected by FL-FWCC/FMRI.
Figure 6. Salinity spatial distributions on the West Florida Shelf. Measurements obtained using continuous flow-through system of surface waters. The months of August 2004, December 2004, and November 2005 were marked by Hurricane Charley, a winter storm event, and Hurricane Wilma, respectively. Ship tracks are shown in black.
Figure 7. Enhanced RGB (R, 551 nm; G, 488 nm; B, 443 nm) for 3 days in August 2004. Imagery supplied by USF Optical Oceanography Laboratory. Also shown are maps of currents and wind data from buoys operated by USF Ocean Circulation Group (http://ocg7.marine.usf.edu/~liu). (left) During the passage of Hurricane Charley and (right) 10 days after the storm.
During the passing of the storm, however, white colors dominated the signal (Figure 8, top right). White colors in the ERGB imagery result from either bottom interference or SPM and in this case is most likely the result of resuspended particles from the storm’s passing. Such increases in particulates can also interfere with the field sensors and result in higher COM values, as well as any dissolved material released from the sediments at the time of resuspension [Boss et al., 2001].

[21] The Fluorescence Line Height (FLH) images show a marked difference from before and during the storm, indicating an increase in CHL during the latter experiment (Figure 8, middle). The water-leaving radiance data of FLH allows for better detecting spatial features due to the
use of three MODIS bands at longer wavelengths, as compared to using to only two shorter-wavelength bands in CHL imagery, therefore only FLH images are shown. This increase during the second field experiment was most likely the result of an observed Karenia brevis bloom in the southern portions of the shelf (Florida Fish and Wildlife Conservation Commission, Florida Wildlife Research Institute website). As evident from the cell count distributions in Figure 5, regions with the highest counts (up to a million cells/L) coincide with highest fluorescence intensity. The CHL imagery (not shown) also suggests that there was significant biomass on the West Florida Shelf at this time. Additionally, the observed increase in COM fluorescence during the second December 2004 field experiment concurs with an increase in adg443 (absorption due to gelbstoff and detritus at 443 nm) in the satellite imagery (Figure 8, bottom). It is also important to note that just as ERGB can be affected by the presence of suspended sediment, so too can the FLH and adg443. As a result of inclement weather, only two discrete samples south of the Caloosahatchee River could be taken during the storm. Comparing those samples to ones taken during the first field experiment showed roughly a 10% increase in CDOM fluorescence intensity. Likewise a comparison of the unfiltered SAFire results to the discrete samples revealed that the percent difference between measurements was 20% prestorm, and 40% poststorm. This suggests that a plausible explanation for the observed poststorm high-COM values is most likely a combination of factors including (1) the presence of suspended particles as the experiment occurred during the passing of the storm, (2) dissolved materials released from red tide, (3) dissolved materials resuspended from the sediments, and possibly even (4) benthic diatoms that may have been put into suspension (C. A. Heil and K. L. Carder, personal communication). Given the data available it is difficult to assess which factor dominated.

Case 3 is Hurricane Wilma. Above, it was shown that storms can drastically alter IOP concentration and distribution on the shelf, but how they are changed and to what extent depends greatly on the characteristics of the storm (from strength, to direction, to storm surge, to wind patterns) and the ambient climate before the storm passes over a region. During November 2005, South Florida was impacted by another major storm, Hurricane Wilma (category 3 at landfall in Cape Romano on 24 October 2005), and the field experiment for this month occurred 8 days after its passing. Highest concentrations of organic matter were observed during this experiment and were widespread over much of the shelf. When reviewing the ERGB imagery (Figure 9) it is apparent that unlike the August and December 2004 experiments, there exist extensive areas of dark colors prior to the passing of the hurricane. This may have resulted from either the accumulation of CDOM delivered to the shelf throughout the wet season and/or the presence of the persistent HAB of K. brevis that blanketed the coast (FWCC-FWRI web site). Again, highest cell counts coincided with highest fluorescence values (Figure 5). The FLH imagery shows widespread phytoplankton signal during this pre-Hurricane Wilma time period. ERGB Imagery from 8 days after the storm shows the presence of lighter colors at the southern portion of the WFS (Figure 9, top right). This is most likely due to bottom sediments, as this region is shallow and the imagery is from more than a week after the storm, thereby giving ample time for particles resuspended during the storm to settle out. This is based on particle settling velocities and Stoke’s equation, where sand and calcium carbonate certainly settle within 1 day and benthic diatoms would take approximately 10 days (0.5 m/d) [Walsh et al., 2003] to settle out of the water column for this region. The FLH imagery shows a concentration effect of the phytoplankton between Tampa Bay and Charlotte Harbor, which is also seen in the adg443 imagery. It also shows high gelbstoff in the southern and inshore portions near Florida Bay. In situ measurements found the highest COM fluorescence and lowest salinities near Florida Bay, but the imagery cannot support or refute this due to the presence of clouds in this region.

If the high COM signal did not result from interference with suspended particles, then an explanation for the high intensities during November 2005 includes the following components: (1) The storm physically concentrated the bloom and any of the dissolved organic material produced by the prolonged K. brevis bloom. (2) Dissolved Organic Matter from the sediments becoming suspended in the water column and remaining in solution long after the particles settled out. (3) The storm occurring at the end of the rainy season, when the shelf and the rivers had exhibited high amounts of organic material. The rain from the storm could have resulted in a flushing of easily transported terrestrial material resulting in higher color on the shelf.

3.2. Spectral Differences

In addition to concentration differences, there exist spectral distinctions of the fluorescence spectra for WFS samples. Table 1 lists the fluorescence intensity, position of humic fluorescence maxima (Fmax) (represents Humic Peaks C and M region), spectral slopes and absorption coefficients for sample types observed during the field experiments. Plotted in Figure 10 are normalized emission spectra from the EEM fingerprints for these same six waters, illustrating spectral differences which serve as proxies for compositional differences of organic matter within sample waters [Coble et al., 1993; McKnight et al., 2001; Stedmon et al., 2003; Chen et al., 2004; Battin et al., 2008; Jaffé et al., 2008]. Fmax for the high-CDOM, low-salinity waters were red-shifted (toward longer wavelengths) compared to high-salinity waters (arrows mark the position). Spectra of this type are found inshore, particularly during wet season months and are representative of Humic Peak C fluorescence [Coble, 1996]. Higher-salinity waters exhibit blue-shifted Fmax and are classified as Humic Peak M. Exposure of this marine CDOM to sunlight results in the flattening of the spectra [Moran et al., 2000] and further blue shifting [Coble, 1996, 2007; Conny, 1999], which is common in offshore waters in the Gulf of Mexico (P. G. Coble and R. N. Conny, unpublished data). Waters sampled after Hurricane Charley were also found to have this spectral shape, even samples collected close to shore. Samples collected after the Winter Storm and Hurricane Wilma exhibit spectra that appear to be a mixture of Peaks C and M. The physical conditions during both events favored resuspension of CDOM from the benthic layer which mixed with material delivered via rivers. A study by Burdige et al. [2004] demonstrated that Humic Peaks A, C and M are found in...
sediment pore waters of coastal zones. In the case of Hurricane Wilma, there was the added production from the HAB. Shown by the dashed line is the spectrum for a sample collected in the bloom just north of Charlotte Harbor (concentration > 1 million cells/l), which represents a newly produced marine CDOM signature.

[25] Plotting FDOM intensity as a function of emission maxima ($F_{\text{max}}$) allows for visualizing coincident changes in concentration and spectral shape for all samples collected (Figure 11). The position of the fluorescence maxima showed the largest wavelength range during high-flow conditions (379–425 nm), where the most red-shifted peaks, corresponded to lowest spectral slopes, lower salinities and higher concentrations of organic material. Peaks at longer wavelengths during the wet season are explained by the occurrence of increased river discharge that delivers

**Figure 9.** Enhanced RGB (R, 551 nm; G, 488 nm; B, 443 nm) (top) for 2 days pre-Hurricane Wilma and post–Hurricane Wilma. (middle) The Fluorescence Line Height (mW/cm$^2$/µm/sr) for the same days. (bottom) Imagery of adg443 (m$^{-1}$). Imagery supplied by USF Optical Oceanography Laboratory.
CDOM of terrestrial origin to the shelf. This material has been shown to be red-shifted, highly colored, labile and compositionally complex \[McKnight et al., 2001; Aiken, 2002; Stedmon and Markager, 2005\] as compared to marine organics. Conversely, the occurrence of peaks at shorter wavelengths during the wet season is the result of warmer temperatures and high sun exposure of these summer months. These conditions are favorable for photodegradation of organic material, which produces smaller, less colored, organically resistant material that results in a blue-shifting of the fluorescence peaks \[Zepp and Schlotzhauer, 1981\]. The most blue-shifted peaks were found after the passage of Hurricane Charley, which also exhibited the highest spectral slope values. These waters had an increase in clarity over much of the shelf. Hypersaline waters also had similar peak positions indicating a marine source, but with higher concentrations. Samples collected during December 2004 exhibited \(F_{\text{max}}\) ranging from 393 to 422 nm with blue-shifted wavelengths prior to the event. Likewise, shelf waters after the passage of Hurricane Wilma possessed peaks between 401 and 418 nm, but with higher fluorescence intensities. Contributing to these spectral properties were the river discharge, resuspended material from the sediments and the presence of new marine organic material from the HAB.

Spatial distributions of \(F_{\text{max}}\) for each field experiment are shown in Figure 12. It is important to note that the contour maps shown previously in Figures 5 and 6 were generated with in situ, unfiltered water, whereas filtered, discrete samples were used in Figures 10–12. Red colors in the spatial map represent terrestrial material, orange colors for new biologically produced marine CDOM and/or the mixing of terrestrial and marine water, and blue colors are indicative of older/possibly photobleached marine CDOM. Blue-shifted \(F_{\text{max}}\) were found after the passage of Hurricane

### Table 1. Fluorescence and Absorption Spectral Properties for the Water Types Shown in Figure 10a

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>Month and Year</th>
<th>Salinity</th>
<th>Ex/Em = 300/430 nm (QSE)</th>
<th>Humic Peak Emission Maximum (F_{\text{max}}) (nm)</th>
<th>Fluorescence Intensity at (F_{\text{max}}) (QSE)</th>
<th>Spectral Slope 280–312 nm (m0/C0)</th>
<th>Spectral Slope 350–440 nm (m0/C0)</th>
<th>(a(280)) (m0/C0)</th>
<th>(a(350)) (m0/C0)</th>
<th>(a(440)) (m0/C0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>High CDOM–low salinity</td>
<td>Aug 2005</td>
<td>24.75</td>
<td>54.61</td>
<td>420</td>
<td>55.73</td>
<td>0.01938</td>
<td>0.01788</td>
<td>33.88</td>
<td>9.54</td>
<td>1.95</td>
</tr>
<tr>
<td>Low CDOM–high salinity</td>
<td>Dec 2003</td>
<td>35.51</td>
<td>1.41</td>
<td>402</td>
<td>1.63</td>
<td>0.03225</td>
<td>0.01294</td>
<td>0.91</td>
<td>0.14</td>
<td>0.04</td>
</tr>
<tr>
<td>Post–Hurricane Charley</td>
<td>Aug 2004</td>
<td>36.03</td>
<td>1.31</td>
<td>383</td>
<td>1.45</td>
<td>0.03074</td>
<td>0.01072</td>
<td>1.29</td>
<td>0.24</td>
<td>0.09</td>
</tr>
<tr>
<td>Post–Hurricane Wilma</td>
<td>Nov 2005</td>
<td>34.02</td>
<td>19.72</td>
<td>407</td>
<td>24.19</td>
<td>0.02219</td>
<td>0.01074</td>
<td>12.94</td>
<td>3.48</td>
<td>1.41</td>
</tr>
<tr>
<td>Post–Winter Storm</td>
<td>Dec 2004</td>
<td>34.66</td>
<td>9.04</td>
<td>414</td>
<td>9.32</td>
<td>0.02189</td>
<td>0.01698</td>
<td>7.44</td>
<td>1.78</td>
<td>0.39</td>
</tr>
<tr>
<td>HAB</td>
<td>Nov 2005</td>
<td>33.90</td>
<td>19.72</td>
<td>404</td>
<td>10.44</td>
<td>0.02219</td>
<td>0.01074</td>
<td>12.94</td>
<td>3.48</td>
<td>1.41</td>
</tr>
</tbody>
</table>

\(a\)Intensity at \(F_{\text{max}}\) represents the Humic Peak C and M region \[Coble, 1996\].

![Figure 10](imageURL). Fluorescence spectra for different water types sampled during field experiments on the West Florida Shelf.
Charley and conversely, red-shifted maxima were observed during August 2005, when discharge was highest. During November 2005, post–Hurricane Wilma, peak positions of longer wavelengths dominated the shelf (peaks > 400 nm) and are most likely related to the flux of organic material from the sediments and from terrestrial runoff due to increased rain brought by the storm. However, waters with blue-shifted spectra were observed, and resulted primarily from the lysis of cells from the phytoplankton bloom. For the case of December 2004, unfortunately, only a few samples were taken south of Charlotte Harbor, so the storm event cannot be documented spatially with discrete samples. At the time of lowest flow (December 2003), patterns similar to August 2004 were found, but with a smaller range in peak position. This pattern would have been expected with April 2005, as well, but because samples were only taken at inshore stations, no offshore blue-shifted material was sampled.

4. Conclusions

[27] In general, waters on the West Florida Shelf exhibited a strong correlation between CDOM and salinity. This suggests that although there are numerous sources of this material to the WFS, to the first order, mixing between freshwater and seawater is the dominant factor controlling CDOM. Temporal variability in distribution patterns of CDOM concentrations and spectral properties is attributed to seasonal differences in river discharge, the presence of local biology and the occurrence of episodic storm events. Three events were highlighted here.

[28] 1. First, the passage of Hurricane Charley in August 2004 resulted in low fluorescence intensities over the entire shelf. Little terrestrial organic matter was detected as evidenced by high spectral slopes, low absorption coefficients and fluorescence intensity, and blue-shifted Fmax.

[29] 2. The Winter Storm event in December 2004 was shown to cause an increase in fluorescence intensity (using in situ instruments) as compared to the field experiment just prior to the storm’s passing. Spectral slope and EEM data showed slight changes in the optical properties of discrete samples prior to and after the event, suggesting that the change measured by in situ sensors was in part due to the presence of particles in the unfiltered seawater [Conmy, 2008]. Contributing to this higher signal was also the presence of a red tide and detrital material released from the sediments.

[30] 3. Last, the highest fluorescence intensities during this study were observed on the shelf during November 2005 after the passing of Hurricane Wilma. Spectral slope values were low, Fmax were red-shifted, and both high- and low-salinity waters were observed indicating that the organic material originated from both riverine and marine sources. Likely marine sources are DOM released from the sediments and the persistent K. brevis bloom that blanketed the shelf at this time.

[31] The work presented here illustrates the dynamic nature of the West Florida Shelf and ways in which discharge patterns and biophysical forcings influence the distribution of CDOM. This is ecologically significant as the these factors determine the degree to which DOM can serve as a nutrient or food source, provide UV shading for plants and animals in shallow environments, impact photosynthesis as plants compete for PAR, and serve as a vector for pollutant transport in the coastal zone. Additionally, CDOM is a critical component of the Dissolved Organic Carbon pool and studies such as the one presented here are necessary for improving carbon budgets and fluxes at the land-ocean margin. Given that CDOM is the only component of this pool that can be measured by remote sensors, and that these results can be used to ground truth ocean color products for a variety of scenarios (discharge patterns, hurricanes, resuspension events, and bloom periods), these
Figure 12. Spatial distributions of $F_{\text{max}}$ for seasonal cruises on the West Florida Shelf. Note that contours were generated using limited discrete samples, but layout was chosen to be consistent with high-resolution in situ data shown in Figures 5 and 6 for ease of comparison.
types of studies advance the field of coastal carbon budgeting and modeling.

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References
CONMY ET AL.: INFLUENCE OF EXTREME EVENTS ON CDOM


