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Dissolved Organic Matter Characteristics Across a Subtropical Wetland's Landscape: Application of Optical Properties in the Assessment of Environmental Dynamics

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Abstract

Wetlands are known to be important sources of dissolved organic matter (DOM) to rivers and coastal environments. However, the environmental dynamics of DOM within wetlands have not been well documented on large spatial scales. To better assess DOM dynamics within large wetlands, we determined high resolution spatial distributions of dissolved organic carbon (DOC) concentrations and DOM quality by excitation–emission matrix spectroscopy combined with parallel factor analysis (EEM–PARAFAC) in a subtropical freshwater wetland, the Everglades, Florida, USA. DOC concentrations decreased from north to south along the general water flow path and were linearly correlated with chloride concentration, a tracer of water derived from the Everglades Agricultural Area (EAA), suggesting that agricultural activities are directly or indirectly a major source of DOM in the Everglades. The optical properties of DOM, however, also changed successively along the water flow path from high molecular weight, peat-soil and highly oxidized agricultural soil-derived DOM to the north, to lower molecular weight, biologically produced DOM to the south. These results suggest that even though DOC concentration seems to be distributed conservatively, DOM sources and diagenetic processing can be dynamic throughout wetland landscapes. As such, EEM–PARAFAC clearly revealed that humic-enriched DOM from the EAA is gradually replaced by microbial- and plant-derived DOM along the general water flow path, while additional humic-like contributions are added from marsh soils. Results presented here indicate that both hydrology and primary productivity are important drivers controlling DOM dynamics in large wetlands. The biogeochemical processes controlling the DOM composition are complex and merit further investigation.

Key words: dissolved organic matter; dissolved organic carbon; fluorescence characteristics; excitation–emission matrix; parallel factor analysis; spatial distribution; wetlands; Everglades.

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Introduction

Substantial amounts of terrestrial dissolved organic matter (DOM) estimated at 0.25 Pg C y^{-1} are conveyed to coastal regions (Hedges and others 1997). Although these values are quite small compared to the oceanic DOM pool (700 Pg C, Hedges and others 1997), they are of the same order of magnitude as the annual production of semi-labile DOM in the open ocean (1.2 Pg C y^{-1}; Hansell and Carlson 1998). Although a major fraction of terrestrial DOM is thought to be degraded photochemically and biologically in coastal regions, DOM plays an important role in riverine and coastal fluvial ecosystems by regulating light penetration (Frenette and others 2003; Hayakawa and Sugiyama 2008), maintaining pH through organic acid buffering capacity (Ceppi and others 1999; García-Gil and others 2004), acting as a substrate for trace metal complexation (Yamashita and Jaffé 2008) and fueling the microbial loop (Hood and others 2009). In oligotrophic environments, a major fraction of macronutrients are known to occur as DOM-associated nitrogen and phosphorus, where, for example, greater than 90% of the total nitrogen and phosphorus in the Florida Coastal Everglades are in an organic form (Boyer and others 1997; Boyer 2006). Thus, knowledge of the environmental dynamics of DOM in terrestrial and coastal environments is essential for a better understanding of ecosystem function and biogeochemical cycling (Findlay and Sinsabaugh 2003; Battin and others 2008). However, our knowledge about the environmental dynamics of DOM on large spatial and long temporal scales remains limited. A significant limitation is the low sample throughput of analytical methods used for DOM characterization (for example, Maie and others 2006a). On the other hand, optical means for characterizing DOM allows for high sample throughput, that is, high sensitively, relatively inexpensive in comparison to other analytical techniques, and thus, recent advances in DOM characterization using optical properties have helped overcome these limitations (Jaffé and others 2008). In addition, this technique allows us to use real-time monitoring of CDOM with in situ instruments (for example, Spencer and others 2007).

The relationships between riverine dissolved organic carbon (DOC) concentration and the percentage of wetlands within its catchment are often reported (Mulholland 2003 and references therein). In addition, recent studies reported the relationship between stream DOM quality/composition and the percentage of wetlands in a catchment, where greater contributions of soil-derived humic-like DOM were observed as the proportion of wetlands increased (Wilson and Xenopoulos 2009; Williams and others 2010). Such enhanced contributions of humic substances to DOM have been suggested to result in decreased biodegradability of DOM (Balcarczyk and others 2009; Fellman and others 2008; 2009). Thus, wetlands are a quantitatively and qualitatively important factor in the determination of DOM quality and quantity in streams, and consequently in coastal areas. However, little is known about the large scale environmental dynamics of DOM in freshwater wetlands, including source assessments and biogeochemical alteration and removal processes (Mladenov and others 2007a).

The important contribution of humic-like DOM from wetlands to streams (Wilson and Xenopoulos 2009; Williams and others 2010) suggests that soils are major contributors to the DOM pool in wetlands. Conversely, exudation and leaching of DOM from aquatic plants and litter has also been considered an important source of wetland DOM (Maie and others 2006b; Mladenov and others 2007b; Osborne and others 2007; Larsen and others 2010). Although plant/litter-derived DOM has usually been considered labile or semi-labile compared to soil-derived DOM (Mladenov and others 2007b), some components of litter leachates seem to be resistant to rapid degradation (Mladenov and others 2007b). Spectroscopic and chemical characterization of fulvic acids, obtained from the Okavango Delta wetland system surface water and plant leachates, showed similar characteristics, suggesting a progressive enrichment of DOM by plant-derived material occurs along the wetland's flow path (Mladenov and others 2007a). Similarly, stable and radio-carbon isotopic signatures of DOM showed clear source changes along the flow path in northern Everglades wetlands (Wang and others 2002; Stern and others 2007). Thus, it has been proposed that DOM quality and quantity is dynamically altered with distance downstream within wetlands. High resolution mapping on spatial and temporal scales of DOM characteristics (quantity and quality) would be helpful in clarifying the alteration of DOM within these ecosystems. However, only a few such studies have been reported in the literature (Mladenov and others 2005).

In this study, we present the spatial variability of DOC concentration and DOM quality across the Everglades landscape, one of the largest subtropical wetlands in the world. The main purpose of this study was to clarify changes in DOM quantity and

quality along a broadly defined southerly water flow path and to determine factors controlling DOM quantity and quality within the Everglades. To achieve this purpose, water samples were collected across the freshwater Greater Everglades Ecosystem (GEE) as part of the U. S. Environmental Protection Agency (USEPA) Everglades Regional Environmental Monitoring and Assessment Program (R-EMAP) Phase III, and high sample throughput optical methods were applied to evaluate the high resolution spatial distribution of DOM quality. Thus, results presented here might be important not only for a better understanding of DOM dynamics in wetlands but also for providing base-line information of DOM dynamics in the GEE as an important biogeochemical parameter in the Everglades restoration plan (Scheidt and Kalla 2007).

Site Description

The original Everglades were the southern terminus of a large watershed (28,205 km^2) that included the Kissimmee River, Lake Okeechobee, and the Everglades. Water seasonally overflowing the southern boundary of Lake Okeechobee moved southward toward Florida Bay in a continuous shallow free-flowing wetland that was the Everglades. Beginning in the early 1880s the Everglades was ditched, diked, and drained to promote agricultural and urban development. Thus, the original Everglades were transformed from a free-flowing wetland into a series of hydrologically isolated surface water impoundments known as Water Conservation Areas (WCAs). The purpose of the WCAs was largely to receive and store agricultural runoff from the Everglades Agricultural Area (EAA), to provide flood prevention for urban areas, to provide recreational benefits, and to supply water for the natural system requirements of Everglades National Park (ENP) (Light and Dineen 1994) (Figure 1). The drainage of the EAA exposed the naturally accumulated organic peat soils to the atmosphere allowing microbial oxidation and compaction and resulted in the loss of over 2 m of soil in some areas (Sklar and others 2005). The use of fertilizers in the EAA and runoff from developed areas added increased nutrients, most notably phosphorus, to the historically nutrient-poor downstream receiving WCAs (McCormick and others 2002). Notable effects have been an increase in the areal coverage of P-loving cattail (*Typha* spp.), and an increase in surficial soil P concentrations (Childers and others 2003). The reduction in the spatial extent of the original Everglades,

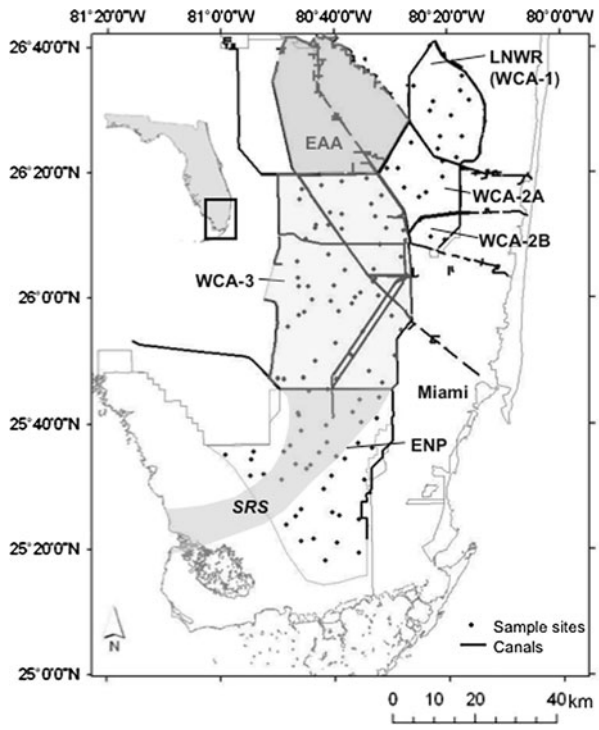

Figure 1. Sampling site locations in the Everglades wetlands. *EAA* Everglades Agricultural Area, *LNWR* Loxahatchee National Wildlife Refuge, *WCA* Water Conservation Area, *ENP* Everglades National Park, and *SRS* Shark River Slough.

ecological damage to large portions of the remaining Everglades, and the need for water supply to ENP and the developed areas of SE Florida prompted passage of the 1994 Everglades Forever Act (EFA) and the subsequent creation of the Comprehensive Everglades Restoration Plan (CERP) (Sklar and others 2005) in an attempt to partially undo past damage. DOM represents a significant pool of carbon, nitrogen and phosphorus in the Everglades ecosystem, and its environmental dynamics, which are expected to be impacted through CERP implementation, are still not well understood. Thus, the main objectives of this work are to shed light on the DOM dynamics of a large wetland on a spatial landscape scale.

Methods

Surface water samples were collected during the wet season (November 2005) at 118 sites stretching over approximately 5500 km^2 of the GEE from the marshes located south and east of the EAA down to ENP, including WCA-1 (Loxahatchee National Wildlife Refuge—LNWR), WCA-2, and WCA-3 (Figure 1) as part of a larger and more inclusive ''Everglades Ecosystem Assessment Phase III'' a

Regional Environmental Monitoring and Assessment Program (R-EMAP) conducted by USEPA Region 4 (Scheidt and Kalla 2007). The sampling design employed was probability-based and used a stratified random sampling design to assure sufficient samplings occurred in each sub-area permitting a quantitative analysis of environmental information across the spatial landscape scale and resulting in an average distribution of 1 sample per 47 km^2 (Scheidt and Kalla 2007). The R-EMAP Project sampled several ecosystem compartments including soil, soil porewater, surface water, detrital layers, vegetation, and periphyton for a multitude of physicochemical parameters, some of which were used in correlation analysis in this study. Details of sampling and analytical procedures can be found in the EPA-related references including Scheidt and Kalla (2007) and Stober and others (2001). Sites were accessed by helicopter and samples were collected using pre-cleaned, brown Nalgene polyethylene bottles and stored on ice during transportation to the laboratory. In the laboratory, samples were filtered through pre-combusted GF/F filters and kept refrigerated (4°C) until analysis.

DOC concentration was determined by high-temperature combustion with a Shimadzu TOC-V_{CSH} TOC analyzer. The UV–Vis absorption spectra were measured from 240 to 800 nm in a 0.01 m quartz-windowed cell using a Varian Cary 50 Bio. A blank scan (Milli-Q water) was subtracted from each sample spectrum. The blank subtracted spectra were baseline-corrected by subtracting average values ranging between 700 and 800 nm from the entire spectra, and then, converted to absorption coefficient, a (λ) (m^{-1}) as follows:

$$a(\lambda) = 2.303A(\lambda)/z$$

where $A(\lambda)$ is absorbance provided by the spectrophotometer and z is the path length of the cuvette, that is, 1 cm. In the present study, the absorption coefficient at 350 nm (a_{350}) was reported as a quantitative parameter of chromophoric DOM (CDOM). As a qualitative parameter of the absorbance spectra, the spectral ratio (S_R) was calculated as the ratio of spectra slope (S) obtained from 275–295 nm and 350–400 nm, respectively (Helms and others 2008). The S_R parameter has been proposed as an index of molecular weight (MW) of DOM with the S_R value inversely related to the MW (Helms and others 2008).

Excitation–emission matrix (EEM) spectra were obtained using a Horiba Jovin Yvon SPEX Fluoromax-3 spectrofluorometer according to procedures described by Maie and others (2006a) and Santín and others (2009). Inner-filter corrections were carried out for each EEM using their absorbance spectrum (McKnight and others 2001), and then, an EEM of Milli-Q water was subtracted from sample EEMs. The specific instrument components were also corrected with excitation and emission correction files supplied by the manufacturers. EEMs were then corrected to the area under the water Raman peak at 350 nm (measured daily) and converted to quinine sulfate units (QSU). The fluorescence index (FI) was estimated as the ratio of the fluorescence intensity at 470 to 520 nm emission excited at 370 nm (Cory and McKnight 2005; Maie and others 2006a).

Parallel factor analysis (PARAFAC) was carried out for the evaluation of the EEM data set. PARAFAC statistically separates the complex EEM measured into its individual underlying fluorescent groups with specific excitation and emission spectra and provides both a qualitative (fluorescent groups) and quantitative (fluorescence intensity of each group) model of the data (Stedmon and Bro 2008). Thus, this technique may be ideally suited to detect small, but potentially significant vitiations in DOM composition in apparently similar aquatic environments. The approach of PARAFAC modeling to EEMs has been described in detail elsewhere (Stedmon and others 2003; Ohno and Bro 2006). The PARAFAC modeling was carried out in MATLAB (Mathworks, Natick, MA) with the DOMFluor toolbox (Stedmon and Bro 2008). For a better understanding of DOM environmental dynamics in the Everglades, we used a large number of samples obtained from the Florida Coastal Everglades including samples reported here for the PARAFAC modeling (n = 1394). After validation of the PARAFAC modeling, we obtained an eight component model (Table 1). Details for the spectral characteristics of these components can be found in Chen and others (2010).

Spatial mapping of quantitative and qualitative parameters was carried out using inverse distance weighted methods in ArcGIS (ver. 9.3) software. Correlations (R) were determined using StatView 5.0. The differences in parameters between sampling area were determined by non-parametric Mann–Whitney U tests using StatView 5.0.

Results

Spatial Distribution of DOC Concentration and Optical Parameters

The distribution of DOC showed spatial variation where DOC concentrations were highest adjacent to the canal in WCA-2A and lowest at the southern

Table 1. Characteristics of the Eight Components Derived from the Florida Coastal Everglades

Component	Excitation maximum	Emission maximum	Stedmon and Markager (2005)	Cory and McKnight (2005)	Assignment
C1	<260 (345)	462	4 (Ter/Aut)	(C1[a] or SQ2[a])	Ubiquitous humic-like
C2	<260	454	1 (Ter)	Q2	Terrestrial humic-like, suggested as photo-refractory
C3	<260 (305)	416	3 (Ter)	C10	Terrestrial humic-like, fulvic acid-type
C4	<260 (305)	376	6 (Ant)	C3[a] or Q3[a]	Microbial humic-like
C5	275 (405)	>500	2 (Ter/Aut)	SQ1	Terrestrial humic-like, humic acid-type
C6	325	406	5 (Ter/Ant)	–	Ubiquitous humic-like, suggested as photo-labile and agricultural land use derived
C7	275	326	8 (Aut)	Tyr	Protein-like
C8	300	342	7 (Aut)	Trp	Protein-like

Ter, Aut, and Ant means origin of terrestrial, autochthonous, and anthropogenic, respectively.
[a]Identified in the Antarctic data set only (Cory and McKnight 2005), indicating microbial origin.

portion of the more pristine wetlands of ENP (Figure 2). The DOC concentrations ranged from 4.6 to 45.0 mg C l^{-1}. Thus, DOC concentrations generally decrease from north to south along the general water flow path, which is partially disrupted by transverse canals, roads and other man-made structures. Such directional patterns of DOC concentration, namely the decrease from the northern to southern Everglades, have previously been observed in the Everglades wetlands (Qualls and Richardson 2003; Larsen and others 2010) and specifically in WCA-2A (Wang and others 2002; Stern and others 2007). Quantitative parameter measures of CDOM (a_{350}) ranged from 4.8 to 81.9 m^{-1} and showed very similar distributional patterns to those of DOC (data not shown). A strong linear relationship was observed between a_{350} and DOC ($R = 0.95$, $P < 0.01$), suggesting that a major fraction of the DOM is colored humic-like OM. Such strong linear relationships have previously been reported for other aquatic environments including large tropical river systems (Yamashita and others 2010) and the Yukon River, Alaska (Spencer and others 2009a).

The FI and S_R values also showed north–south gradients in the Everglades wetlands (Figure 2). The FI was originally proposed to assess the DOM sources and the aromaticity of fulvic acids (McKnight and others 2001). FI ranged from 1.28 to 1.47 for Everglades wetlands. FI values commonly range from 1.0 to 1.8 over a wide range of aquatic environments and where low and high values indicate terrestrial derived (higher plant originated), high aromatic DOM and microbially

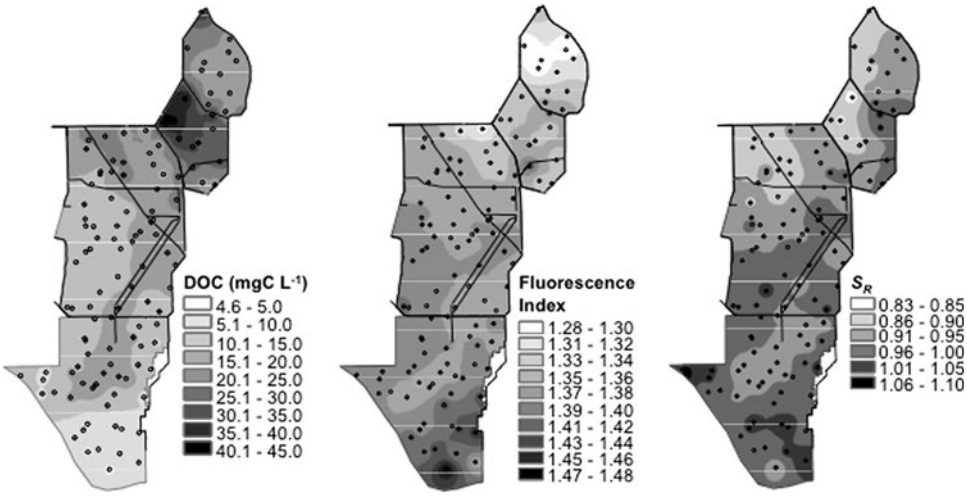

Figure 2. Spatial distribution of DOC, fluorescence index (FI), and S_R in the Everglades wetlands.

derived low aromatic DOM, respectively (Cory and McKnight 2005; Jaffé and others 2008). Thus the FI values observed here indicate that CDOM in the Everglades wetlands is a mixture of terrestrial and microbial CDOM. The values of S_R ranged from 0.83 to 1.07 for the Everglades. These values were similar to values observed for the Great Dismal Swamp on the NC/VA border, USA (Helms and others 2008), Yukon River, Alaska (Spencer and others 2009a) and to those of large tropical river systems (Spencer and others 2009b; Yamashita and others 2010; Spencer and others 2010).

Even though a general north–south gradient was evident for DOC, FI, and S_R values, trends in the spatial distribution in the northern part of the Everglades wetlands (that is, LNWR and WCA-2A) were different among parameters (Figure 2). In the Everglades wetlands, DOC concentration was highest at WCA-2A, but FI was lowest at LNWR. DOC concentration and FI at WCA-2A were significantly higher than those at LNWR ($P < 0.01$). The values of S_R were similar between LNWR and WCA-2A ($P > 0.05$).

Interestingly, relatively high DOC concentrations, low FI, and low S_R values were evident along the canal in the WCA-3 and along the general water flow path (Shark River Slough) in the ENP (Figure 2). These distributional patterns suggest that elevated concentrations of high molecular weight (HMW), terrestrial (soil-derived) DOM are being transported from north to south by canals and pumping stations. Similarly, the transport of abundant, relatively HMW DOM from EAA to northern WCA-2A by canals is evident (Figure 2). Such transport processes through the existing canal network were also suggested through the study of chloride ion concentrations and dissolved mercury species (Scheidt and Kalla 2007; Liu and others 2009). Additionally, high aromaticity for DOM in canals on the Everglades has previously been reported (Lu and others 2003).

Spatial Distribution of PARAFAC Components

PARAFAC modeling resulted in five terrestrial (ubiquitous) humic-like, one microbial humic-like, and two protein-like components as characteristic fluorescence components in the Everglades (Table 1). Consistent with the abovementioned linear relationship between DOC and a_{350}, the fluorescence intensities of PARAFAC components were strongly related to DOC concentration ($R = 0.85$-0.96, $P < 0.01$) except for component 3 ($R = 0.59$, $P < 0.01$). Conversely, the relative abundance of individual components (% fluorescence intensity of individual components relative to total fluorescence intensity) was differently distributed for each PARAFAC component (Figure 3). C1 represented 24.8–34.1% of eight PARAFAC components and was usually the most abundant component in the Everglades wetlands (Figure 3). The spectral characteristics of C1 are similar to the previously reported ubiquitous, fulvic acid-like component which occurs commonly in diverse aquatic environments (for example, component 4 in Stedmon and Markager 2005). This component is also relatively similar to PARAFAC components obtained from an Antarctic lake where no higher plant OM inputs were evident (C1/SQ2, Cory and McKnight 2005). The distributional pattern of the relative abundance of humic-like C5 is similar and correlated to that of C1 (Figure 3) ($R = 0.73$, $P < 0.01$). The spectral characteristics of C5 were similar to those of a terrestrial reduced quinone-like component (SQ2; Cory and McKnight 2005). Also, C5 is similar to a humic acid-type component extracted from soils and sediments in coastal environments (Santín and others 2009). The highest values of relative abundance (%) of C1 and C5 were only 1.4 and 1.5 times higher than the minimum values, and thus, the relative percentages of C1 and C5 are fairly uniformly distributed in the Everglades (Figure 3). The most notable feature in their distributional patterns was the difference between LNWR and WCA-2A, where relative abundances of C1 and C5 in LNWR were significantly higher compared to those in WCA-2A ($P < 0.01$).

The spectral characteristics of C3 are similar to other terrestrial PARAFAC components previously reported (C3, Stedmon and Markager 2005; C10, Cory and McKnight 2005). The relative abundance (%) of C3 in LNWR was also significantly higher than that in WCA-2A ($P < 0.01$), however, differences in the relative abundance (%) of C3 between these two areas were greater than those of humic-like C1 and C5 (Figure 3). Interestingly, clear differences were also evident across the canal between WCA-2A and WCA-3A.

A good correlation between the distributional patterns of the other humic-like components C2 and C6 were observed ($R = 0.64$, $P < 0.01$; Figure 3). From its spectral characteristics, C2 could be assigned to a terrestrial humic-like, oxidized quinone-like component (component 1, Stedmon and Markager 2005; Q2, Cory and McKnight 2005). Conversely, spectral characteristics of C6 were similar to another ubiquitous humic-like component (component 5, Stedmon and Markager 2005). Highest relative abundances (%) of these components were found in WCA-2A, and decreased

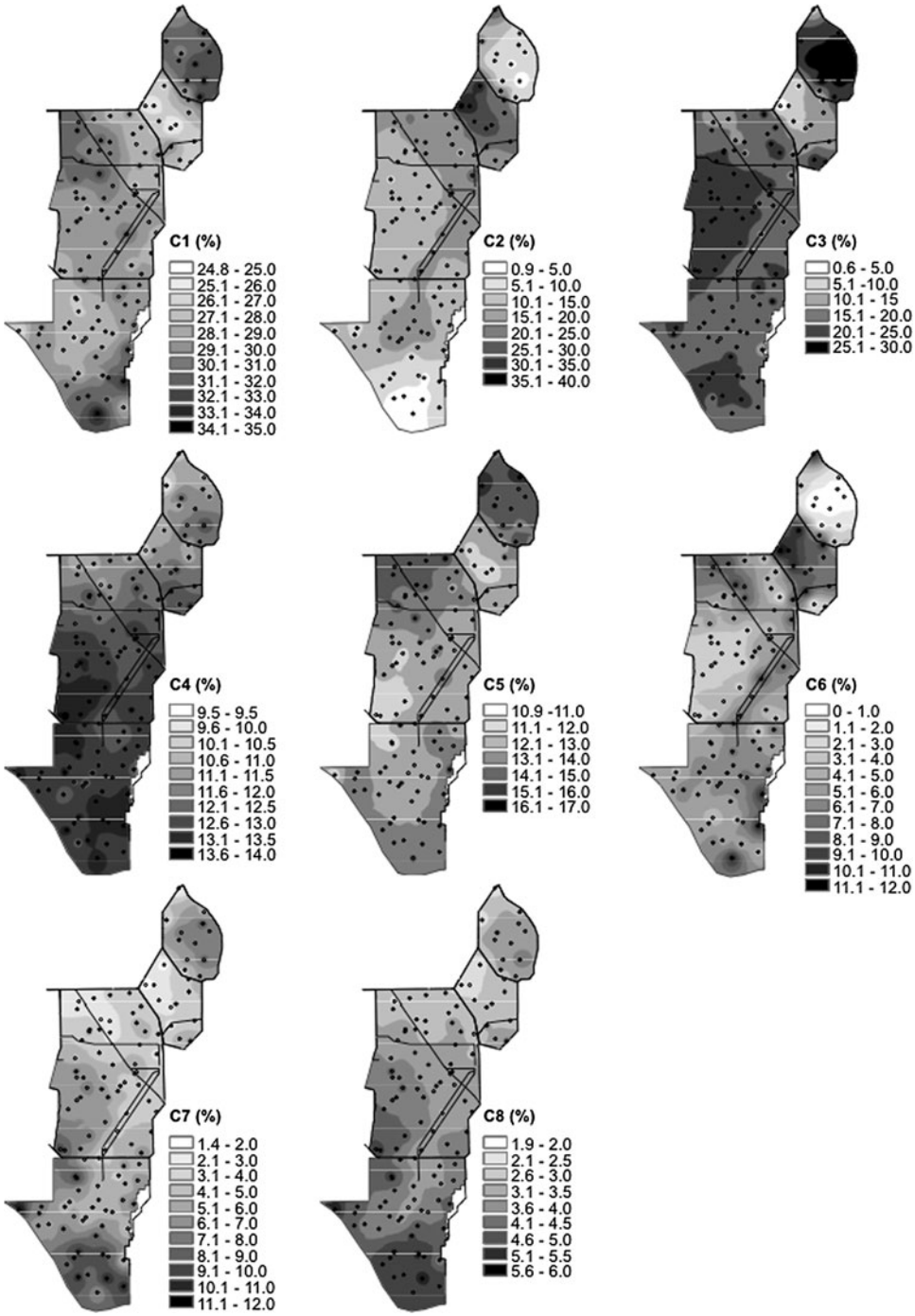

Figure 3. Spatial distribution of eight PARAFAC components in the Everglades wetlands. The scales of relative abundance (%) are different for each component.

toward the southern part of the wetland. Similar to the distributional patterns for DOC values (Figure 2), higher relative abundances of these components were found along the canals. Contrary to humic-like C1, C3, and C5, the relative abundance (%) of C2 and C6 were significantly lower in LNWR compared to WCA-2A ($P < 0.01$).

C4 showed similar spectral characteristics to other previously reported microbial humic-like PARAFAC components (Cory and McKnight 2005; Yamashita and others 2008), and was distributed relatively uniformly throughout the Everglades. The highest value of C4 relative abundance (%) was only 1.4 times higher than its lowest value (Figure 3). The differences in %C4 between LNWR and WCA-2A were not significant ($P > 0.05$). Although the variability in the C4 percentage was small, clear north–south gradients (that is, lower % in northern wetlands) were evident between WCA-2 and ENP (Figure 3).

The spectral peak positions of C7 and C8 were similar to protein-like PARAFAC components previously reported (Stedmon and Markager 2005; Cory and McKnight 2005; Yamashita and others 2008), and the spatial distribution patterns of two protein-like components were well correlated ($R = 0.90$, $P < 0.01$; Figure 3). The spatial distribution of these components was also related to that of the microbial humic-like C4 ($R = 0.54$, $P < 0.01$ for C7; $R = 0.80$, $P < 0.01$ for C8). The relative abundance (%) of C7 and C8 in LNWR were, however, significantly higher than those in WCA-2A ($P < 0.01$).

Discussion

Variations in Everglades DOM Characteristics Originate from Autochthonous or Allochthonous (Agriculturally Influenced) Sources

Pedogenic development and accretion of organic soils in the Everglades occurred earlier and to a greater extent in the northern Everglades with decreasing age and thickness southward (Richardson 2009). Measurements made early (circa 1910) in the development of the EAA and in the northern Everglades showed peat depths greater than 3 m (Sklar and others 2005; Richardson 2009). These deep peat soils were subsequently drained to create the EAA and to facilitate agricultural production of sugar cane, citrus, and vegetable crops (Scheidt and Kalla 2007). By 1988 only 17% of the EAA had peat soils thicker than 1.3 m largely due to drainage causing increased aerobic decomposition (Tate 1980). In contrast, the peat soils remain thick (2.5–3.0 m) in most of the LNWR (Scheidt and Kalla 2007). Water draining the EAA is commonly pumped into a series of canals and then into the WCAs. However, not all WCAs receive EAA discharge to the same extent. For instance, most of the water budgets of LNWR and WCA-3 are from direct rainfall whereas WCA-2A has received the majority of its water from surface water inflows including drainage from the EAA and outflows from LNWR (Sklar and others 2005). Additionally, the LNWR is designed with perimeter canals adjacent to but inside the levee system which effectively causes the discharged canal water to move through the outside edges of this area without significantly affecting the marsh interior (Light and Dineen 1994). Thus, differences in DOM characteristics between WCA-2A and LNWR could partially be dependant upon the sources of the DOM, with the DOM in WCA-2A originating largely allochthonously (that is, in the EAA) and that in LNWR originating in situ. Consequently, DOC values in WCA-2A were significantly higher than those in LNWR (Figure 2). High DOC values in WCA-2A are likely the result of the combination of inputs of DOM from the EAA, as mentioned above, and in situ production (Qualls and Richardson 2003; Stern and others 2007). Lower value of $\Delta^{14}C$ in canals compared to WCA-2A were observed during the late dry season (May), suggesting changes in DOM sources in WCA-2A from 'old' EAA soil-derived to recently produced organic matter (Wang and others 2002). In contrast, the $\Delta^{14}C$ values of DOC in the canals were similar to those in WCA-2A during the wet season (August; Stern and others 2007). This might be due to a greater contribution of DOM derived from plant and/or plant litter during the dry season compared to higher canal and EAA soil-derived inputs during the wet season. Higher contributions of peat leachate during the dry season to early wet season compared to the wet season were also observed in Everglades wetlands (Larsen and others 2010). In the present study, sampling was carried out during the late wet season (November), and thus the contribution of DOM from plant and/or plant litter might be proportionally small compared to EAA soil-derived sources as previously suggested (Stern and others 2007).

Although S_R values were similar between LNWR and WCA-2A, the FI in LNWR was significantly lower than those in WCA-2A (Figure 2), suggesting a greater contribution of microbial-derived CDOM in WCA-2A compared to LNWR. The increase in FI of riverine DOM with an increase in the proportion of crop land in riparian zones was also observed in Ontario, Canada (Wilson and Xenopoulos 2009). Relative abundances of microbial humic-like C4 were, however, similar between LNWR and WCA-2A (Figure 3). The spectral characteristics of C4 might not significantly affect FI values, because the excitation and emission peak wavelengths are shorter than those fluorophores affecting the FI calculation (Table 1). A component similar to the microbial humic-like C4 was observed in estuarine regions where autochthonous organic matter generation was active (Yamashita and others 2008). Such data suggest that the microbial humic-like C4 may actually represent an autochthonously derived product of microbial activity in the water column. The above-mentioned information suggests that the relatively lower abundances of C4 in the EAA soil-derived DOM regions is expected, and that C4 is primarily autochthonously produced by microbial activity in the water column in these wetlands.

Linear relationships between protein-like fluorescence intensity and the concentration of total hydrolyzable amino acids have been reported (Yamashita and Tanoue 2003), although non-proteinous compounds have also been suggested to contribute to the protein-like fluorescence signal (Maie and others 2007; Hernes and others 2009). In addition, the abundances of protein-like components were recently reported to be related to bioavailability of DOM (Balcarczyk and others 2009; Fellman and others 2008, 2009). Thus, the protein-like components could be considered to represent freshly produced, semi-labile DOM. The relative abundance of protein-like components was higher in LNWR compared to WCA-2A suggesting that the DOM in the LNWR may contain a higher relative contribution of autochthonous DOM (that is, plant leachates and periphyton OM inputs) compared to WCA-2A (Figure 3). Alternatively, such results might be explained by the differences in the concentration of phosphorus. The concentration of phosphorus in the canals discharging from the EAA was shown to be much greater than in interior marshes with significantly decreasing P concentration with distance from the canals and when coupled with the interior canal design of LNWR suggest that canal waters seldom intrude into the marsh interior (McCormick and others 2002; Childers and others 2003). Thus, protein-like components might be greatly degraded in the canals in EAA and WCA-2A compared to LNWR due to high microbial activity caused by high concentrations of phosphorus which is typically limited in oligotrophic Everglades wetlands.

The relative abundances of terrestrial (higher plant derived) and ubiquitous humic-like components were also different between WCA-2A and LNWR (Figure 3). The higher relative abundance in WCA-2A compared to LNWR is evident for C2 and C6, but vice versa for components C1, C3, and C5. In ENP, C6 was enriched in the groundwater compared to surface water, suggesting that C6 is easily photodegradable compared to other humic-like components (Chen and others 2010). Thus, the low relative abundance of C6 at LNWR might result from more extensive photo-degradation compared to WCA-2A. In contrast, a comparative study between Everglades surface and groundwater DOM suggested C2 to be photo-refractory compared to other humic-like components (Chen and others 2010). Spectral characteristics of C2 are similar to an oxidized quinone-like component (Cory and McKnight 2005). The loss of peat soil at the EAA is due largely to aerobic decomposition, as mentioned above. Thus, the high relative abundance of C2 at WCA-2A might be the result of DOM derived from highly oxidized peat soils.

Factors Controlling DOM Concentration and Composition in Everglades Wetlands

In the Everglades water generally flows from north to south, that is, from WCA-2A to the ENP. As discussed above, the major factor controlling DOM concentration and composition in WCA-2A and LNWR appears to be different. Thus, further evaluation of changes in DOM quantity and quality within the Everglades were conducted excluding the LNWR.

It is well known that the concentration of chloride (Cl^- ion) in the canals in the EAA is high compared to the surrounding area (Chen and others 2006; Scheidt and Kalla 2007). The median Cl^- ion concentration in 10 farm canals within the EAA during the period between 1999 and 2003 was reported to range from 72 to 174 mg l^{-1} (Chen and others 2006). Conversely, Cl^- ion concentration in precipitation was reported to be only approximately 1.5 mg l^{-1} (Scheidt and Kalla 2007; Harvey and McCormick 2009). Thus, the concentration of Cl^- ion will be a potentially useful indicator to trace regional water sources from rainwater and water from the EAA (Scheidt and Kalla 2007). In addition to waters discharging from the EAA, ground water is another potential source for Cl^- ion in surface water, where discharge of groundwater to surface water is dominant in the coastal region of ENP (Price and Swart 2006; Price and others 2008), whereas recharge of surface water to groundwater is dominant in the area from WCA-2A to the northern ENP (Price and Swart 2006; Harvey and McCormick 2009). Thus, Cl^- ion concentration is useful as a semi-conservative tracer of water from the EAA for comparison of DOM environmental dynamics.

The concentration of Cl^- ion was highest in WCA-2A and higher concentrations were found along canals in WCA-3 and ENP compared to freshwater marsh environments (Scheidt and Kalla 2007). Interestingly, DOC concentrations were strongly correlated to Cl^- ion concentrations (Figure 4). Even though DOC concentrations in rainwater around the Everglades wetlands have not been reported, the linear relationship between DOC concentration and Cl^- ion concentration seems to imply that simple mixing of high DOC and high chloride concentrations in water derived from the EAA with rainwater low in DOC and low in chloride might be an important factor controlling the north–south gradient of DOC concentration. In

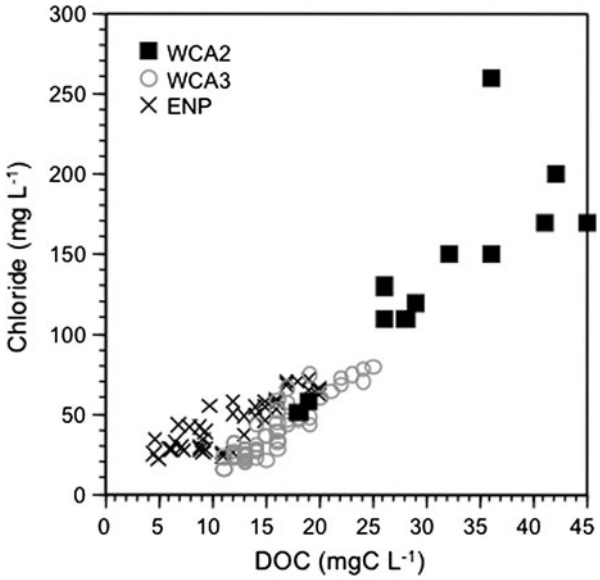

Figure 4. Relationships between DOC concentration and chloride concentration at WCA-2 (*closed square*), WCA-3 (*open circle*), and ENP (*cross*).

addition to further dilution, this gradient might be the result of ground-to-surface discharge in ENP, where groundwater having a relatively lower DOC concentration compared to surface waters has been reported (Chen and others 2010).

The FI and S_R values were negatively correlated to Cl^- ion concentration (Table 2). However, correlations of the FI and S_R values with DOC concentration were better than those with Cl^- ion concentration (Table 2), suggesting that simple mixing of water from the EAA and rainwater alone could not explain changes in DOM quality and quantity. That is, DOM source changes, such as variations in inputs of soil-derived, HMW DOM to microbial/plant-derived, low molecular weight (LMW) DOM within the wetland gradient are also important factors in addition to simple dilution. Such a change in DOM quality from the northern to southern Everglades seems to be in agreement with the clear differences in ^{14}C ages of DOC between WCA-2A (705–840 BP) and the ENP ('modern') previously reported (Stern and others 2007). In addition to source changes, degradation experiments using DOM in pore waters from WCA-2A showed that 25% of the DOC was degraded by sequential photo- and bio-degradation (Qualls and Richardson 2003). Although Qualls and Richardson (2003) suggested that decomposition of DOM balances its production, a clear change in DOM quality was observed along the north to south transect (Figures 2, 3).

Interestingly, FI and S_R values were positively correlated to mineral content of the soil (Table 2). Mineral content of the soil is controlled to hydroperiod, that is, the greater the mineral content with the shorter the hydroperiod and vice versa. The mineral content of the soil is also positively correlated to peryphyton dry weight ($R = 0.77$, $P < 0.01$) and negatively to DOC ($R = -0.43$, $P < 0.01$). These correlations indicate that longer-hydroperiod locations have an enriched humic-like DOM composition due to enhanced peat formation/accumulation, whereas the shorter-hydroperiod, marl-dominated locations have a higher microbial contribution due to greater periphyton abundances. Some of these geomorphological aspects are clearly observed in Figures 2 and 3 where landscape features such as water depth/hydroperiod are depicted along the longer-hydroperiod, peat-dominated Shark River Slough (SRS) for example. Thus, DOM seems to be dynamically generated and removed through a variety of biogeochemical processes along the north to south flow path in the Everglades, where hydroperiod and hydrological transport and mixing of DOC are all drivers contributing to the spatial distribution patterns of DOM across this landscape.

To confirm this hypothesis, the correlation between relative abundances (%) of PARAFAC components and other parameters were determined (Table 2). Seven components were linearly

Table 2. Correlations Between Biogeochemical Parameters and Optical Parameters and Relative Abundance of PARAFAC Components in WCA-2, WCA-3, and ENP

	FI	S_R	%C1	%C2	%C3	%C4	%C5	%C6	%C7	%C8
DOC (mg C l^{-1})	−0.46	−0.58	−0.48	0.96	−0.80	−0.71		0.60	−0.70	−0.79
Chloride (mg l^{-1})		−0.38	−0.38	0.84	−0.85	−0.59		0.71	−0.54	−0.60
Alkaline-phosphatase activity			−0.31			0.48	−0.30	−0.29	0.42	0.47
Periphyton dry weight (g m^{-2})	0.46						0.39			0.43
Mineral content of soil (%)	0.47	0.30	0.29	−0.41			0.28		0.40	0.50

Only significant correlations ($P < 0.01$) were listed in the table.

related to Cl^- ion concentrations and also to DOC concentrations. PARAFAC components C1, C3, C4, C7, and C8 were negatively correlated to DOC and thus to Cl^- ion concentration, again suggesting a change in the source of DOM from EAA soil-derived DOM to pristine wetlands soil-derived DOM and/or recently produced DOM, that is, plant leachate and inputs from peryphyton, along with water flow from north to south. No significant relationship was evident between DOC concentration and %C5, identified as a humic acid-type component (Table 1, Santín and others 2009). The lack of a significant correlation between DOC and C5 (Table 2), as well as its relatively uniform distribution within the wetland (Figure 3), suggests that the generation and removal rates of C5 through biogeochemical processing along the studied north–south gradient are relatively constant.

Positive correlations between DOC and the relative abundance of PARAFAC components were only found for humic-like C2 and C6, suggesting that these components undergo mixing/dilution and/or extensive removal along the N–S gradient. They show the highest enrichment of all components in the northern Everglades, particularly that under the influence of the EAA (excluding LNWR). Thus, it seems reasonable to assume that C2 and C6 are mainly produced in the EAA. It has been suggested that C6 may be a microbial degradation product found in watersheds under agricultural influence (Stedmon and Markager 2005) and it is also presumed to be photo-sensitive (Chen and others 2010). Thus, this component may be enriched in EAA effluents carrying soil organic matter derived DOM, whereas photochemical removal processes might dominate the dynamics of this component along the N–S gradient. In contrast, C2 is suggested to be relatively photo-refractory compared to other components (Chen and others 2010), but also seems primarily derived from or is strongly enriched in DOM from the EAA. Similar to C6 the major source of C2 in the Everglades is likely from highly oxidized peat soils in the EAA. However, C2 is also negatively correlated to the mineral content of the soil (Table 2), implying that it may have an additional source in the peat soils of the long hydroperiod freshwater marshes.

Recently, a positive correlation between a protein-like component and leucine-aminopeptidase activity was observed at streams in southern Ontario, Canada (Williams and others 2010), suggesting that microbial activity controls the production of such components. In the present study, the relative abundance (%) of the microbial humic-like C4 and protein-like C7 and C8 were positively correlated to alkaline-phosphatase activity (Table 2). However, none of these components were correlated to chlorophyll *a* concentration, suggesting that primary productivity of phytoplankton in the Everglades is not controlling the distribution of microbial and protein-like components. Similarly, although periphyton dry weight was significantly correlated to FI, it was not correlated to microbial humic-like %C4 (Table 2). However, periphyton dry weight was significantly correlated to protein-like C8, but not to protein-like C7 (Table 2). Thus, the microbial component C4 may be mainly derived from heterotrophic activity, whereas the protein-like component C7 and C8 are generated by both microbial communities, periphyton and leachates from higher plants (Scully and others 2004). These components seem to be dynamically produced and consumed and therefore, contribute to fueling the microbial loop in this aquatic environment. The production of protein-like components might exceed degradation due to phosphorus limitation within the oligotrophic southern Everglades.

In summary, the application of optical property measurements on extensive spatial scales for the assessment of DOM dynamics in large wetlands can provide important information on qualitative changes in DOM. In the specific case of the Everglades, it was found that 'old', HMW, oxidized humic-enriched DOM, which originates largely in the agricultural areas (EAA), is transported southwards through canals or surface water flow while subjected to photo-degradation and possibly bio-degradation. During the general southward transport, this DOM becomes diluted through rainwater inputs and alternative DOM sources from biological origin and soils, thus resulting in a gradual change to more 'modern', lower MW, protein-enriched DOM in the southern Everglades. Results presented here indicate that DOM is dynamically produced and degraded within large wetlands, and the detailed determination of the biogeochemical processes involved in this complex cycling need more attention for a better understanding of DOM dynamics in wetland-associated terrestrial and coastal environments. It is expected that as the CERP advances, and water delivery to the ENP region increases, DOM residence times in the system, and consequently DOM quantity and quality will change as well. The effects of such changes on the biogeochemical cycles of this ecosystem and the adjacent estuarine areas of Florida Bay and the Florida Shelf are unknown and need to be assessed. The application of high sample throughput spectroscopy based optical properties

measurements such as EEM fluorescence, in combination with multivariate statistics, seem, as presented here, ideally suited for ecosystem studies targeting the assessment of ecological and physical processes driving the biogeochemistry of DOM on large spatial and temporal scales.

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