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Photo-dissolution of flocculent, detrital material in aquatic environments: Contributions to the dissolved organic matter pool

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ABSTRACT

This study shows that light exposure of flocculent material (floc) from the Florida Coastal Everglades (FCE) results in significant dissolved organic matter (DOM) generation through photo-dissolution processes. Floc was collected at two sites along the Shark River Slough (SRS) and irradiated with artificial sunlight. The DOM generated was characterized using elemental analysis and excitation emission matrix fluorescence coupled with parallel factor analysis. To investigate the seasonal variations of DOM photo-generation from floc, this experiment was performed in typical dry (April) and wet (October) seasons for the FCE. Our results show that the dissolved organic carbon (DOC) for samples incubated under dark conditions displayed a relatively small increase, suggesting that microbial processes and/or leaching might be minor processes in comparison to photo-dissolution for the generation of DOM from floc. On the other hand, DOC increased substantially (as much as 259 mgC gC^{-1}) for samples exposed to artificial sunlight, indicating the release of DOM through photo-induced alterations of floc. The fluorescence intensity of both humic-like and protein-like components also increased with light exposure. Terrestrial humic-like components were found to be the main contributors (up to 70%) to the chromophoric DOM (CDOM) pool, while protein-like components comprised a relatively small percentage (up to 16%) of the total CDOM. Simultaneously to the generation of DOC, both total dissolved nitrogen and soluble reactive phosphorus also increased substantially during the photo-incubation period. Thus, the photo-dissolution of floc can be an important source of DOM to the FCE environment, with the potential to influence nutrient dynamics in this system.

1. Introduction

Dissolved organic matter (DOM) comprises the largest pool of organic matter (OM) in a wide range of aquatic environments and plays a key role in the biogeochemical cycles affecting processes such as metal complexation, pH buffering, light attenuation, nutrient availability, microbial and phytoplankton activity, and ecosystem productivity (Findlay and Sinsabaugh, 2003). The optical properties of chromophoric DOM (CDOM), the fraction of DOM that absorbs ultraviolet

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(UV) and visible light, have been extensively investigated in various aquatic ecosystems to determine the sources and transformations of this material in the environment (Coble, 1996, 2007).

Photochemical effects on DOM dynamics have also been studied. CDOM containing numerous chromophoric moieties can undergo important photo-induced processes including photolysis of higher molecular weight to lower molecular weight compounds (Lou and Xie, 2006), generation of free radicals (Holder Sandvik et al., 2000), photo-mineralization reactions (Clark et al., 2004), and photo-bleaching (Shank et al., 2010). Photo-reactions have also been shown to help in the formation of biologically labile compounds, making the organic material more available for both autotrophic and heterotrophic biological activity (Moran and Zepp. 1997).

More recently, the effects of light on the dissolution of particulate organic matter (POM) have been studied (Kieber et al., 2006; Mayer et al., 2006 , 2009a). It has been well established that POM can absorb light at similar wavelengths as DOM (Kirk, 1980; Kieber et al., 2006) allowing the particulate material to undergo similar photo-induced reactions. Such reactions can induce processes that break down larger molecules into smaller photo-products through the absorption of light (Miller and Moran, 1997). These reactions can influence the transition between the particulate and the dissolved phase of organic material (Mayer et al., 2006) and therefore the frequent exposure of particulates and sediments to light can ultimately lead to the transfer of particulate carbon to the dissolved phase. Kieber et al. (2006) irradiated sediments from the Cape Fear River estuary in North Carolina and found that on average, the dissolved organic carbon (DOC) photo-production rate was 0.0056 mmol DOC g^{-1} dry sediment h^{-1}, and suggested this value was larger than local riverine discharge and benthic flux sources of DOC to the ocean. Mayer et al. (2006) irradiated sediments from the Mississippi River and found that under optimal conditions two thirds of the exposed particulate organic carbon (POC) underwent photo-dissolution after several days. Shank et al. (2011) irradiated suspended sediments from Florida Bay and found that after 24 h of light exposure, the DOC concentration increased from 0.5 to 3.0 mgC L^{-1}. This potential generation of DOM through photo-induced mechanisms can play a significant role inorganic carbon and other biogeochemical cycles of aquatic environments, affecting both nutrient dynamics (Kieber et al., 2006; Zhang et al., 2009) and biological activity (Miller and Moran, 1997).

In the Florida Coastal Everglades (FCE), the majority of the POM occurs at the sediment-water interface as flocculent detritus (floc, 0.02–1.4 mg L^{-1}). This material has been previously studied (Neto et al., 2006; Gao et al., 2007; Larsen et al., 2009; Troxler and Richards, 2009) and is known to be composed mainly of an assembly of periphyton, higher plant detritus and carbonates. With the application of molecular biomarkers, Neto et al. (2006) found that floc composition is primarily controlled by local vegetation inputs and early diagenetic transformations of OM. Using isotopic characterization, Troxler and Richards (2009) determined that detrital remains of *Utricularia* species comprise the primary components of floc materials found in deep sloughs of the FCE. Isoprenoid hydrocarbons known as botryococcenes, and believed to be produced by the microalga *Botryococcus braunii* or by filamentous green algae, have also been reported in floc from the FCE (Gao et al., 2007). However, little is still known about the biogeochemical dynamics of floc in this environment.

Detritus is known to be a source of energy and nutrients to living organisms in many food webs (Moore et al., 2004). In the FCE, floc and periphyton mats have been proposed as primary energy sources driving local trophic dynamics (Williams and Trexler, 2006). For this reason alone, it is important to understand floc dynamics in the waters of this oligotrophic, subtropical wetland. In the shallow waters of the FCE, floc is naturally re-suspended through wind and bio-turbation (Larsen et al., 2009), allowing it to be exposed to intense sunlight (light penetration in FCE waters can reach 1745 $\mu E\ cm^{-2}\ s^{-1}$; F. Tobias, personal communication). In the Everglades, floc is not entrained by water flow (entrainment threshold of 1.0×10^{-2} Pa; Larsen et al., 2009) because the flow is not sufficient for significant floc transport. However, some authors have suggested that floc is mobile enough to reach the estuarine areas of the FCE (Jaffé et al., 2001). With the implementation of the Comprehensive Everglades Restoration Plan (CERP) there will be an increase in water flow through the Shark River Slough (SRS) to the Gulf of Mexico (www.evergladesplan.org). This increase in water delivery can potentially increase floc transport from the freshwater marshes to the mangrove fringe and out to the Gulf, where the flocculent material will be exposed to intense sunlight. Light exposure can initiate a series of reactions and alterations in detrital OM (Kieber et al., 2006; Mayer et al., 2006, 2009a and 2009b), and therefore in floc, potentially affecting its environmental dynamics and ecosystem functions. Thus it is important to determine the photochemical reactivity of floc in the FCE and aquatic environments in general, in order to estimate the potential contribution of such processes to the DOM pool and its overall influence on the biogeochemistry of detrital rich ecosystems.

The specific objectives of this study were to quantitatively assess the amount and quality of DOM that is photo-produced from floc of different composition/origin on both spatial and seasonal scales (i.e. freshwater marsh vs. mangrove fringe; wet season vs. dry season).

2. Methods

2.1. *Site description*

The Florida Coastal Everglades (FCE) is a subtropical wetland located on the southern tip of the Florida peninsula. The FCE extends west to the Gulf of Mexico and south to Florida Bay. This oligotrophic wetland is characterized by very low dissolved nutrient concentrations in the water column. There are two main drainage basins in the FCE; Shark River Slough (SRS) drains to the southwest coast of Everglades National Park (ENP) and into the Gulf of Mexico, while Taylor Slough (TS) drains to the southeast and into Florida Bay. Water discharge to the southwest coast of ENP through SRS has been shown to be substantially larger than discharge through TS (Woods, 2010).

Floc samples were collected in SRS at sites that have been previously described by the on-going Florida Coastal

Everglades-Long Term Ecological Research program (FCE-LTER), namely at a freshwater marsh site (SRS2) and at an estuarine mangrove site (SRS6) (Fig. 1). The former is a long hydroperiod site characterized by peat soils where the dominant vegetation is *Cladium jamaicense* (sawgrass), *Eleocharis cellulosa* (gulfcoast spikerush) and calcareous periphyton, an assemblage of cyanobacteria, green algae, diatoms and higher plant detritus. The latter site, located on the coastal fringe, is dominated by *Rhizophora mangle* (red mangrove). This site may receive in addition to the dominant mangrove detritus, some marine OM inputs from seagrasses and phytoplankton (Hernandez et al., 2001) through tidal exchange. Basic water quality and floc parameters are summarized in Table 1.

2.2. *Sample collection*

Floc samples were collected according to Neto et al. (2006). Briefly, floc samples were collected using a transparent plastic corer (inner diameter of 2.5 cm). The core was pushed about 10 cm below the sediment surface, capped to create suction, and retrieved. The floc layer was visible in the core and was decanted from the consolidated surface of the soil/sediment using a plunger with a smaller diameter to that of the core tube to hold the bottom layer in place. Excess water was decanted and the floc was collected in pre-rinsed 1 L Teflon jars (Nalgene). This procedure was repeated at randomly selected locations at each site enough times to obtain about 1 L of floc composite for each sampling event.

Eight L of natural water were also collected at each site in Nalgene bottles sequentially pre-washed with 0.5 N HCl and 0.1 N NaOH. Water samples were kept on ice and upon return to the laboratory, they were filtered through pre-combusted (450 °C for 4 h) 0.7 μm glass-fiber filters (GF/F) (Whatman International Ltd.) and 0.22 μm Durapore Membrane filters (Millipore) to remove POM from water samples. The filtrate was passed through an activated carbon filter cartridge (Whatman) to remove much of the DOM from the natural water (%DOC removed was 46–64%; %absorbance at 254 nm removed was 57–93%). This step was needed to reduce the background DOC levels, and thus be able to better determine its photo-generation rates, as Everglades waters are commonly enriched in DOC (Table 1).

Table 1 – Natural water and floc bulk chemical parameters.

Site	Season	Natural water				Floc		
		Salinity	DOC (mgC L^{-1})	TDN (mgN L^{-1})	SRP (mgP L^{-1})	Density (g mL^{-1})	TOC (%)	TN (%)
SRS2	Dry	0	32.8	1.33	0.008	0.067	25.6	3.02
	Wet	0	22.3	0.23	n.a.[a]	0.71	37.3	3.25
SRS6	Dry	34.4	6.7	0.31	0.018	n.a.[b]	14.9	0.54
	Wet	17.1	7.9	0.25	n.a.	n.a.	11.4	0.41

a n.a. = not analyzed.

b The density for SRS6 floc could not be measured due to low tide at the time of sample collection.

2.3. *Experimental setup*

Floc samples were mixed with natural water (after DOM removal) to give solutions with a final floc concentration of about 24 g floc L^{-1} (dry weight). Such high initial concentrations were used to simulate the floc layer in the natural environment which can reach concentrations of up to 710 g floc L^{-1} (unpublished data). These solutions were prepared in pre-combusted glass jars (in triplicate), covered with quartz plates for light exposure, or wrapped in black plastic bags for dark controls. Light and dark controls were performed in the solar simulator's water circulating bath (26 °C), to maintain

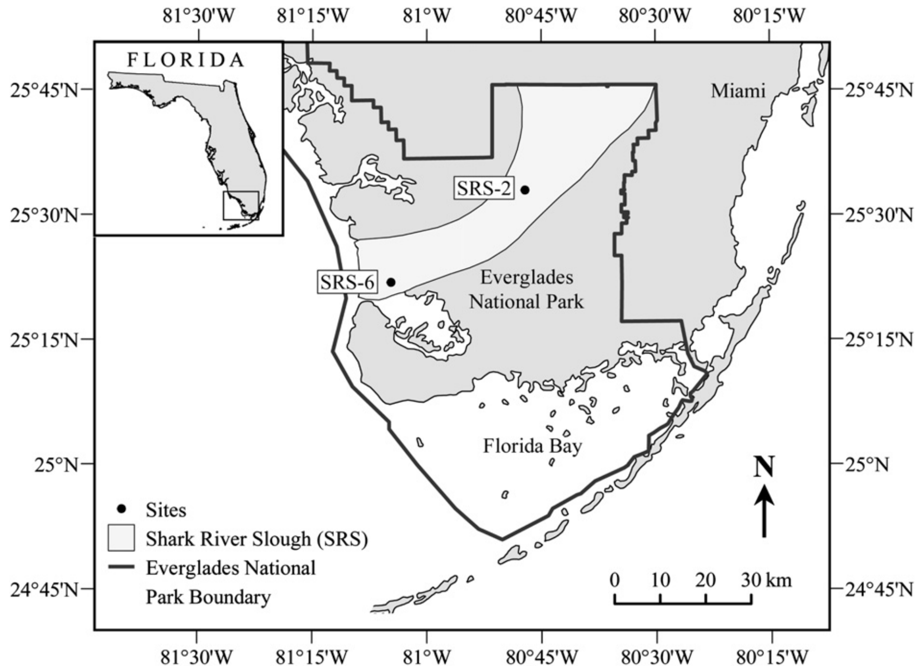

Fig. 1 – Florida coastal Everglades map showing sampling site locations along the Shark River Slough (SRS).

similar temperature conditions for all experiments. Flat top glass jars were used instead of beakers to obtain a better seal with the quartz cover plates in order to avoid sample contamination by dust particles. True dark blanks were not performed as poisoning with either mercuric chloride or sodium azide would result in fluorescence quenching. Samples were incubated for different periods of time (0, 0.5, 1, 2, 4, and 7 days) in a solar simulator (Suntest XLS+, Atlas Material Testing Technology LLC) set at 765 W m^{-2}. These conditions correspond to about 1.2 times solar noon in South Florida (Maie et al., 2008). After photo-exposure, samples were filtered (0.7 μm GF/F) to separate the aqueous phase for DOM analysis, and to recover the detrital fraction. The filtered particulates were dried overnight in a 60 °C oven and the recovered floc was ground and saved for elemental analysis. The filtrate was analyzed for DOC, total dissolved nitrogen (TDN) and soluble reactive phosphorus (SRP), and the optical properties were examined using UV–vis spectroscopy and excitation emission matrix (EEM) fluorescence spectroscopy.

2.4. *Elemental analysis*

About 8–10 mg of floc sample was weighed in silver cups and de-carbonated by exposure to hydrochloric acid vapors overnight (Harris et al., 2001). Samples were dried in a 60 °C oven overnight and analyzed for total organic C (%TOC) and total N (%TN) concentrations. Triplicate samples were measured using a Carlo Erba NA 1500 nitrogen/carbon analyzer with a reproducibility of ±1.07% for TOC and ±0.09% for TN on average.

DOC concentration was measured with a Shimadzu TOC-V total organic carbon (TOC) analyzer. Prior to analysis, the samples were acidified ($pH < 2$) and purged with CO_2-free air for 5 min to remove inorganic C. Total dissolved nitrogen (TDN) was measured on an ANTEK 9000 nitrogen analyzer.

2.5. *UV–vis and fluorescence spectroscopy*

UV–visible absorption spectra were obtained using a Varian Cary-50 Bio spectrophotometer at wavelengths between 250 and 800 nm. Samples were measured in a 1 cm quartz cuvette using Milli-Q® water as the blank.

EEM Fluorescence was measured on a Horiba Jobin-Yvon Fluoromax-3 spectrofluorometer equipped with a 150-W Xenon arc lamp according to Chen et al. (2010) and Yamashita et al. (2010). Briefly, scans were acquired in a 1 cm quartz cuvette at excitation wavelengths (λ_{ex}) between 260 and 455 nm at 5 nm intervals. Emission wavelengths (λ_{em}) were scanned from $\lambda_{ex} + 10$ nm to $\lambda_{ex} + 250$ nm at 2 nm intervals. The individual spectra were concatenated to form a three-dimensional matrix. All spectra were acquired in *S*/*R* mode and were corrected for inner filter effects and instrument bias. Finally, fluorescence intensity values were converted to quinine sulfate units (QSU) to facilitate inter-laboratory comparisons.

2.6. *Parallel factor analysis (PARAFAC)*

Parallel factor analysis (PARAFAC) is a three-way multivariate statistical method that has been used to decompose EEMs of complex mixtures into their individual fluorescent components (Stedmon et al., 2003). The EEMs of 75 incubated floc and natural water samples were fitted to an existing PARAFAC model created with *ca* 1400 surface water samples collected from the Everglades and Florida Bay (Chen et al., 2010). PARAFAC analysis was performed using MATLAB 7.0.4 (Mathworks, Natick, MA) with the DOMFluor toolbox (Stedmon and Bro, 2008). Obvious residual peaks were not found after fitting our samples to this eight component model, indicating that the fluorophores produced from the irradiation of floc are similar to those of surface waters from the Everglades. The spectral characteristics of the eight components are summarized below.

3. Results & discussion

3.1. *Natural water & floc chemical characteristics*

Spatial differences in the initial DOC concentration for the two water samples are summarized in Table 1. As expected, the higher DOC values were obtained for the freshwater site (SRS2) compared to the mangrove site (SRS6), where a contribution of DOM to the former derive from the abundant macrophytes, periphyton mats and organic rich soils (peat) (Yamashita et al., 2010), while the latter is mostly influenced by mangrove derived sources and diluted by tidal mixing (Jaffé et al., 2003). Seasonal differences were also observed; water collected at the freshwater site was found to have 32.8 mgC L^{-1} in the dry season and 22.3 gC L^{-1} in the wet season. The smaller DOC concentration obtained in the wet season could be indicative of a dilution effect due to an increase in rainfall. The DOC content of natural water collected at the mangrove site was found to be seasonally similar, at 6.7 mgC L^{-1} in the dry season and 7.9 mgC L^{-1} in the wet season.

TDN was found to be higher in the natural water at the freshwater site during the dry season, indicative of a concentration effect. In addition, the abundant periphyton mats found at SRS2 contain numerous N-fixing cyanobacteria which may be contributing to the local TDN pool. SRP was higher at the mangrove site which receives phosphorus inputs from the adjacent Gulf of Mexico, while the SRS2 site is a typically P-limited FCE freshwater marsh site (Childers et al., 2006).

The floc collected in the freshwater marsh had higher %TOC and %TN compared to the mangrove floc, probably due to increased accumulation of OM at the former long hydroperiod site. The mangrove site is strongly influenced by tidal activity and the floc found there may not have the opportunity for significant accumulation. In fact, the sediment accretion rate at this particular site has been estimated to be 0.30 ± 0.03 cm $year^{-1}$ (Castañeda-Moya et al., 2009) while accretion rates in the SRS2 vicinity have been estimated at 0.50 cm $year^{-1}$ (Saunders et al., 2006). Floc collected at SRS2 during the wet season had higher %TOC and %TN than the floc collected in the dry season, indicative of higher inputs from increased local biomass productivity. The floc at SRS6 had a higher %TOC and %TN in the dry season, probably due to a decreased dilution effect, and higher nitrogen immobilization by bacteria associated with leaf litter decomposition (Twilley et al., 1986).

3.2. Photochemical production of DOC from floc

Photo-exposure of floc collected at both the freshwater and the mangrove sites caused the generation of significant amounts of DOC (Fig. 2). Normalized to the initial POC content, the floc collected at the freshwater site (SRS2) photo-generated up to 259 mgC gC^{-1} while SRS6 floc produced up to 173 mgC gC^{-1} with exposure to sunlight (corrected for dark treatments). This is in agreement with recent studies on the generation of DOM from re-suspended sediments in shallow aquatic environments (Shank et al., 2011). The authors found that upon solar irradiation, the sediments with the highest %OC content, exhibited the largest increases in DOC and terrestrial humic components. It should be noted that DOC in surface water samples may photo-degrade during photo-irradiation, and thus, values of photo-produced DOC reported here would be underestimated. However, it is important to mention that floc has been reported to contain some live benthic periphyton, including cyanobacteria (Neto et al., 2006). These organisms upon light exposure could generate DOM through enhanced primary productivity. However, it has been reported that microbial activity in solutions exposed to intense sunlight (such as in the solar simulator) is significantly inhibited (Xie et al., 2009) and therefore unlikely to make significant contributions to the DOC pool. While the overall trend is one of increasing DOC with exposure time, some variations were observed after several days of light exposure. This was particularly the case for the data from the dry season floc from both locations. While the DOC generation curve for floc from the wet season was relatively constant with time for both freshwater and mangrove floc, the data for floc from the dry season showed a fast increment in DOC generation during the first two and four days for the freshwater and mangrove samples respectively, followed by an overall decrease. These variations in DOC concentration with incubation time could be due to several mechanisms including re-adsorption onto particles, flocculation (von Wachenfeldt et al., 2009) and/or photo-mineralization of DOC to yield dissolved inorganic carbon (DIC) (Clark et al., 2004), and seem more pronounced for the dry season samples (see Fig. 2). Regardless of this trend, the difference in DOC production between the two sites suggests enrichment in photo-labile material at the freshwater site (SRS2) compared to the mangrove site (SRS6). The former is dominated by marsh vegetation (sawgrass and spikerush) and abundant periphyton mats which seem to control the main sources of OM to the floc layer (Neto et al., 2006). The organic rich, peat soils at SRS2 may also contribute OM to the floc layer. As such, floc at SRS2 is expected to be lower in lignin phenol content compared to that at SRS6 where mangrove derived detrital OM in the form of decaying leaf and root materials are likely the main OM sources to the floc (Neto et al., 2006). Consequently, the floc at SRS6 is expected to feature more biologically recalcitrant organic matter. However, lignin phenol is photodegradable (Opsahl and Benner, 1998), and sunlight intensity is not considerably different throughout the year in South Florida. Thus, considering that its lignin phenol content is larger at SRS6 floc the lower reactivity to photo-exposure is somewhat unexpected.

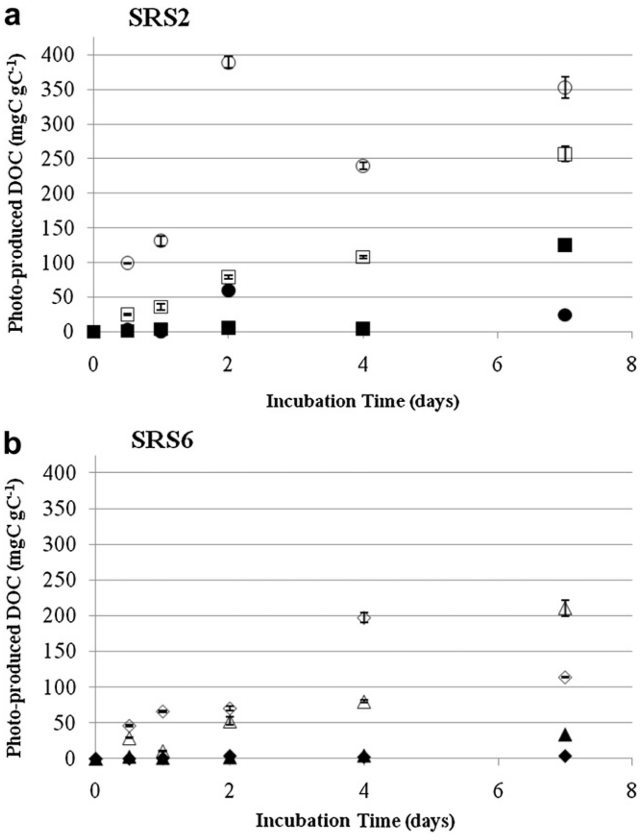

Fig. 2 – Photo-dissolution induced changes in DOC concentrations normalized to initial floc POC content for floc at SRS2 (a) and SRS6 (b). Photo-produced DOC at day = t was calculated by subtracting the DOC values at t = 0: photo-produced DOC (t) = DOC (t) − DOC (0). Error bars are for triplicate experiments. Open and filled symbols correspond to light and dark treatments, respectively. (●: dry and ■: wet season for SRS2; ◆: dry and ▲: wet season for SRS6).

Samples that were incubated under dark conditions also produced measurable amounts of DOC (126 mgC gC^{-1} for SRS2 floc and 34 mgC gC^{-1} for SRS6 floc) but significantly less compared to the photo-exposed samples. While leachates from some common Everglades biomass, such as sawgrass and spikerush blades, periphyton and mangrove leaves, have been reported to be important contributors to the DOC pool, leaching between 8 and 51 mgC g^{-1} of dry biomass during the early stages of decomposition (Maie et al., 2006), the floc from the freshwater site leached up to 79 mgC g dry floc. Such experimental results indicate that leaching from floc may be a more important source of this dissolved material than previously believed, although the photo-induced generation of DOC clearly dominates.

Exposure of flocculent material to artificial sunlight also caused the production of dissolved nutrients at both sites, showing photo-generation of TDN (5.2 and 0.98 mgN g^{-1} floc for SRS2 and SRS6, respectively) and SRP concentrations (0.07 and 0.19 mgP g^{-1} floc for SRS2 and SRS6, respectively). Because these parameters were only measured for floc collected in the dry season, seasonal effects will not be addressed. However, the photo-generation of DOM-associated N and P can greatly affect food web dynamics and biogeochemical cycles, especially in the oligotrophic waters of the FCE where most of the dissolved nutrients are found in the organic form (Noe and Childers, 2007).

Seasonal differences (wet vs. dry season) in DOC photo-production from floc were also observed (Fig. 2). Throughout the length of the incubation period, site SRS2 floc collected in the dry season produced 97 mgC gC^{-1} more than floc collected at the same site in the wet season. Photo-exposure of floc collected at SRS6 during the dry season also produced more DOC during the first 4 days of incubation, but fell below the levels of photo-produced DOC from the wet season floc after 7 days of exposure. Similarly, SRS2 floc from the dry season was significantly more photo-productive of DOC during the first 2 days of exposure (see above). The higher (initial) photo-production rates of DOC for the dry season samples may be due to the presence of more degraded, aged OM in the floc layer during this period. An increase in mangrove litterfall during the wet season has been observed at SRS6 (Twilley et al., 1986), contributing fresher inputs of OM to the floc layer. Similarly, the abundant periphyton mats found at SRS2 have been shown to display an increase in primary productivity at the onset of the wet season (Ewe et al., 2006), contributing significant amounts of more labile, fresh OM to the floc layer. The older, more degraded floc present during the dry season however, seems to be more photo-reactive. This is in agreement with Mayer et al. (2009a) who showed that photo-dissolution is greatly enhanced by microbial decay, suggesting that older, more humified OM is more photo-labile. Therefore, seasonal primary productivity variations may result in changes in the floc OM quality and consequently its photo-reactivity.

While Mayer et al. (2006) reported that light exposure of freshwater suspended particulates could result in a loss of 64% of the POC over a 15 d period of 6 h d^{-1} irradiation, in the present study, the POC content did not change significantly during incubation of both the light and the dark treatments. This is likely due to an analytical artifact, since very high initial concentrations of POC (up to 3 gC L^{-1}) were used to simulate the natural floc layer conditions. As a result, the POC carbon loss through DOC photo-dissolution was a very small fraction of the total and consequently within the analytical error of the POC analysis. Thus, POC loss data and potential correlations with DOC production are not presented here. However, and in agreement with the literature (Kieber et al., 2006; Mayer et al., 2006 and 2009a) floc exposed to light generated a significant amount of DOC.

3.3. *Composition of photo-produced DOM*

Fluorescence properties of natural waters have been used for determining the sources of DOM as well as its transformations in different aquatic environments and have been extensively applied for the quantification of fluorescent DOM (FDOM) in natural waters (Coble, 1996). EEM fluorescence can provide detailed information on the types of fluorescent compounds present in complex mixtures such as DOM (Coble, 1996). This fluorescence technique has been coupled with parallel factor analysis (PARAFAC), a statistical modeling approach, to decompose the EEMs into individual fluorescent components (Stedmon et al., 2003). Applying this approach, a total of eight fluorescent components had previously been obtained through PARAFAC modeling for the Everglades ecosystem (Chen et al., 2010; Yamashita et al., 2010). The fluorescence characteristics of these components were assigned to be characteristic for terrestrial humic-like (C1, 3 and 5), microbial humic-like (C4), protein-like (C7 and 8) and two unknown components (C2 and 6) which have recently been suggested to represent a humic-like component derived from soil oxidation and a ubiquitous humic-like component, respectively (Yamashita et al., 2010).

In this study, the fluorescence intensity of the three humic-like and the two protein-like components were combined into two groups for simplicity reasons. The fluorescence intensity of the three humic-like components, C1 ($\lambda_{ex} = 260$ (345) nm, $\lambda_{em} = 462$ nm), C3 ($\lambda_{ex} = 260$ (305) nm, $\lambda_{em} = 416$ nm) and C5 ($\lambda_{ex} < 275$ (405) nm, $\lambda_{em} > 500$ nm), increased for floc samples irradiated with artificial sunlight, suggesting that these components are photo-generated. These three components comprised a large portion (46–70% after 7 d of light exposure) of the total fluorescence, suggesting that the majority of the CDOM produced from irradiation of floc has humic-like optical characteristics. Two protein-like components were identified, a tyrosine-like component (C7; $\lambda_{ex} = 275$ nm, $\lambda_{em} = 326$ nm) and a tryptophan-like component (C8; $\lambda_{ex} = 300$ nm, $\lambda_{em} = 342$ nm) which also increased during photo-incubation. However, unlike the terrestrial humic-like components, these protein-like components comprised a smaller portion (10–16% after 7 d of light exposure) of the CDOM produced during photo-incubation of floc. The photo-generation of these protein-like components is in agreement with previous findings that tannin compounds leached from abscised mangrove leaves and other types of vegetation can form insoluble complexes with proteins, which upon photo-exposure have been shown to break up and re-release the N-containing compounds (Maie et al., 2008). Fluorescence intensity of protein-like components in DOM has also been reported to be strongly structure dependent (Mayer et al., 1999), and thus, could in part explain an increment in fluorescence intensity after photo-exposure. However, detailed EEM-PARAFAC based photo-degradation studies of Everglades DOM have not shown such effects, but instead show a decrease in intensity of protein-like fluorescence with increasing light exposure (Chen and Jaffé, unpublished). Thus, the increase in protein-like fluorescence observed in this study is most likely the result of photo-dissolution of floc. The increase in TDN during these experiments seems to agree with this suggestion. However, overall, the fluorescence signature was dominated by photo-generated humic-like compounds.

To look at the generation rates of the different fluorescent components we plotted the sum of the fluorescence intensity of the terrestrial humic-like components (C1, 3 and 5) and the protein-like components (C7 and 8), normalized to POC content, versus incubation time (Fig. 3). Differences in generation rates between samples, PARAFAC components and season are evidenced by significant differences in the slope of the linear correlations shown in Fig. 3 (see Table 2). When exposed to artificial sunlight, the floc collected at SRS2 produced more terrestrial humic-like material compared to the floc collected at SRS6 on a per-g POC basis. Shank et al. (2011) characterized the fluorophores generated from photo-irradiation of Florida Bay suspended sediments, and found that the most organic rich sediments exhibited the largest increases in terrestrial humic-like components. Similarly, photo-production of the protein-like components, where the presence of labile floc components from periphyton may be an important source of dissolved nitrogen, was higher in freshwater than in mangrove floc exposure experiments. Seasonal differences were similar to those previously described for DOC (see above), where higher initial (2–4 days) generation of humic- and protein-like components in the dry season was observed (Fig. 3), suggesting that aged floc is more photo-reactive. Because the maximum photo-production of CDOM differed for the floc collected at the two sites, the slopes of the best-fit line for the linear portion of the experiment were compared (2 days for SRS2 and 4 days for SRS6). The generation of the humic-like and protein-like components was significantly different between sites and between seasons (Table 2). Humic-like components were generated at a much faster rate than the protein-like components, and during the wet season, these components were generated at a lower rate than during the dry season. This seasonal difference could be explained by the fact that unprocessed, fresher material incorporated into the floc layer during the wet season, is less photo-reactive, while older, more degraded material found in floc during the dry season is more reactive to sunlight. This is in agreement with recent studies by Mayer et al. (2009a) which showed that the photochemical reactivity of algal detritus increases with increasing microbial decay and/or humification of OM. This data suggests that potentially both OM sources and degree of degradation (age) control the resulting composition of photo-generated DOM. The exact mechanism for these processes is presently not known.

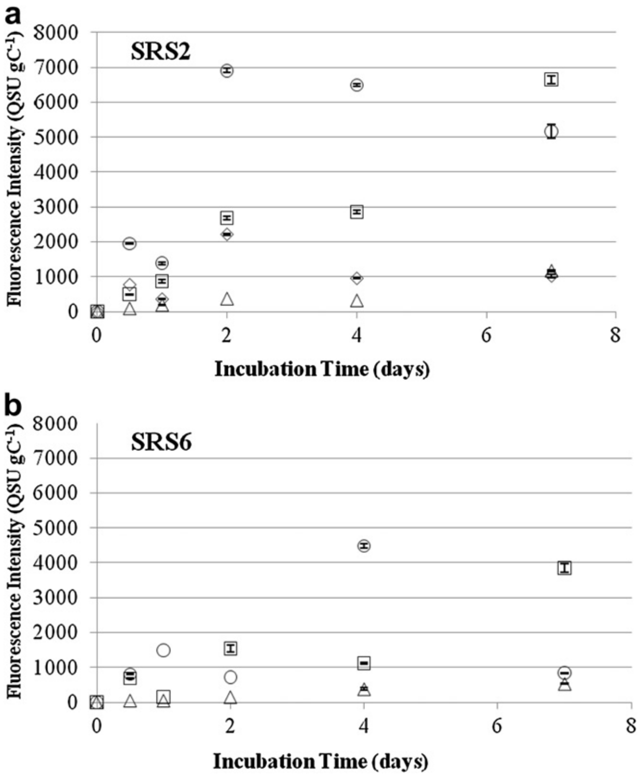

Fig. 3 – Photo-production of terrestrial humic-like components, C1, C3 and C5 were combined (○: Dry season, □: Wet season) and protein-like components, C7 and C8 (◇: Dry season, △: Wet season) from SRS2 (3a) and SRS6 (3b) floc. Fluorescence intensities were normalized to the initial floc POC content. Photo-produced fluorescent components at day = t was calculated by subtracting the fluorescence intensity at t = 0: photo-produced fluorescent intensity (t) = fluorescence intensity (t) − fluorescence intensity (0).

Table 2 – Regression analysis for CDOM generation rates. Linear regressions were determined between incubation time and fluorescence intensities of terrestrial humic-like and protein-like components for 0–2 and 0–4 days for SRS2 and SRS6, respectively.

Components	Site	Season	Generation rate (QSU gC^{-1} d^{-1})	p
Humic-like	SRS2	Dry	3.30 ± 0.88	0.065
		Wet	1.35 ± 0.18	0.018
	SRS6	Dry	1.00 ± 0.27	0.034
		Wet	0.28 ± 0.17	0.199
Protein-like	SRS2	Dry	1.03 ± 0.35	0.097
		Wet	0.19 ± 0.00	<0.001
	SRS6	Dry	0.14 ± 0.04	0.027
		Wet	0.09 ± 0.01	0.002

4. Conclusions

In summary, the data presented above show that flocculent detritus in the FCE generates significant amounts of DOM as well as TDN and SRP when exposed to artificial sunlight. In the shallow waters of the FCE, floc is naturally re-suspended (Larsen et al., 2009), and can easily be exposed to intense sunlight. This is particularly critical for floc from freshwater marshes where the dominant vegetation is composed of short grasses and sedges, with minimal tree cover and consequently low shading effects. The resulting light exposure of the floc can aid in the transfer of POM into the dissolved phase through photo-dissolution processes (Kieber et al., 2006; Mayer et al., 2006) and as such fuel the microbial loop. This is especially important in the oligotrophic waters of the FCE where the concentrations of dissolved nutrients are naturally very low, but where most of the dissolved N and P are in an organic form (Noe and Childers, 2007).

Regarding the composition of the photo-generated DOM, terrestrial humic-like components were the main contributors to the CDOM fluorescence, indicating a preferential photo-dissolution of humic moieties. Shank et al. (2011) reported that terrestrial humic-like components were preferentially photo-desorbed from re-suspended estuarine sediments, indicating that photo-generated materials seem to be preferentially dominated by organics with a more terrigenous character. The generation rate of the terrestrial humic- and protein-like components was higher for floc collected at the freshwater site compared to the mangrove site, suggesting that there are differences in floc composition between the freshwater and mangrove sites that are reflected in differences in their photo-reactivity. Similarly, the generation rate of the terrestrial humic- and protein-like components was higher during dry season than wet season for both sites. It has recently been reported that older, partially degraded material can be significantly more photo-reactive compared to unprocessed, fresh material (Mayer et al. 2009a). Floc receives much of its OM input during the wet season when periphyton mats are more productive and mangrove litterfall increases. Consequently, floc present during the wet season is expected to be fresher, while it is more aged during the dry season, therefore increasing its potential photo-reactivity during the latter. While floc collected during the dry season clearly showed higher photo-dissolution rates during the first 2–4 days of exposure for freshwater and mangrove floc respectively, the overall DOC production after one week of exposure was not too different between wet and dry season samples.

The Florida Coastal Everglades is an oligotrophic subtropical wetland, where detrital carbon pools are critical components of the food web and control to a significant extent the trophic dynamics in this system (Williams and Trexler, 2006). This study suggests that floc photo-dissolution has the potential to generate high amounts of DOC as well as TDN and SRP and thus can affect the biogeochemical cycling and productivity of this system. The efficiency of these photo-dissolution processes is dependent on floc quality, which seems dependent on biomass type inputs and primary productivity on both spatial and temporal scales. Potential changes, such as increased water delivery, particularly through Shark River Slough as a result of the implementation of the Comprehensive Everglades Restoration Plan may induce changes in floc dynamics in this system. A better understanding of the effects of light exposure to POM, suspended sediments or floc is needed to assess carbon dynamics in shallow and/or turbid aquatic ecosystems.

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REFERENCES

Castañeda-Moya, E., Twilley, R.R., Rivera-Monroy, V.H., Zhang, K., Davis III, S.E., Ross, M., 2009. Sediment and nutrient deposition associated with hurricane Wilma in mangroves of the Florida Coastal Everglades. Estuaries and Coasts 33 (1), 45–58.

Chen, M., Price, R.M., Yamashita, Y., Jaffé, R., 2010. Comparative study of dissolved organic matter from groundwater and surface water in the Florida coastal Everglades using multi-dimensional spectrofluorometry combined with multivariate statistics. Applied Geochemistry 25, 872–880.

Childers, D.L., Boyer, J.N., Davis, S.E., Madden, C.J., Rudnick, D.T., Sklar, F.H., 2006. Relating precipitation and water management to nutrient concentrations in the oligotrophic "upside-down" estuaries of the Florida Everglades. Limnology and Oceanography 51 (1/2), 602–616.

Clark, C.D., Hiscock, W.T., Millero, F.J., Hitchcock, G., Brand, L., Miller, W.L., Ziolkowski, L., Chen, R.F., Zika, R.G., 2004. CDOM distribution and CO_2 production on the southwest Florida Shelf. Marine Chemistry 89, 145–167.

Coble, P.G., 1996. Characterization of marine and terrestrial DOM in seawater using excitation-emission matrix spectroscopy. Marine Chemistry 51, 325–346.

Coble, P.G., 2007. Marine optical biogeochemistry: the chemistry of ocean color. Chemical Reviews 107, 402–418.

Ewe, S.M.L., Gaiser, E.E., Childers, D.L., Iwaniec, D., Rivera-Monroy, V.H., Twilley, R.R., 2006. Spatial and temporal patterns of aboveground net primary productivity (ANPP) along two freshwater-estuarine transects in the Florida Coastal Everglades. Hydrobiologia 569, 459–474.

Findlay, S.E.G., Sinsabaugh, R.L., 2003. Aquatic Ecosystems: Interactivity of Dissolved Organic Matter. Academic Press, San Diego.

Gao, M., Simoneit, B.R.T., Gantar, M., Jaffé, R., 2007. Occurrence and distribution of novel botryococcene hydrocarbons in freshwater wetlands of the Florida Everglades. Chemosphere 70, 224–236.

Harris, D., Horwath, W.R., van Kessel, C., 2001. Acid fumigation of soils to remove carbonates prior to total organic carbon or carbon-13 isotopic analysis. Soil Science Society of America Journal 65, 1853–1856.

Hernandez, M.E., Mead, R., Peralba, M.C., Jaffé, R., 2001. Origin and transport of *n*-alkane-2-ones in a subtropical estuary: potential biomarkers for seagrass-derived organic matter. Organic Geochemistry 32, 21–32.

Holder Sandvik, S.L., Bilski, P., Pakulski, J.D., Chignell, C.F., Coffin, R. B., 2000. Photogeneration of singlet oxygen and free radicals in dissolved organic matter isolated from the Mississippi and Atchafalaya River plumes. Marine Chemistry 69, 139–152.

Jaffé, R.J., Mead, R., Hernandez, M.E., Peralba, M.C., DiGuida, O.A., 2001. Origin and transport of sedimentary organic matter in two subtropical estuaries: a comparative, biomarker-based study. Organic Geochemistry 32, 507–526.

Jaffé, R., Boyer, J.N., Lu, X., Maie, N., Yang, C., Scully, N.M., Mock, S., 2003. Source characterization of dissolved organic matter in a subtropical mangrove-dominated estuary by fluorescence analysis. Marine Chemistry 84, 195–210.

Kieber, R.J., Whitehead, R.F., Skrabal, S.A., 2006. Photochemical production of dissolved organic carbon from resuspended sediments. Limnology and Oceanography 51 (5), 2187–2195.

Kirk, J.T.O., 1980. Spectral absorption properties of natural waters: contribution of the soluble and particulate fractions to light absorption some inland waters of south-eastern Australia. Australian Journal of Marine and Freshwater Research 31, 287–296.

Larsen, L.G., Harvey, J.W., Noe, G.B., Crimaldi, J.P., 2009. Predicting organic floc transport dynamics in shallow aquatic ecosystems: Insights from the field, the laboratory, and numerical modeling. Water Resources Research 45, W01411. doi:10.1029/2008WR007221.

Lou, T., Xie, H., 2006. Photochemical alteration of the molecular weight of dissolved organic matter. Chemosphere 65, 2333–2342.

Maie, N., Jaffé, R., Miyoshi, T., Childers, D.L., 2006. Quantitative and qualitative aspects of dissolved organic carbon leached from senescent plants in an oligotrophic wetland. Biogeochemistry 78, 285–314.

Maie, N., Pisani, O., Jaffé, R., 2008. Mangrove tannins in aquatic ecosystems: their fate and possible influence on dissolved organic carbon and nitrogen cycling. Limnology and Oceanography 53 (1), 160–171.

Mayer, L.M., Schick, K., Loder III, T.C., 1999. Dissolved protein fluorescence in two Maine estuaries. Marine Chemistry 64, 171–179.

Mayer, L.M., Schick, L.L., Skorko, K., Boss, E., 2006. Photodissolution of particulate organic matter from sediments. Limnology and Oceanography 51 (2), 1064–1071.

Mayer, L.M., Schick, L.L., Hardy, K.R., Estapa, M.L., 2009a. Photodissolution and other photochemical changes upon irradiation of algal detritus. Limnology and Oceanography 54 (5), 1688–1698.

Mayer, L.M., Schick, L.L., Bianchi, T.S., Wysocki, L.A., 2009b. Photochemical changes in chemical markers of sedimentary organic matter source and age. Marine Chemistry 113, 123–128.

Miller, W.L., Moran, M.A., 1997. Interaction of photochemical and microbial processes in the degradation of refractory dissolved organic matter from a coastal marine environment. Limnology and Oceanography 42 (6), 1317–1324.

Moore, J.C., Berlow, E.L., Coleman, D.C., de Ruiter, P.C., Dong, Q., Hastings, A., Johnson, N.C., McCann, K.S., Melville, K., Morin, P.J., Nadelhoffer, K., Rosemond, A.D., Post, D.M., Sabo, J. L., Scow, K.M., Vanni, M.J., Wall, D.H., 2004. Detritus, trophic dynamics and biodiversity. Ecology Letters 7, 584–600.

Moran, M.A., Zepp, R.G., 1997. Role of photoreactions in the formation of biologically labile compounds from dissolved organic matter. Limnology and Oceanography 42 (6), 1307–1316.

Neto, R.R., Mead, R.N., Louda, W.J., Jaffé, R., 2006. Organic biogeochemistry of detrital flocculent material (floc) in a subtropical, coastal wetland. Biogeochemistry 77, 283–304.

Noe, G.B., Childers, D.L., 2007. Phosphorus budgets in Everglades wetland ecosystems: the effects of hydrology and nutrient enrichment. Wetlands Ecology and Management 15, 189–205.

Opsahl, S., Benner, R., 1998. Photochemical reactivity of dissolved lignin in river and ocean waters. Limnology and Oceanography 43, 1297–1304.

Saunders, C.J., Gao, M., Lynch, J.A., Jaffé, R., Childers, D.L., 2006. Using soil profiles of seeds and molecular markers as proxies for sawgrass and wet prairie slough vegetation in Shark River Slough, Everglades National Park. Hydrobiologia 569, 475–492.

Shank, G.C., Zepp, R.G., Vähätalo, A., Lee, R., Bartels, E., 2010. Photobleaching kinetics of chromophoric dissolved organic matter derived from mangrove leaf litter and floating Sargassum colonies. Marine Chemistry 119, 162–171.

Shank, G.C., A. Evans, Y. Yamashita and R. Jaffé. Solar radiation-enhanced dissolution of particulate organic matter from coastal marine sediments. Limnology and Oceanography in press.

Stedmon, C.A., Bro, R., 2008. Characterizing dissolved organic matter fluorescence with parallel factor analysis: a tutorial. Limnology and Oceanography Methods 6, 572–579.

Stedmon, C.A., Markager, S., Bro, R., 2003. Tracing dissolved organic matter in aquatic environments using a new approach to fluorescence spectroscopy. Marine Chemistry 82, 239–254.

Troxler, T.G., Richards, J., 2009. δ^{13}C, δ^{15}N, carbon, nitrogen and phosphorus as indicators of plant ecophysiology and organic matter pathways in Everglades deep slough, Florida, USA. Aquatic Botany 91 (3), 157–165.

Twilley, R.R., Lugo, A.E., Patterson-Zucca, C., 1986. Litter production and turnover in basin mangrove forests in southwest Florida. Ecology 67 (3), 670–683.

von Wachenfeldt, E., Bastviken, D., Tranvik, L.J., 2009. Microbially induced flocculation of allochthonous dissolved organic carbon in lakes. Limnology and Oceanography 54 (5), 1811–1818.

Williams, A.J., Trexler, J.C., 2006. A preliminary analysis of the correlation of food-web characteristics with hydrology and nutrient gradients in the southern Everglades. Hydrobiologia 569, 493–504.

Woods, J. 2010. Surface Water Discharge and Salinity Monitoring of Coastal Estuaries in Everglades National Park, USA, in support of the Comprehensive Everglades Restoration Plan. In: Proceedings of the 3rd International Perspective on Current & Future State of Water Resources & the Environment, Chennai, India.

Xie, H., Zafiriou, O.C., 2009. Evidence for significant photochemical production of carbon monoxide by particles in coastal and oligotrophic marine waters. Geophysical Research Letters 36, L23606. doi:10.1029/2009GL041158.

Yamashita, Y., Scinto, L.J., Maie, N., Jaffé, R., 2010. Dissolved organic matter characteristics across a subtropical wetland's landscape: application of optical properties in the assessment of environmental dynamics. Ecosystems 13, 1006–1019.

Zhang, Y., van Dijk, M.A., Liu, M., Zhu, G., Qin, B., 2009. The contribution of phytoplankton degradation to chromophoric dissolved organic matter (CDOM) in eutrophic shallow lakes: field and experimental evidence. Water Research 43, 4685–4697.