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# Using fluorescence spectroscopy to trace seasonal DOM dynamics, disturbance effects, and hydrologic transport in the Florida Everglades

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[1] Dissolved organic matter (DOM) quality reflects numerous environmental processes, including primary production and decomposition, redox gradients, hydrologic transport, and photochemistry. Fluorescence spectroscopy can detect groups of DOM compounds sensitive to these processes. However, different environmental gradients (e.g., redox, DOM provenance) can have confounding effects on DOM fluorescence spectra. This study shows how these confounding effects can be removed through discriminant analyses on parallel factor modeling results. Using statistically distinct end-members, we resolve spatiotemporal trends in redox potential and DOM provenance within and between adjacent vegetation communities in the patterned ridge and slough landscape of the Everglades, where biogeochemical differences between vegetation communities affect net peat accretion rates and persistence of landscape structure. Source discrimination of DOM in whole-water samples and peat leachates reveals strong temporal variability associated with seasonality and passage of a hurricane and indicates that hurricane effects on marsh biogeochemistry persist for longer periods of time (>1 year) than previously recognized. Using the DOM source signal as a hydrologic tracer, we show that the system is hydrologically well mixed when surface water is present, and that limited transport of flocculent detritus occurs in surface flows. Redox potential discrimination shows that vertical redox gradients are shallower on ridges than in sloughs, creating an environment more favorable to decomposition and diagenesis. The sensitivity, high resolution, rapidity, and precision of these statistical analyses of DOM fluorescence spectra establish the technique as a promising performance measure for restoration or indicator of carbon cycle processes in the Everglades and aquatic ecosystems worldwide.

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## 1. Introduction

[2] Dissolved organic matter (DOM), composed of a complex mixture of molecules, is ubiquitous in environmental waters, where it has a major influence on carbon cycling, redox processes, and the transport of contaminants and nutrients. DOM quantity and quality is in turn controlled by a variety of biological (e.g., primary production, decomposition [*McKnight et al.*, 1985; *Findlay and Sinsabaugh*, 2003; *Wickland et al.*, 2007]), chemical (e.g., photodegradation [*McKnight et al.*, 2001; *Cory and McKnight*, 2005]), redox reactions [*Fulton et al.*, 2004; *Miller et al.*, 2006], and physical (e.g., hydrology [*Maie et al.*, 2006a; *Lapworth et al.*, 2008; *Mladenov et al.*, 2008]) processes and therefore can serve as a comprehensive indicator of ecological and environmental conditions over space and time. Use of DOM as an environmental tracer requires analytical techniques to measure its variability and statistical techniques to independently resolve the influences of chemical, biological, and physical processes.

[3] Techniques commonly used to characterize variability in DOM quality are isolation and chemical characterization of fractions with different chemical properties [*Aiken et al.*, 1992; *Aiken and Leenheer*, 1993], nuclear magnetic resonance spectroscopy [*Benner et al.*, 1992], and optical/ultraviolet spectroscopy [*McKnight et al.*, 2001; *Stedmon et al.*, 2003; *Weishaar et al.*, 2003]. Of these, optical spectroscopy is emerging as a particularly powerful technique for analyzing large quantities of samples because of its rapidity, cost-effectiveness, and information density. A

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fraction of the DOM pool (chromophoric DOM) absorbs light in the ultraviolet and can be characterized by its specific ultraviolet absorbance (SUVA), which correlates with DOM aromaticity and reactivity [*Weishaar et al.*, 2003], and spectral slope, which relates to photobleaching and algal productivity [*Twardowski et al.*, 2004]. This measurable fraction of the DOM pool is typically assumed to be representative of the reactivity and provenance of the DOM pool as a whole. Similarly, the fluorescent fraction of the DOM pool is also assumed to be indicative of DOM reactivity, provenance, and redox state of the surrounding environment [*Lovley et al.*, 1996, 1998; *Scott et al.*, 1998]. These qualities influence the shape of DOM fluorescence excitation and emission spectra [*Senesi et al.*, 1989, 1991; *Matthews et al.*, 1996], typically obtained from three-dimensional scans that produce an excitation-emission matrix (EEM).

[4] Although techniques for measuring variability in the optical properties of DOM are relatively well established, statistical techniques for interpreting EEMs and other data-rich measurements are still being refined. Fluorescence index, calculated from two points in a fulvic acid-influenced region of EEMs, is a relatively simple measure of the degree of allochthonous or autochthonous influence in DOM processing [*McKnight et al.*, 2001]. Other analyses use all of the information available in EEMs and multivariate statistics such as hierarchical clustering [*Jiang et al.*, 2008], partial least squares regression [*Persson and Wedborg*, 2001; *Hall et al.*, 2005], and principal component analysis [*Persson and Wedborg*, 2001; *Rinnan et al.*, 2005; *Hall and Kenny*, 2007] to determine the similarity between samples or groups of samples. A more mechanistic interpretation of EEMs involves qualitative identification of peaks that correspond to different classes of molecules (e.g., humic acids, fulvic acids, amino acids) and use of the dissolved organic carbon (DOC) normalized fluorescence at each peak as a proxy for the abundance of the corresponding class of molecules [*Coble et al.*, 1990; *Chen et al.*, 2003; *Merritt and Erich*, 2003]. Parallel factor analysis (PARAFAC) of EEMs evolved from the need to more quantitatively identify spectral features and associated fluorophore concentrations [*Stedmon et al.*, 2003]. The algorithm, analogous to a trilinear principal component analysis, makes no assumptions about the number of components or the shapes of their absorption and emission spectra, and simulates EEMs by optimizing the absorption spectra, emission spectra, and concentrations of independent groups of fluorophores in the sample [*Stedmon and Bro*, 2008].

[5] PARAFAC analysis of DOM samples (whole water, fulvic acids, hydrophilic fraction, and ultrafiltered DOM) acquired from aquatic environments worldwide revealed that redox-reactive quinone-like components, amino acid-like components, and a few unnamed fluorophore groups are repeatedly responsible for the spectral features of EEMs [*Cory and McKnight*, 2005]. Resolution of the excitation and emission spectra of these 13 ubiquitous components (Table S1, available as auxiliary material) has enabled a simpler implementation of PARAFAC, in which the algorithm is run as an error minimization procedure to choose the concentrations of these 13 components [*Miller et al.*, 2006; *Jaffe et al.*, 2008; *Mladenov et al.*, 2008].[1] A recent comparison between the full and Cory/McKnight methods of implementing PARAFAC found that both techniques explain a similar amount of variability in the EEMs and provide similar chemical and functional information about the DOM. Still, because residual spectra are slightly larger and/or more coherent when the prevalidated Cory/McKnight model is used, the full PARAFAC implementation often retains greater sensitivity [*Fellman et al.*, 2009]. However, the Cory/McKnight model enables direct comparison between different studies, produces concentrations of components with a known relationship to redox potential that are thus highly interpretable [*Cory and McKnight*, 2005], and can resolve low-frequency components that vary with subtle environmental gradients but would not be statistically significant in a full PARAFAC analysis of a relatively small number of samples.

[6] Because of spectral overlap in the excitation and emission signatures of fluorophores, multivariate analyses such as principal component analyses performed on whole EEMs identify sample groups less distinctly than multivariate analyses performed on PARAFAC model results [*Ohno and Bro*, 2006; *Jaffe et al.*, 2008]. Even when sample groups are identified based on PARAFAC model results, their positions in multivariate space are a function of provenance, redox potential, and reactivity gradients. How each gradient independently controls observed differences in DOM fluorescence can be unclear.

[7] Wetlands commonly exhibit distinct spatiotemporal gradients in both redox potential and DOM provenance and reactivity. The long-term persistence of saturated soils often results in vertical redox gradients near the soil surface [*Thomas et al.*, 2009], and depth heterogeneity resulting from wetland microtopography can establish horizontal gradients in soil redox potential [*Vivian-Smith*, 1997; *Ahn et al.*, 2009]. Horizontal gradients in DOM provenance and reactivity can result from heterogeneity in local vegetation community composition, though hydrologic transport may change or obscure those gradients [*Neto et al.*, 2006; *Saunders et al.*, 2006]. Meanwhile, nonconservative behaviors of DOM including photobleaching, metabolic processes, and sorption can contribute to vertical gradients in DOM quality [*McKnight et al.*, 1992; *Benner and Biddanda*, 1998; *McKnight et al.*, 2002]. Seasonal wet-up/drydown processes and disturbance events such as hurricanes contribute to temporal gradients in DOM quality that are reflected in fluorescence spectra [*Lu et al.*, 2003; *Maie et al.*, 2005; *Mladenov et al.*, 2005; *Maie et al.*, 2006a]. In particular, hurricanes may resuspend sediments, disrupt or shift ecosystem metabolism, and produce large quantities of organic detritus [*Greening et al.*, 2006; *Mallin and Corbett*, 2006; *Williams et al.*, 2008]. Studies performed in coastal wetlands suggest that these effects can last for up to a year following passage of the storm [*Greening et al.*, 2006].

[8] An objective of this paper is to use discriminant analyses on PARAFAC results from the 13-component Cory/McKnight model to achieve a process-based understanding of how redox potential, hydrology, primary production, and decomposition can independently control the seasonal and spatial dynamics of DOM. We apply this new technique to the ridge and slough landscape of the Florida Everglades, where ecologically critical landscape dynamics are driven by redox, transport, and vegetation processes that

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[1] Auxiliary materials are available in the HTML. doi:10.1029/2009JG001140.

govern the carbon balance and spatial distribution of peat accretion rates [*Science Coordination Team* (*SCT*), 2003; *Larsen et al.*, 2007]. By resolving independent DOM provenance and redox potential gradients over space and time, we test and confirm the hypotheses that particulate organic material (POM) is redistributed from sloughs to ridges by flow, that ridges and sloughs exhibit differences in pore water biogeochemistry that have implications for rates of organic matter decomposition, and that regular (e.g., seasonal drydowns) or infrequent (e.g., hurricanes) disturbances have long-duration impacts on DOM quantity and quality that result from the disruption of periphyton communities. Our method is broadly applicable to achieving a process-based understanding of DOM dynamics in other systems where multiple environmental gradients are likely to have confounding influences on excitation-emission matrices or spectral indices. Likewise, our findings suggest that DOM quantity, quality and associated processes exhibit wide variation over a monthly timescale, and that hurricane effects on the biogeochemistry of coastal wetlands may persist for longer than has previously been recognized.

## 2. Site Description

[9] The ridge and slough landscape is a patterned, 2700 year-old [*Bernhardt and Willard*, 2009] peatland within the nontidal Everglades, where pH values are circumneutral (7.0–7.1), and the substrate is approximately 90% organic [*Gleason and Stone*, 1994]. Here, elevated ridges colonized by *Cladium jamaicense* (sawgrass) are regularly distributed among sloughs that are dominated by *Eleocharis* spp. (spikerush), *Nymphaea odorata* (water lily), floating and epiphytic forms of periphyton, and *Utricularia* spp. (bladderwort). Whereas sawgrass, which has a relatively high lignin content [*Saunders et al.*, 2006], dominates OM production on ridges, floating periphyton mats typically dominate OM production in sloughs [*Maie et al.*, 2006b]. Landscape features are aligned parallel to the flow direction, with a wavelength on the order of hundreds of meters in the direction perpendicular to flow. This configuration promotes high habitat and species diversity and high total secondary production [*Ogden*, 2005]. However, the ridge and slough landscape has experienced degradation over the past century, coincident with drainage, levee construction, and nutrient enrichment that has caused eutrophication, redox potential shifts, and loss of topographic relief and habitat heterogeneity [*SCT*, 2003].

[10] It is thought that two feedback processes historically maintained the peat elevation differences between ridge and slough. An autogenic feedback process, sensitive to local redox potentials and pore water biogeochemistry, would promote differential peat accretion rates in different vegetation communities [*SCT*, 2003; *Larsen et al.*, 2007]. Meanwhile, an allogenic feedback process, redistribution of organic bed sediment from sloughs to ridges, would be critical to maintaining a carbon balance at ridge edges that prevented ridges from spreading indefinitely over time [*Larsen et al.*, 2007]. Diminished flow velocities and drainage of the Everglades may have contributed to widespread landscape degradation by perturbing these feedback mechanisms [*SCT*, 2003]. However, these hypotheses have been poorly tested because factors controlling carbon cycling in this environment are not well understood.

[11] Our study used pore water, surface water, and surficial peat samples collected from U.S. Geological Survey long-term monitoring station WCA-3A-5 (80°42′19″W, 26°3′24″N). The site is located within the best preserved portion of the ridge and slough landscape, where ridge-slough elevation differences are approximately 20 cm [*Harvey et al.*, 2009]. An 11.3 m sampling platform bridges a ridge/slough transition, providing access to both landscape elements. Water levels at the site range from 80 cm above slough peat during the wet season (May–October) to 40 cm below slough peat during the dry season (November–April). Surface water flows are laminar to transitional in nature, with a mean daily velocity of 0.32 cm $s^{-1}$ [*Harvey et al.*, 2009]. Shallow groundwater flow velocities in the greater Everglades are orders of magnitude lower, ranging from 0 to 1.5 cm $d^{-1}$ [*Krest and Harvey*, 2003]. Surface-subsurface exchange fluxes vary in magnitude and direction across the Everglades, with typical magnitudes on the order of 0.05-0.5 cm $d^{-1}$ [*Harvey et al.*, 2004]. The highest measured surface-flow velocities at site WCA-3A-5 (4.9 cm $s^{-1}$ [*Harvey et al.*, 2009]) occurred during the category 3 Hurricane Wilma, which passed directly over the site on Julian day 297–2005 (24 October 2005). One of the most prominent effects of the storm was its elimination of floating periphyton and *Utricularia* mats, which remained absent through the end of sampling in November 2006.

## 3. Methods

### 3.1. Field Methods

[12] Sampling from permanent ridge and slough stations occurred on 14 dates between 9 August 2005 (Julian day 221–2005) and 7 November 2006 (Julian day 311–2006) on an approximately monthly basis. An array of seven miniature drivepoint (minipoint) piezometers [*Duff et al.*, 1998] was deployed to simultaneously sample surface water (2–8 cm above the peat/surface water interface) and six pore water depths, ranging from 2 to 45 cm beneath the peat surface. Minipoint piezometers were pumped at 1.5 mL $\min^{-1}$, and water was filtered in-line through 0.2 $\mu$m Pall polyethersulfone (DOM samples) or 0.1 $\mu$m Whatman Anotop (Fe samples) filters. The volume of the piezometers was purged by continuous pumping for 2 min prior to sampling. An additional 45 mL was pumped for other analyses prior to collection of Fe and DOC samples. During the dry season in 2006, dissolved oxygen was measured in-line with an oxygen electrode (Microelectrodes, Inc., Bedford, NH). Permanent piezometers (2.5 cm diameter) screened 60 cm beneath the ridge peat surface and 48 cm beneath the slough peat surface were installed in December 2005 for deeper pore water sampling and were purged prior to each use.

[13] All samples were collected with minimal headspace, stored on ice in a dark environment for transport to the laboratory, refrigerated, and analyzed within days of collection. Fe samples were preserved with 100 $\mu$L 12-M HCl. DOC samples were not processed in an anoxic environment, but studies have found that reduced quinones can be stable over a timescale of weeks without precautions to limit oxygen exposure [*Scott et al.*, 1998; *Klapper et al.*, 2002].

Nonetheless, we consider our procedure to produce a conservative estimate of gradients in redox potential.

[14] Surficial cores (10 cm long) were collected from central ridge (8 cores) and slough (12 cores) locations in March 2006 by manually driving 4.8 cm diameter plastic core sleeves with a sharpened end into the peat, stoppering the exposed end, and extracting the tube. Prior to transport to the laboratory, the unconsolidated layer of flocculent organic sediment was decanted from the cores, and suction was applied to a 0.32 mm diameter steel tube inserted along the edge of the core to remove interstitial water. In October 2006, additional coring was performed along an 11.6 m-ridge/slough transect. Eight core samples were acquired along the transect with a spacing most dense across the vegetation transition zone. Additional cores were obtained from slough and ridge centers (5 each). At each coring location, water depth was measured using a PVC rod with an "I"-shaped foot. Cores were stored upright in a dark, refrigerated environment and processed in October 2006. Live and senescent samples of *Eleocharis elongata*, *Cladium jamaicense*, *Utricularia purpurea*, *Bacopa caroliniana*, and *Nymphaea odorata* were also harvested during October 2006 for leaching experiments.

### 3.2. Laboratory Methods

[15] DOC concentrations in the filtered samples were measured on an OI Model 700 Total Carbon analyzer with a mean standard error of 0.3 mg $L^{-1}$ and a detection limit of 0.2 mg $L^{-1}$. UV absorption spectra were measured between 190 and 1100 nm at 1 nm resolution on an HP Chem spectrophotometer with a standard error of $6 \times 10^{-4}$ AU (based on $n = 10$ measurements). Using a Horiba-JY Fluoromax-3 spectrofluorometer with DataMax software, EEMs were acquired for excitation wavelengths between 240 nm and 450 nm at a 5 nm increment and for emission wavelengths between 300 nm and 600 nm at 2 nm increment. Samples were diluted to a UV absorbance of 0.4 AU prior to obtaining EEMs. Blank EEMs were obtained using MilliQ water. Sample EEMs were blank-subtracted, Raman-normalized, and corrected for the inner-filter effect [*McKnight et al.*, 2001]. From the fluorescence and UV spectra, fluorescence index [*McKnight et al.*, 2001], SUVA at 254 nm [*Weishaar et al.*, 2003], and spectral slope within 3 wavelength ranges (200–250 nm, 250–300 nm, 350–600 nm [*Twardowski et al.*, 2004]) were calculated. In addition, 3 L samples of ridge and slough surface water collected in August 2005 and pore water collected in January 2006 were fractionated in duplicate on XAD-8 and XAD-4 columns in accordance with *Aiken et al.* [1992]. Precision tests revealed a standard error of 0.009 in fluorescence index values ($n = 5$).

[16] Ferrous and total iron concentrations of samples were determined on a Shimadzu UV2101 spectrophotometer using the modified ferrozine method [*Viollier et al.*, 2000]. Eight-point calibration curves were obtained using standard solutions of $Fe^{2+}$ ($(NH_4)_2Fe(SO_4)_2$: concentrations of 0–0.1 mM) and total Fe ($FeCl_3$: concentrations of 0–1 mM). The detection limit for the method is 0.3 $\mu$M, and tests with a 20 $\mu$M $FeCl_3$ standard produced predicted concentrations of 20.1 ± 0.2 $\mu$M $Fe^{3+}$ and 0.1 ± 0.1 $\mu$M $Fe^{2+}$ ($n = 5$) [*Viollier et al.*, 2000].

[17] Peat and vegetation leaching experiments were performed to assess the fluorescent character of potential DOM sources in the ridge and slough landscape and to differentiate origins of ridge and slough peat. In the peat core leaching experiments, the surface 2.5 cm of the cores (which reflect the most recent depositional processes) were extruded and homogenized. Pore water was removed by centrifuging 7.0 g of peat at 3500 rpm for 10 min. After decanting the supernatant, water with concentrations of $HCO_3^-$ (0.001 N), $Ca^{2+}$ (75 mg $L^{-1}$), $SO_4^{2-}$ (5 mg $L^{-1}$), and $Cl^-$ (76 mg $L^{-1}$) adjusted to match Everglades surface water was added to the peat, bringing the total volume to 50 mL. The peat was leached at room temperature under agitation for 48 h. Postleaching, samples were centrifuged, and supernatants were filtered through 0.2 $\mu$m Pall polyethersulfone filters. Vegetation leaching experiments were performed similarly, with leaching taking place in aerated 1 L covered beakers filled with the amended water. After 48 h, a 40 mL sample of the leachate was extracted, filtered, and analyzed.

### 3.3. Statistical Analyses

[18] Normalized and corrected EEMs were processed with PARAFAC using the 13-component model of *Cory and McKnight* [2005]. Based on the criteria of *Mladenov et al.* [2008], PARAFAC results carried on for further analysis captured more than 90% of the total variance present in measured EEMs and had low residual EEMs with little coherent structure (i.e., maximum residual intensity was less than 5–10% of the measured fluorescence intensity; see Figure S1). Relative concentrations of the 13 PARAFAC model components, spectral slope, and fluorescence index from 233 samples were then used as inputs to further multivariate analyses (Figure 1). First, we used a principal component analysis with a Varimax rotation to guide our selection of end-member samples to use in the resolution of independent DOM provenance and redox potential gradients. We defined these two respective pairs of end-member samples as: (1) peat core leachates from the ridge center and the slough center (the "peat leachate" end-members), and (2) surface water and pore water (the "surface water/pore water" end-members). Second, eigenvectors that maximized the separation (Mahalanobis distance) between the end-members were computed in two univariate discriminant analyses [*Hair et al.*, 1998] (Table S1). Using each eigenvector ($\boldsymbol{c}$) as the weighting coefficients for the vector ($\boldsymbol{L}$) of relative fluorescent component loadings determined from PARAFAC and the values of the spectroscopic indices, we constructed discriminant scores for each sample as $\boldsymbol{c} \cdot \boldsymbol{L}$. Each sample was assigned two discriminant scores (a peat leachate discriminant score and a pore water/surface water discriminant score) that specified the location of the sample along the gradients between the pertinent end-members.

[19] For the peat leachate discriminant analysis to remove the confounding effect of redox potential and the pore water/surface water discriminant analysis to remove the confounding effect of DOM provenance, our data needed to meet the following requirements: (1) discriminant variables had to vary linearly with source and redox potential, (2) variables related to both source and redox potential had to be correlated with at least one other variable along the axis targeted for removal so that the correlated variable(s) could be weighted to remove the confounding influence (see TextS1),

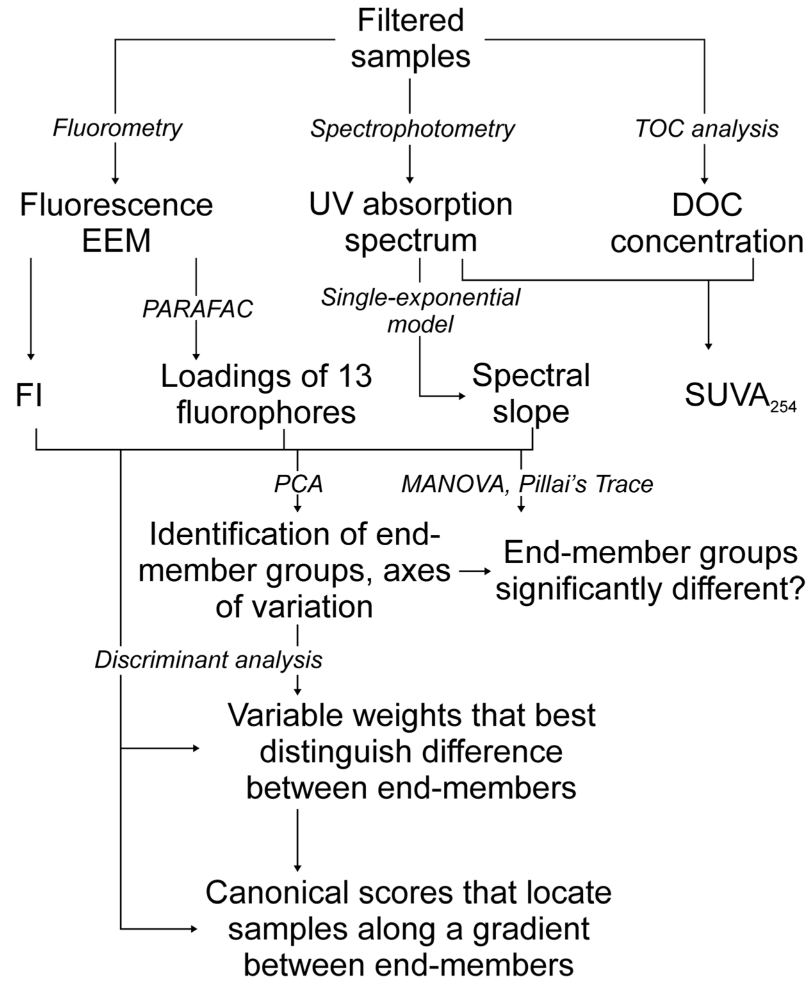

**Figure 1.** Inputs and outputs for the analytical and statistical methods used in this study. Methods are indicated in italic font, and inputs and outputs are shown in normal font.

and (3) both end-member groups needed to exhibit some systematic, multivariate noise along the axis designated for removal by the discriminant analysis so that variables correlated with this axis could be identified.

## 4. Results

### 4.1. Spatiotemporal Changes in DOC Concentration

[20] DOC concentrations increased with depth in both ridge and slough (Figure 2a), with the vertical gradient tending to be steeper in the slough ($-0.1 \pm 0.2$ mg L$^{-1}$ cm$^{-1}$) than in the ridge ($0.0 \pm 0.2$ mg L$^{-1}$ cm$^{-1}$). DOC concentration also varied seasonally over the drying/rewetting cycle (Figure 3). Immediately prior to the loss of surface water during the 2006 dry season, surface and near-surface concentrations of DOC increased. At the beginning of the subsequent rewetting event, pore water DOC concentrations in ridge and slough reached a maximum, with the highest concentrations (40 mg L$^{-1}$) occurring in the slough. As rewetting continued, DOC concentrations gradually attenuated in surface water and near-surface pore water.

### 4.2. Dominant Gradients in Everglades DOM Quality

[21] DOM samples acquired from Everglades surface water and pore water exhibited gradients in spectroscopic properties that varied continuously along two principal component axes (Figure 4). Rotated principal component 1, which explained 34.8% of the data set variance, separated samples by origin and prehurricane versus posthurricane time period. Ridge samples had a lower principal component 1 value than slough samples, and samples collected after Hurricane Wilma had lower values than prestorm samples. Rotated principal component 2, explaining 32.7% of data set variance, separated samples by depth, with surface water samples exhibiting the lowest values and deep pore water samples exhibiting the highest values.

[22] Principal component analysis showed that the principal component 1 value of DOM became increasingly distinct with depth beneath the peat/surface water interface. The principal component 1 value of all pore water samples decreased with depth, but the decrease was steeper in ridge compared to slough and steepened further following Hurricane Wilma. Slough pore water samples achieved more extreme values of principal component 2 than ridge pore

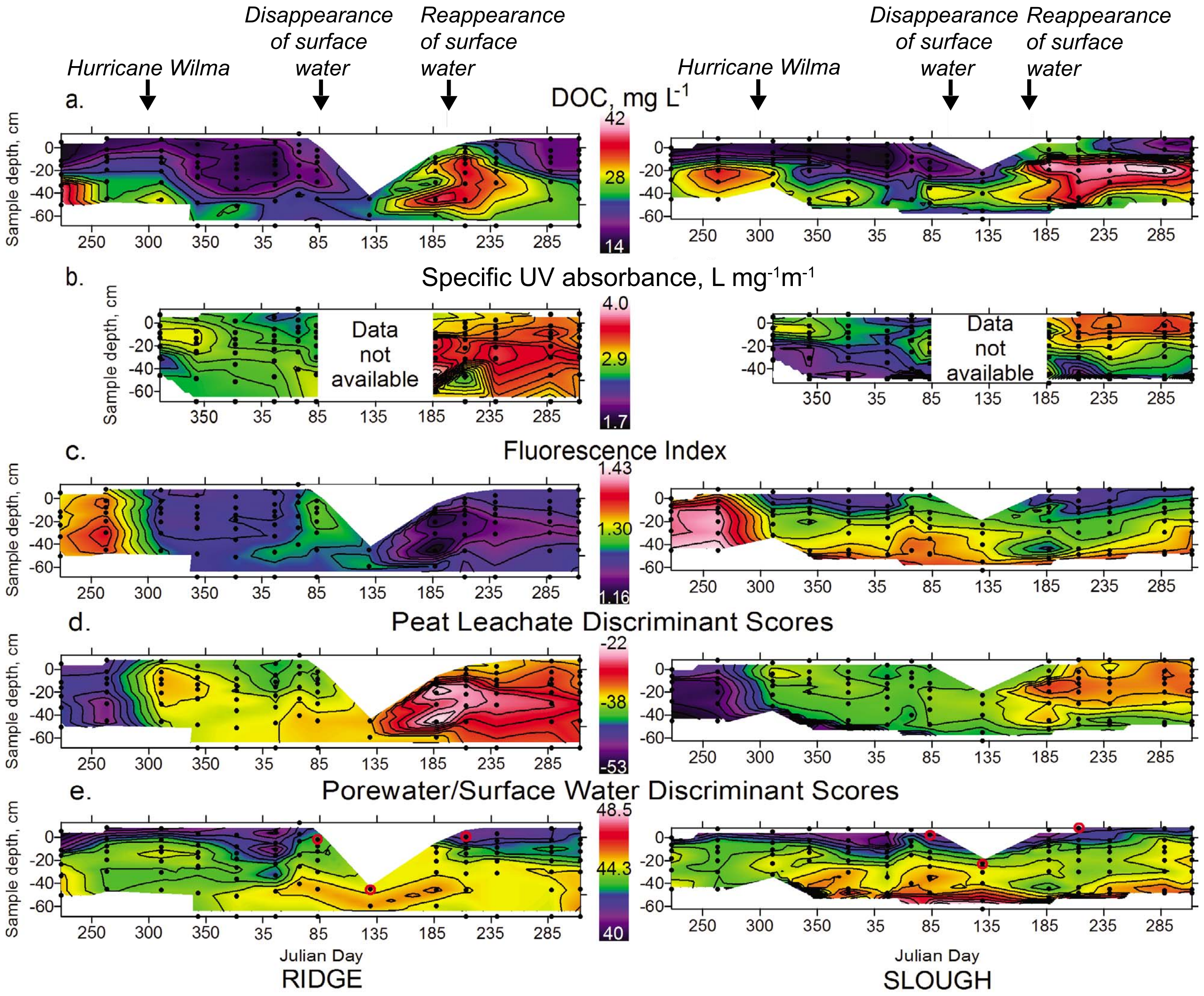

**Figure 2.** Spatiotemporal changes in DOM and water quality variables at permanent ridge and slough sampling sites. (a) DOC concentrations (contour interval 2 mg $L^{-1}$), (b) SUVA, corrected for dissolved $Fe^{2+}$ and $Fe^{3+}$ absorption (not available for the whole period of record; contour interval 0.1 L $mg^{-1}$ $m^{-1}$), (c) fluorescence index (contour interval of 0.015), (d) peat leachate discriminant scores (contour interval of 1.5), and (e) pore water/surface water discriminant scores (contour interval of 0.5). Black circles show sample dates and depths, and reference lines show the dates of Hurricane Wilma's passage and the disappearance and reemergence of surface water. Sampling began on 9 August 2005 (Julian day 221–2005) and continued to 7 November 2006 (Julian day 311–2006). Supplemental dissolved oxygen measurements are available for sample points circled in red (Table 1).

water samples, indicating greater separation along this pore water/surface water gradient.

[23] Based on the apparent gradients in the principal component analysis, we chose end-members to discriminate between the ridge influence and slough influence on DOM provenance (central ridge and slough peat core leachates, as described above) and between the relatively oxygen-rich surface water and oxygen-poor [*Qualls et al.*, 2001] deep pore water. Within each pair, the end-members were significantly different (Pillai's Trace test, $F = 11.9832$, d.f. = 15, 205, $p < 0.0001$ for peat core leachates; $F = 6.70$, d.f. = 15, 33, $p < 0.0001$ for pore water/surface water samples). Among other variables (see Text S1), fluorescence index was a dominant contributor to the higher peat leachate discriminant score of ridge peat compared to slough peat (Figure 2d). Dominant contributors to pore water/surface water discriminant scores (Figure 2e) were redox-reactive [*Cory and McKnight*, 2005] hydroquinone-, semiquinone-, and quinone-like components (see Text S1). Relative concentrations of the reduced hydroquinone- and semiquinone-like components increased with depth, while concentrations of the oxidized quinone-like component decreased with depth. Water table measurements of dissolved oxygen during the dry season of 2006 were consistent with trends in redox-reactive quinones and pore water/surface water discriminant scores: low dissolved oxygen values corresponded to high pore water/surface water discriminant scores, and vice versa (Figure 2e and Table 1).

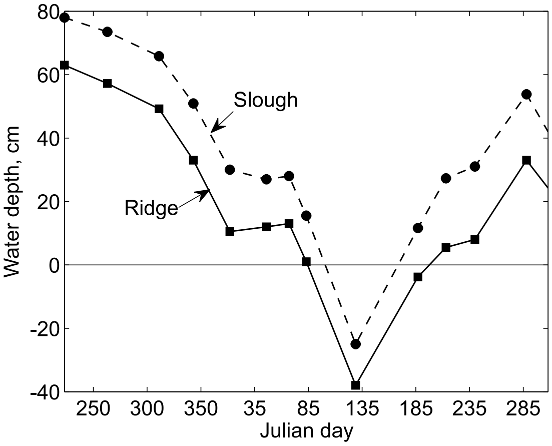

**Figure 3.** Ridge and slough water depths over the sampling period. Fluctuations in water depth, from below the peat surface (at zero) to tens of centimeters above the peat surface, result from the natural seasonality of rainfall in the Everglades.

**Table 1.** Dry Season Dissolved Oxygen Concentration at Site 3A-5[a]

| Julian Day | Ridge (mg L$^{-1}$) | Slough (mg L$^{-1}$) |
|---|---|---|
| 83–2006 | 2.2 ± 0.2 | 2.6 ± 0.2 |
| 129–2006 | 0.3 ± 0.2 | 1.7 ± 0.2 |
| 213–2006 | 3.8 ± 0.2 | 4.4 ± 0.2 |

[a] Samples correspond to the points circled in Figure 2e.

### 4.3. Spatial Variability in DOM Dynamics

[24] Different DOM metrics exhibited different degrees of variation with depth and across ridge and slough vegetation communities (Figure 2). Like DOC concentrations, pore water/surface water discriminant scores increased with depth (Figures 2a and 2e). As with the DOC concentrations, this vertical gradient in the upper 20 cm of the pore water was steeper in slough (0.14 ± 0.03 cm$^{-1}$) than ridge (0.09 ± 0.02 cm$^{-1}$). Steeper pore water/surface water discriminant score gradients in the slough were observed at sampling stations spaced at both the 10 m scale and the 50 m scale (Figures 5a and 5b). In contrast, peat leachate discriminant scores were less variable with depth for most sample dates (Figure 2d), especially in comparison to their seasonal variability. Within surface water (when present), peat leachate discriminant scores were statistically indistinguishable between ridge and slough (paired $t$ test, $p = 0.33$, $t = 0.98$, d.f. = 29). Likewise, XAD8/XAD4 column fractionation results for ridge surface water samples were within 1–3% of those for slough surface water samples (Table 2).

[25] Despite their surface water similarities, peat leachate discriminant scores differed between the ridge and slough subsurface (Figure 2d and Figures 5c and 5d) at both the 10 m scale (paired $t$ test, $p < 0.001$, $t = 8.94$, df = 14) and 50 m scale. During the relatively dry period following hurricane Wilma, peat leachate discriminant score gradients were most pronounced in the ridge ($-0.10 \pm 0.05$ cm$^{-1}$ ridge versus $-0.04 \pm 0.07$ cm$^{-1}$ slough). Still, XAD8/XAD4 column fractionation results from deep pore water samples acquired in January 2006 were equivalent to within 2% for the ridge and slough (Table 2). However, when surface water levels were below the ridge surface, ridge pore water peat leachate discriminant scores diverged more substantially, particularly at the ridge center sampling station, which had the shortest hydroperiod (Figures 5c and 5d).

### 4.4. Temporal Variability in DOM Dynamics

[26] Changes in DOM dynamics over time were associated with the seasonal drydown/wet-up cycle and the passage of Hurricane Wilma. As water levels declined at the end of the 2005 wet season, the near-surface zones of low pore water/

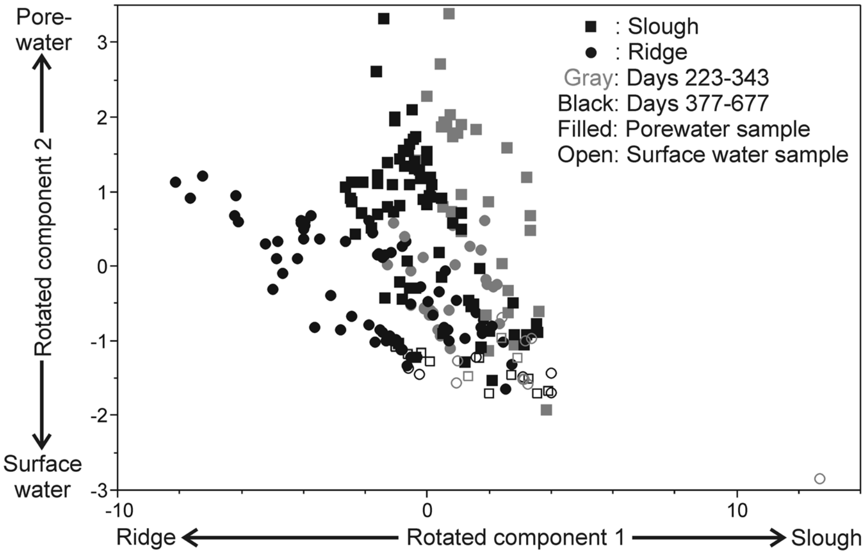

**Figure 4.** Varimax rotation of principal components of the DOM quality data set, constructed from PARAFAC model components, fluorescence index, and spectral slope within the 350–600 nm range. A shift in sample positions occurs as a result of Hurricane Wilma, following a 50 day response period; preresponse and postresponse samples are distinguished by gray scale.

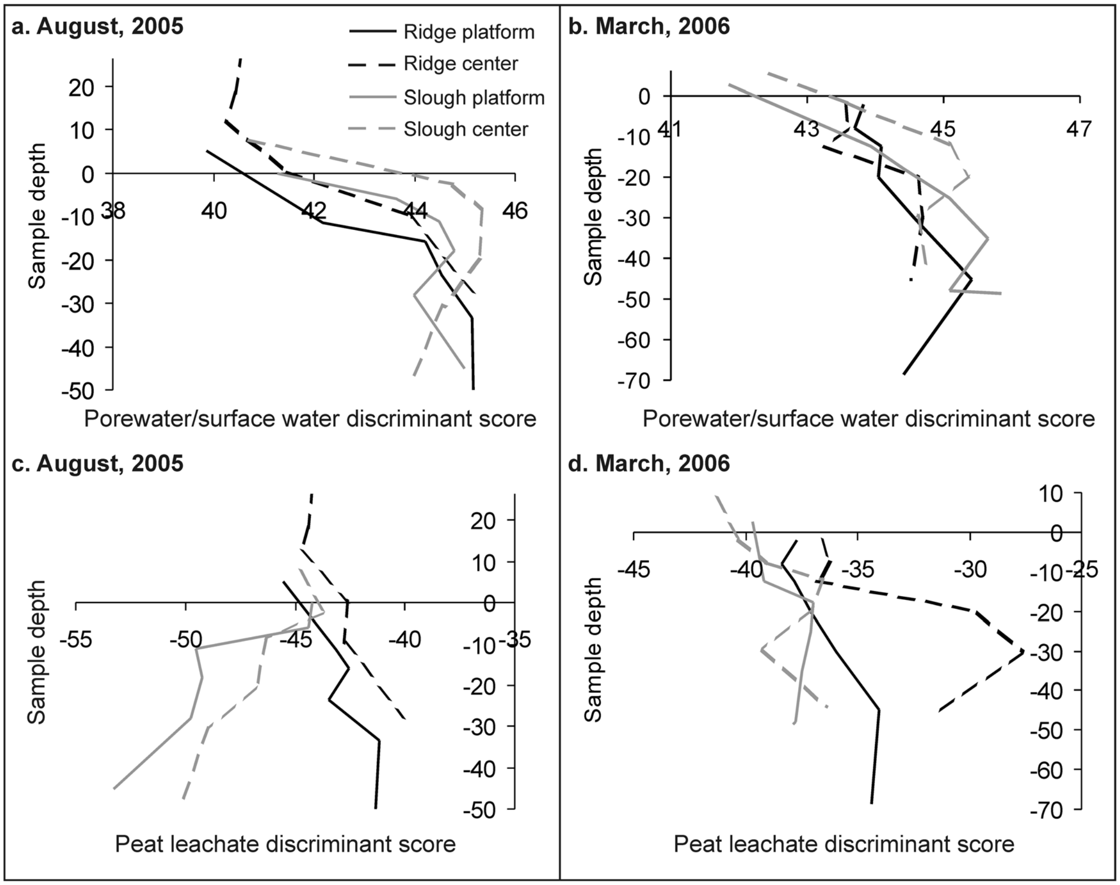

**Figure 5.** Vertical profiles of discriminant scores from peat leachate and pore water/surface water discriminant analyses among ridge and slough sites sampled in duplicate during (a, c) August 2005 and (b, d) March 2006. Each discriminant score profile was obtained from a single sample profile. Samples were acquired from the ridge and slough ends of an 11 m platform at site WCA-3A-5 and from more central locations within the ridge and slough, spaced ~50 m apart.

surface water discriminant scores expanded, mirroring drydown-related changes in DOC concentrations (Figure 2). When water levels again rose following the drydown, the zone of low pore water/surface water discriminant scores contracted. However, higher values of SUVA (Figure 2b) and peat leachate discriminant scores (approaching the mean peat leachate discriminant score of vegetation leachates: −23.4 ± 9.07) and lower values of fluorescence index accompanied the pulse of high DOC that occurred during this time, reaching more extreme values in the ridge than in the slough. Hurricane effects were most prominent in the pore water/surface water discriminant score data set and the fluorescence index data set. Immediately following the storm, fluorescence index declined in both ridge and slough, while peat leachate discriminant scores increased. These intermediate values of fluorescence index and peat leachate discriminant scores persisted until the 2006 rewetting event.

### 4.5. Variability in Peat Leachate Quality Along a Ridge/Slough Transect

[27] Across the small spatial scales of the ridge/slough coring transect, peat leachate discriminant scores had more statistical power to resolve gradients in surface organic matter provenance than any other DOM quality metric (spectral slope, SUVA, fluorescence index) (Table 3). Peat leachate discriminant scores of leachates from cores along the transect were qualitatively correlated to vegetation distribution (Figure 6). However, small-scale variability of

**Table 2.** XAD8/XAD4 Column Fractionation Results

| Sample | Sample Location | Julian Day | Hydrophobic Organic Acids (%) | Hydrophobic Organic Neutrals (%) | Hydrophilic Organic Matter (%) | Transphilic Acids (%) | Transphilic Neutrals (%) |
|---|---|---|---|---|---|---|---|
| Ridge | surface water | 223–2005 | 42 | 15 | 19 | 16 | 2 |
| Slough | surface water | 223–2005 | 41 | 18 | 17 | 15 | 3 |
| Ridge | −69 cm | 12–2006 | 52 | 8 | 14 | 19 | 0 |
| Slough | −49 cm | 12–2006 | 50 | 6 | 15 | 21 | 0 |

**Table 3.** Significance of the Difference Between Ridge and Slough Peat Core End-Member Groups

| DOM Quality Metric | $t$ | Degrees of Freedom | $p$[a] |
|---|---|---|---|
| SUVA | −3.721 | 34.91 | 0.0007* |
| Fluorescence index | 2.045 | 42.85 | 0.0470* |
| Spectral slope (200–250 nm range) | 2.469 | 33.84 | 0.0188* |
| Spectral slope (250–300 nm range) | 2.142 | 44.95 | 0.0376* |
| Spectral slope (350–600 nm range) | 1.751 | 47 | 0.0865 |
| Peat leachate discriminant score without SUVA | −12.64 | 46.74 | <0.0001* |
| Peat leachate discriminant score with SUVA | −12.61 | 46.99 | <0.0001* |

[a] Asterisks denote significant results.

discriminant scores within vegetation communities was also apparent. For example, the F, G, and H core sites had nearly identical *Cladium* densities, yet site H had a discriminant score higher than those of sites F and G by about 44% of the total range. Conversely, site E, which contained a considerably lower *Cladium* density, had a discriminant score approximately equal to those of sites F and G.

## 5. Discussion

[28] One of the goals of this study was to demonstrate a new technique for deconvolving environmental gradients in redox potential and DOM provenance from fluorescence spectra. Multiple lines of evidence suggest that this objective was accomplished through application of discriminant

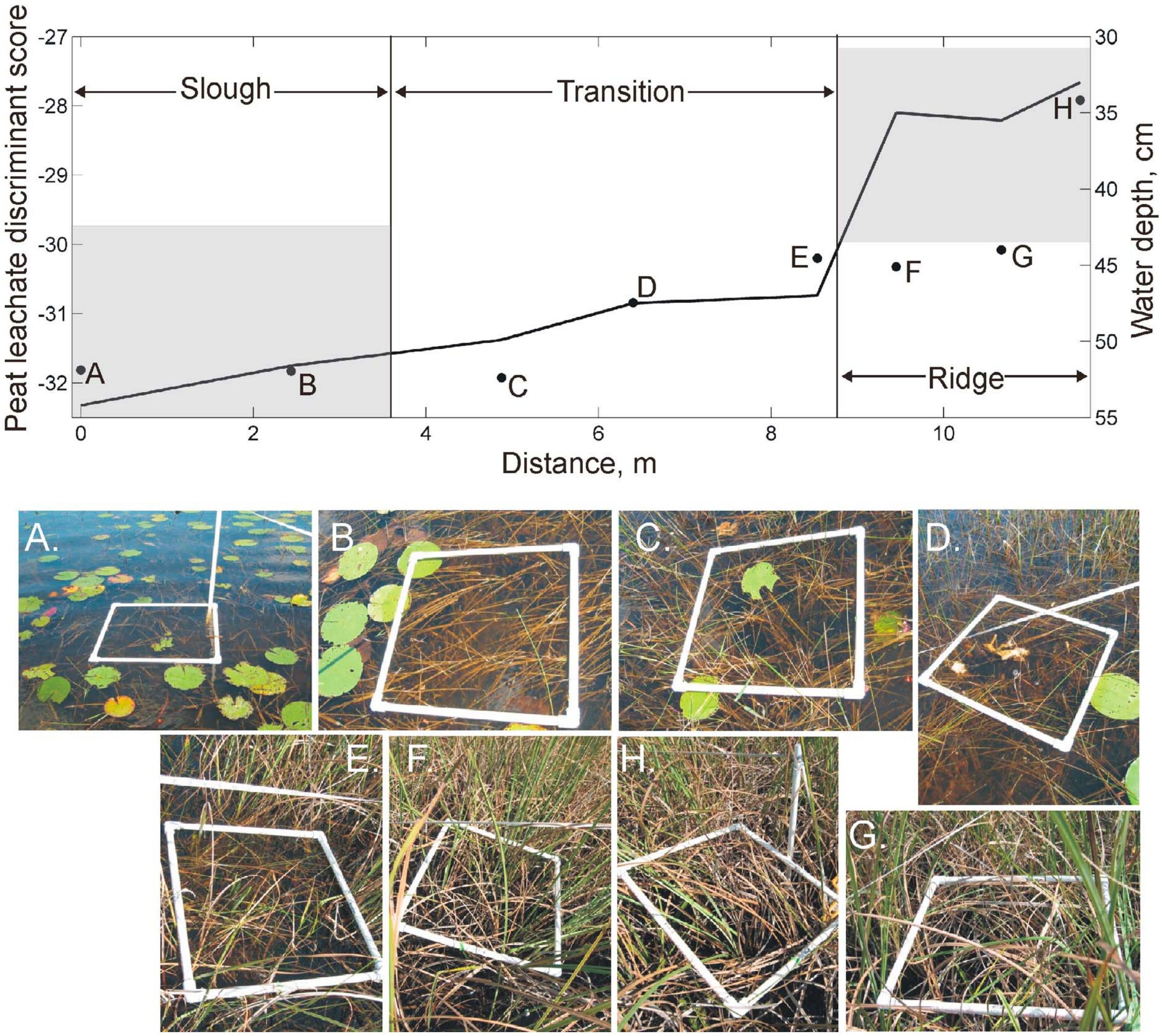

**Figure 6.** Peat leachate discriminant scores for surface peat samples and vegetation distribution along a ridge/slough transect. Local water depths, in centimeters above the peat surface, are inversely related to the peat topography along the transect and are thus plotted on an inverted axis. Shaded regions bracket the range of discriminant scores for replicate peat core samples acquired within ridge and slough centers in October 2006. Vegetation composition corresponding to coring locations is as follows: very open, sparse *Nymphaea odorata* and *Eleocharis* spp (site A); *Nymphaea* and *Eleocharis* (sites B and C); *Eleocharis*, sparse *Nymphaea*, near edge of *Cladium jamaicense* zone (site D); transitional, with *Cladium*, sparse *Eleocharis*, *Crinum americanum*, and *Panicum hemitomon* (site E); dense *Cladium* (sites F, G, and H).

analyses to PARAFAC model results, which enabled resolution of DOM dynamics that were not immediately apparent from other spectral indices, or that were poorly delineated (Table 3).

[29] Our interpretation of the pore water/surface water discriminant score gradient as a redox potential gradient is consistent with oxygen electrode measurements (Table 1), the strong influence of the resolved redox-reactive quinone moities on score values, and the way in which oxidized moities decrease in abundance with sample depth while reduced moities increase (Figure S3). Seasonal changes in discriminant scores suggest that water level was a dominant control on redox potential (Figure 2e), consistent with previous findings in the Everglades [*Thomas et al.*, 2009] and other environments [*de Mars and Wassen*, 1999]. Likewise, the long-term redox potential study of *Thomas et al.* [2009] found that Everglades redox potentials remain roughly constant to a depth of about 10 cm beneath the peat surface but decrease at greater depth, consistent with the vertical gradients in the pore water/surface water discriminant scores.

[30] In the peat leachate discriminant analysis, redox-reactive quinone moieties resolved by PARAFAC contributed to discriminant scores in a way that removed the confounding influence of redox potential in the provenance signal without contributing to the ridge/slough differences in peat leachate discriminant scores (see Text S1). To first order, ridge discriminant scores mirrored the salient features in the fluorescence index record, supporting the interpretation of the discriminant score gradient as a DOM provenance gradient. Both data series were consistent with an interpretation of the more “slough-like” end-member as having more of a microbial influence and the “ridge-like” end-member as having more of a higher plant influence [*McKnight et al.*, 2001], which is in turn consistent with vegetation distributions.

[31] Even so, discriminant scores were more consistent with other metrics of DOM provenance than was fluorescence index, which has significant correlations with redox-reactive quinone moieties (Figure S3 [*Cory and McKnight*, 2005; *Fellman et al.*, 2009]). For instance, the substantial change in the peat leachate discriminant scores in the slough (where redox gradients are steep) from predrydown to postdrydown (Figure 2d) was consistent with the SUVA record (Figure 2b) but undetected in fluorescence index (Figure 2c). Even in the relatively well-aerated surface water and on the ridge, the peat leachate discriminant score reflected this change in DOM quality, while the fluorescence index did not.

[32] Likewise, XAD8/XAD4 column fractionation results were more consistent with the peat leachate discriminant scores than with fluorescence index. Fractionation results from Julian day 12–2006 reflected strong similarities between deep ridge and slough pore water, and the corresponding difference between the ridge and slough peat leachate discriminant scores, normalized by the range in discriminant score values, was 0.15. However, the normalized difference in fluorescence index was twice as large (0.31). Meanwhile, fractionation results indicated substantial differences between slough pore water from that date and slough surface water from Julian day 223–2005 (Table 2). While the corresponding normalized difference in peat leachate discriminant score was 0.18, the normalized difference in fluorescence index was only 0.12. Thus, both the peat leachate and pore water/surface water discriminant scores were uniquely suited for discerning real patterns in DOM dynamics across multiple environmental gradients to a level of accuracy necessary to draw inferences about ecosystem function and landscape-forming processes.

## 5.1. Drivers of Temporal Variability in DOM Quality

[33] During the 2005 wet season, when floating periphyton mats were present in sloughs, peat leachate discriminant scores and fluorescence index patterns reflected a DOM pool strongly influenced by microbial processes. However, after hurricane Wilma eliminated the periphyton mats, peat leachate discriminant scores and fluorescence indices reflected a less microbial DOM source, likely a combination of macrophytes and remnant free microbes or periphyton attached to plant stems, the benthos, or detrital floc. During the 2006 rewetting event, this remnant microbial signal also disappeared, and peat leachate discriminant scores more characteristic of peat dominated. The shift accompanied a release of high-SUVA (i.e., aromatic [*Weishaar et al.*, 2003]) DOC from the upper 30–50 cm of the peat that had been previously unsaturated (Figure 2b).

[34] A third shift in DOC source occurred after Julian day 240–2006, when surface and near-surface peat leachate discriminant scores approached the mean peat leachate discriminant score of Everglades vegetation leachates, while DOC concentrations decreased (Figures 2a and 2d), implying a shift in the dominant DOM source to macrophytes. Unlike the 2005 wet season, microbial production of DOM by slough periphyton remained very low, reflecting the continued absence of periphyton mats. Because the DOC leached from fresh *Cladium jamaicense* detritus on ridges is an order of magnitude greater than that leached from *Eleocharis cellulosa* detritus in sloughs [*Davis et al.*, 2006], the relative importance of ridges and sloughs as sources DOM and nutrient production can fundamentally shift when slough periphyton mats are absent.

[35] Previous studies have shown that hurricanes cause a release of nutrients from soils and organic detritus in wetlands that causes short-term (weeks to months) eutrophication and increased biochemical oxygen demand [*Hagy et al.*, 2006; *Mallin and Corbett*, 2006; *Tomasko et al.*, 2006; *Williams et al.*, 2008]. Our study shows that although Hurricane Wilma may have caused a slight decrease in ridge redox potential that persisted for a maximum of one month (Figure 2e), the hurricane was not associated with a pulse release of DOC; instead, the drydown/rewetting cycle was a more dominant influence on DOC concentrations. However, through its effects on the periphyton mat and DOC quality, the hurricane had a substantially more long-term (>1 year) impact on carbon cycling, with additional repercussions for nutrient cycling and ecosystem processes. Periphyton communities, which typically form the base of Everglades food webs [*Browder et al.*, 1994], are sites of intense autotrophic and heterotrophic activity. Water column microbes have the shortest uptake timescale for phosphorus of Everglades biota [*Noe et al.*, 2003]. Elimination of periphyton mats and a shift to more refractory organic substrate may thus simultaneously reduce heterotrophic activity and increase phosphorus spiraling length scales. In this way, hurricanes may

disrupt carbon and nutrient cycling in wetlands for longer periods of time than previously recognized.

### 5.2. DOM Spectral Characteristics as an Indicator of Hydrologic Mixing

[36] Because distinct OM sources in the Everglades persisted for several months (Figure 2d), peat leachate discriminant scores could be used as a semiconservative tracer of flow and mixing. Indistinguishability of the peat leachate discriminant scores within surface water suggested that surface water was well mixed between ridge and slough. Rapid transitions (nearly vertical contours, Figure 2d) in peat leachate discriminant score profiles following shifts in DOM provenance in surface water implied a short (1 month or less) timescale of vertical flushing. Relative to the ridge, deep (>40 cm) pore water mixing timescales within the slough were long, indicated by the persistence of distinct source signals (e.g., prehurricane periphyton signal, Figures 2c and 2d) at depth after the dominant surface water source had shifted. Lateral pore water mixing also occurred on a slower timescale than surface water mixing, evident in the distinctness of discriminant scores in ridge and slough pore water, particularly during the dry season, when the surface water connection was absent (Figures 2d and 5d).

### 5.3. Detection of Organic Matter Diagenesis

[37] General similarity between pore water/surface water discriminant score gradients and DOC gradients implied that vertical redox potential gradients exerted a dominant control on spatiotemporal variations in organic matter decomposition in the Everglades. In the 2005 posthurricane wet season, when zones of low DOC concentrations and low pore water/surface water discriminant scores penetrated deeper into the ridge subsurface than the slough subsurface, stronger peat leachate discriminant score gradients were found on the ridge, suggesting that diagenetic processes were faster on the ridge than in the slough. As flushing transported DOC that originated within surface water downward, labile compounds were removed in the relatively aerobic ridge subsurface, leaving the remnant DOM pool preferentially enriched in refractory components (as in the works of *Wickland et al.* [2007] and *Lapworth et al.* [2009]) and shifting pore water discriminant scores closer to those of peat. Ridge/slough differences in diagenetic processing tied to redox gradients were not apparent in the fluorescence index data set (Figure 2c), possibly due to spectroscopic confounding, but were consistent with the principal component analysis (Figure 4).

### 5.4. Implications of DOM and POM Dynamics for Ridge and Slough Landscape Processes

[38] Consistent with previous conceptual models [*Larsen et al.*, 2007], our results suggest that both autogenic and allogenic processes affect the topographic and vegetation differentiation of the ridge and slough landscape. Pore water/surface water discriminant score trends suggested that near-surface redox potential gradients are steeper in slough than in ridge (Figure 2e and Figures 5a and 5b), with implications for differences in the rates of redox-regulated diagenetic processing and decomposition. Since pore water and surface water remains well mixed laterally and vertically during the wet season (Figure 2d), the dominant contributors to ridge-slough differences in autogenic peat accretion rates are likely to be redox potential and the lignin content, nutrient content, microbial enzyme activity, and rate of supply of the detrital source material [*Graneli and Solander*, 1988; *DeBusk and Reddy*, 1998; *Penton and Newman*, 2007, 2008]. In the managed Everglades system, landscape differentiation could be reinforced by establishment of conditions that decrease the existing difference in redox potential between ridge and slough and raise slough redox potentials. This change would decrease the net rate of peat accretion within sloughs and the tendency toward slough infilling [*Larsen et al.*, 2007].

[39] Analysis of the peat leachate discriminant score trends along a ridge-slough transect of peat cores (Figure 6) suggested some allochthony in the origin of peat at transitional elevations. The elevated discriminant score of site E (transitional vegetation) compared to discriminant scores of comparable vegetation communities is consistent with gravitational transport of ridge detritus down the topographic gradient of the transition zone; simultaneously, the depressed discriminant scores of sites F and G relative to other dense *Cladium* sites is consistent with hydraulic transport of slough material to the *Cladium* zone at the ridge edge. Ridges can expand sloughward through gravity-driven spreading of flocculent *Cladium* detritus from higher elevations to lower elevations, unless the detritus is entrained by flow before contributing to peat accretion, transported further downstream, and eventually redeposited within dense sawgrass [*Larsen et al.*, 2007, 2009]. The redeposited detritus would have a more slough-like signal than native ridge detritus, due to the entrainment of particles from within sloughs as well as the transition zone. Our observations provide preliminary support for the redistribution of detrital matter at the 5 m scale in the vicinity of ridge-slough transition zones in a way that promotes long-term lateral ridge stability and reinforces the topographic distinctness of ridge and slough.

[40] The peat core transect analysis is broadly consistent with other studies of POM transport in the Everglades that employ a variety of molecular markers and biomarker proxies. Sampling at 10 m intervals across a ridge to wet prairie transect, *Saunders et al.* [2006] found that the $P_{aq}$ (an n-alkane based biomarker proxy that differentiates between organic matter from submerged and emergent vegetation) of shallow peat samples is significantly correlated with local vegetation community and biomass, which was also consistent with the larger-scale $P_{aq}$ study of *Mead et al.* [2005]. As in our study, *Neto et al.* [2006] found that although floc populations predominantly have a local origin, some decoupling exists in provenance-related molecular markers between the floc and underlying peat, possibly evidencing limited hydrodynamic transport.

### 5.5. Limitations of Approach

[41] In this analysis, we elected to fit our EEMs to a previously validated PARAFAC model [*Cory and McKnight*, 2005] primarily for the enhanced interpretability of the results (i.e., the known relationship between the resolved fluorescent components and redox-reactive quinone moieties, which aided in understanding how the discriminant analyses deconvolved redox and provenance gradients (Text S1)). The relatively small size of our data set

(233 samples) compared to others for which the full version of PARAFAC has been successfully implemented [e.g., *Cory and McKnight*, 2005; *Stedmon and Markager*, 2005], also contributed to this decision. Broad consistency between our results and multiple other measured and reported indicators of redox potential and provenance gradients in this environment provide confidence in our use of this technique. However, the technique presents several limitations.

[42] Most importantly, rigorous comparison between the full version of PARAFAC and the 13-component Cory/McKnight model showed that the latter tends to have the highest residuals in the region most sensitive to the fluorescence of amino acids and polyphenols [*Fellman et al.*, 2009]. In other words, the fluorescent signature of proteinaceous and phenolic compounds tends to be unique across different environments. These compounds are typically highly reactive, with proteinaceous compounds prone to rapid microbial uptake and phenolic compounds to photooxidation [*Scully et al.*, 2004]. Because the Cory/McKnight PARAFAC model has limited ability to resolve these compounds across different environments, approaches that employ this technique have limited ability to detect photodegradation processes or the initial, most rapid stages of DOM diagenesis. In the Everglades, these limitations may have contributed to the lack of a strong vertical gradient in peat leachate discriminant scores between surface water and near-surface pore water. Expectedly, labile compounds initially leached from freshly wetted detritus, particularly during rewetting events, would undergo rapid uptake by microbes in the surface water and near-surface peat before penetrating to deeper levels of the subsurface [*Maie et al.*, 2005, 2006b]. Although beyond the scope of the present study goals, future implementation of our discriminant analysis approach using results of a full PARAFAC model could better resolve early diagenesis and photodegradation processes.

## 6. Conclusions and Implications

[43] Recent advances in DOM fluorescence spectroscopy have resulted in rapid and relatively cost-effective options for assessing DOM quality that have enabled detection of processes important for carbon cycling that cannot be resolved from bulk DOC measurements. In our study, the information contained within DOM fluorescence spectra revealed significant shifts in DOM provenance and lability that occurred not just in response to a hurricane disturbance but also as a result of seasonal changes in water levels and leaching from vegetation and detritus. Changes in vertical redox potential gradients that affected DOM diagenesis also occurred over these monthly timescales, adding to a growing awareness of the large degree of temporal variability in DOM signal that many rivers, wetlands, and coastal zones exhibit worldwide [*Spencer et al.*, 2007; *Hernes et al.*, 2008; *Jaffe et al.*, 2008; *Spencer et al.*, 2008].

[44] It is now common practice to resolve large-scale spatial changes in DOM provenance and redox potential using fluorescence index and/or spectroscopic indices constructed from equally weighted PARAFAC model component concentrations (e.g., redox indices [*Miller et al.*, 2006]). However, at small spatial scales (e.g., between adjacent vegetation communities), changes in redox potential can spectroscopically confound source signatures, and vice versa, making trends in simple spectroscopic indices difficult to interpret. We found that discriminant analyses using PARAFAC model results, fluorescence index, spectral slope, and SUVA had the greatest power to deconvolve gradients in redox potential and DOM provenance in the ridge and slough landscape, providing insight into hydrologic mixing, effects of a hurricane, relative rates of OM decomposition, and POM redistribution to an extent not possible using simple spectroscopic indices alone. Because its sensitivity, fluorescence spectroscopy, combined with appropriate statistical postprocessing, could be used in concert with other biomarker proxies as a performance indicator in the Everglades to determine whether POM transport, redox gradients, and diagenetic processes are changing in a way that is favorable to landscape restoration. In ecosystems throughout the world, the sensitivity, relative rapidity, and cost-effectiveness of fluorescence measurements combine to make fluorescence spectroscopy an excellent tracer of disturbance effects on carbon cycling and of the effectiveness of restoration and management strategies.

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