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Dissolved Organic Matter Biogeochemistry Along a Transect of the Okavango Delta, Botswana

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Abstract Biogeochemical processing of dissolved organic matter (DOM) in aquatic environments can alter its chemical quality and its bioavailability to the microbial loop. In this study, we evaluated the relative importance to DOM character of allochthonous and autochthonous DOM inputs and photo-degradation in a large, pristine wetland, the Okavango Delta of Botswana. We performed an intensive spatial sampling of surface water and analyzed for chemical and physical parameters (pH, conductivity, dissolved oxygen saturation, temperature, and channel depth), dissolved organic matter (DOM), and particulate organic matter (POM). We used UV–vis absorbance, fluorescence spectroscopy, and parallel factor analysis of excitation emission matrix data (EEM-PARAFAC) to characterize DOM. Our findings from principal component analysis (PCA) show downstream changes in DOM chemistry to be dominated by photo-degradation, suggesting that DOM in the Okavango Delta is transformed photo-chemically in shallower downstream reaches after being mobilized from the permanent swamp and seasonal floodplains. Additionally, we found that the PARAFAC model developed for the Everglades, a large, anthropogenically-altered wetland in North America, was well suited to tracking DOM dynamics in the Okavango Delta and may be useful for characterizing DOM in other sub-tropical, seasonally flooded wetlands.

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Introduction

Dissolved organic matter (DOM) is found in all natural waters and varies in concentration and chemical character depending on the biogeochemistry of a system. DOM can be produced within a water body (e.g., autochthonous plankton and microbial exudates) or can be transported from the surrounding land area (e.g., allochthonous DOM leached from terrestrial biomass and soils). In flood pulsed wetlands, DOM concentrations can increase by two-fold or more as organic matter from dry or frozen soils and senescent vegetation is flushed into the aquatic system with surface runoff water or as a result of overland flow through a system of floodplains (Qualls and Richardson 2003; Mladenov et al. 2005; Fellman et al. 2009a; Miller et al. 2009). Once in the system, DOM is an important component of wetland biogeochemistry that can provide a substrate for microbial growth (Kalbitz et al. 2003; Wiegner and Seitzinger 2004), form complexes with metals (Yamashita and Jaffé 2008), and absorb light (Zafiriou et al. 1984; Lou and Xie 2006). Thus, understanding the DOM dynamics of an aquatic ecosystem gives insights into the dominant biogeochemical processes in a water body.

Although recent studies based on DOM characterization have begun to clarify the processes driving the biogeochemistry of wetlands, the linkages between DOM source materials and

their cycling within wetland ecosystems is still not well understood and may be important with regard to climatic shifts (Mitsch et al. 2010). A comprehensive study of DOM optical properties within the greater Florida Everglades ecosystem has been instrumental in understanding DOM biogeochemistry within this large, pulsed wetland (Yamashita et al. 2010). Yamashita et al. (2010) found that DOM fluorescence characteristics could be used to track recalcitrant, soil-derived, organic matter from the northern, peat-dominated, anthropogenically influenced areas into the southern, less impacted areas of Everglades National Park. In the Okavango Delta, another large tropical wetland, Mladenov et al. (2005) measured water chemistry and used optical analyses to show that the annual flood "flushed" DOM with terrestrial plant origins into the Delta where DOM was most likely photo-degraded and microbially processed before being sequestered in groundwater (Mladenov et al. 2007b). Subsequently, Mladenov et al. (2007a) studied isolated fulvic acids from the Okavango Delta using EEM-PARAFAC, ^{13}C stable isotopes, and ^{13}C NMR analysis to show that these techniques were able to distinguish fresh DOM from photo- and bio-degraded organic matter. However, no study to date has performed a spatial assessment in the Okavango Delta in which DOM optical properties measurements have been paired with a detailed suite of chemical characteristics during the seasonal flood to determine drivers for DOM chemical character.

In order to better understand how DOM is transformed in wetland ecosystems and how local anthropogenic activities and climate change will influence wetland DOM dynamics, large geographically scaled studies based in relatively pristine and unaltered wetlands are needed. In this study, we present comprehensive results from the Okavango Delta, a meso-oligotrophic wetland located in northwestern Botswana that is relatively pristine (Shunthirasingham et al. 2010), with no significant water diversions, dams, or impoundments within or upstream of it. As such, the Okavango Delta offers an opportunity to study DOM dynamics in a wetland with a flood-pulse dominated hydrology (Junk et al. 2006) without the confounding effects of anthropogenic impacts such as pollution, hydrologic modifications, and land use change, which were shown to have overprinting effects on DOM quality (Baker 2002; Williams et al. 2010; Zhuo et al. 2010; Yamashita et al. 2011).

The main goal of this study was to understand the primary drivers for changes in DOM character (e.g., DOM source and transformation) within the Okavango Delta along a complete transect of the wetland. Results presented here, for what may be considered a large wetland reference site, may be important for understanding natural DOM biogeochemistry in sub-tropical and tropical wetlands, which support much of the world's biodiversity and suffer from a variety anthropogenic pressures including water diversion, land-use change, pollution, and climate change.

Site Description

The Okavango Delta is a large wetland located in semi-arid northwestern Botswana (Fig. 1). It is subject to an annual flood event generated by water of the Okavango River flowing south from Angola through Namibia. During the flooding event, the inundated area in the Delta expands in size from the annual minimum of 3,500–6,000 km^2 to the annual maximum of 9,000–13,000 km^2 (Gieske 1997; McCarthy et al. 2003). During our campaign (August 2010) peak flood had passed all sampling points except for the last four (those downstream of 380 km) by the final date of sampling. Differences in hydro-period resulting from seasonality of inundation are manifested mostly in a longitudinal direction (i.e., upstream-downstream rather than channel-floodplain margin) and are often schematized in the form of hydro-ecological units, referred to as hydrotones (Mladenov et al. 2005), including the Panhandle (approximately 0 to 130 km), permanent swamp (approximately 130 to 265 km), seasonal floodplains (approximately 265 to 340 km), and occasional floodplains (approximately 340 to 390 km) (Gumbricht et al. 2004). The boundaries of these units are not well defined, particularly in view of the long-term variability of inundation in the system with gradual expansion of the size of flood. Thus, migration of these units in the downstream direction as has been observed in the last 15 years (Wolski unpublished). The seasonal swamp upstream of 371 km is a protected area separated by a buffalo fence from the more anthropogenically- and agriculturally-influenced downstream areas, which also have cattle grazing. Only 2% of inflowing water leaves the wetland through terminal rivers; the remainder evaporates to the atmosphere through three pathways: from open water, through aquatic vegetation or from shallow groundwater (Wolski et al. 2006). See Mladenov et al. (2005) for a very extensive description of the wetland system and Mmualefe and Torto (2011) for a review of water quality in the Okavango Delta.

Methods

Field measurements of dissolved oxygen (DO) were collected with a YSI 550A meter; pH measurements were made with an Accument AP85 meter; conductivity (EC) and temperature measurements were made with a YSI 30 meters. Turbidity was measured using a LaMatte 2020e meter calibrated with a 1 NTU standard. Mid-channel depth was measured using an ultrasound sounding device. DO, pH, EC, channel depth, and temperature measurements were collected every ~2 km down the Okavango-Jao-Boro (BJO) river channel over the course of 4 days (Figs. 2 and 3).

Surface water was collected by bucket from approximately 0.2 m depth and immediately syringe-filtered through a pre-combusted and pre-rinsed Whatman GF/F filter (~0.7 μm
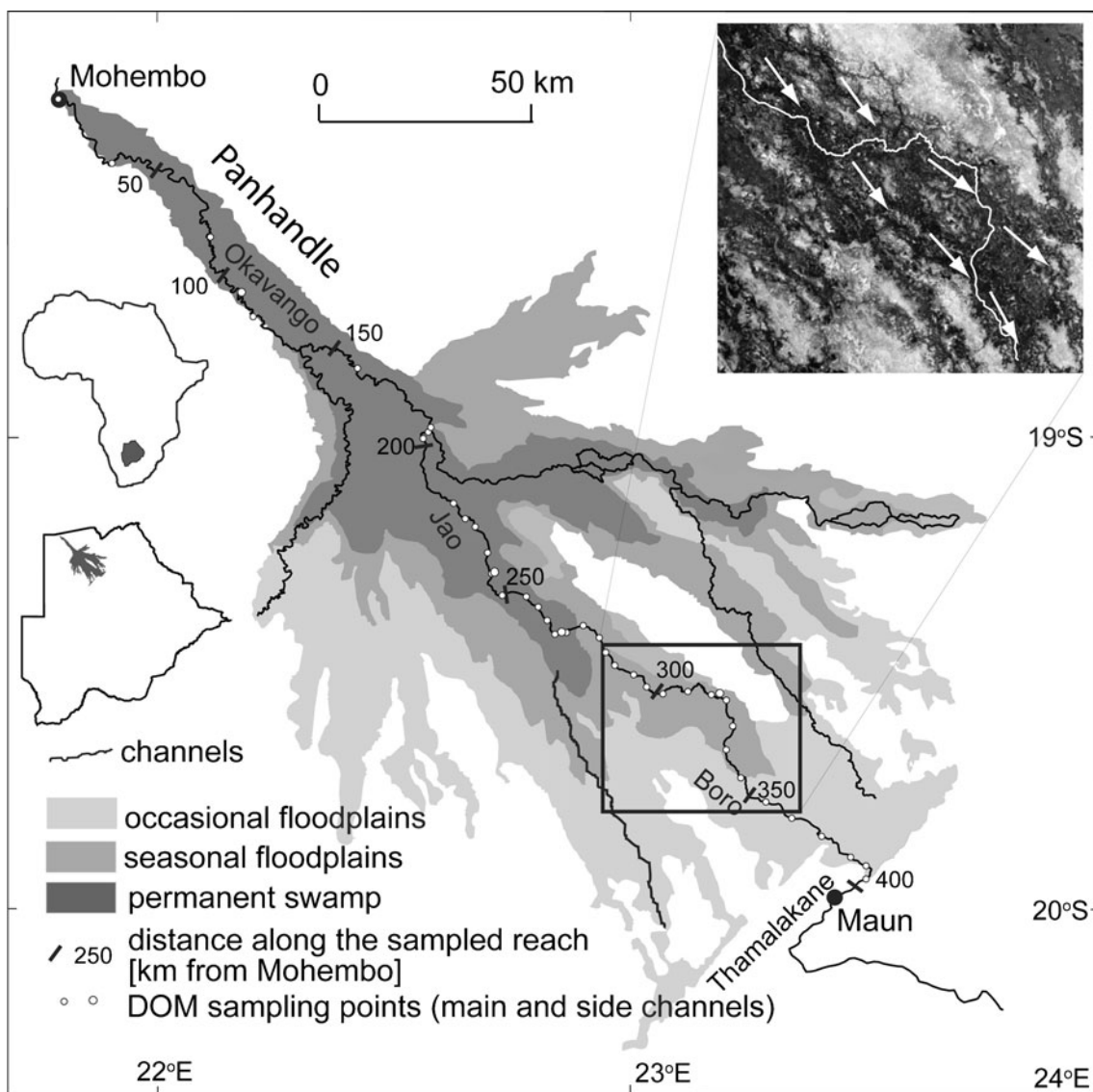
Fig. 1 Map showing the Okavango Delta, Okavango-Jao-Boro River reaches, and approximate locations of the Panhandle, permanent swamp, seasonal floodplains, and occasional floodplains hydrotones. White dots represent sample locations. Larger white dots are samples collected outside of the main stream channel. Hash marks mark distance downstream of Mohembo every 50 km. Inset is a magnification of a change in channel direction where water chemistry changes

nominal pore size) and stored in pre-cleaned and rinsed 60 mL brown plastic bottles. Replicates were not collected. DO, pH, EC, channel depth, and temperature measurements were collected at every site where water samples were collected. Water samples collected outside of the main stream channel were from lagoons and small channels accessible by boat from the main channel. Samples were kept on ice until shipment, and then about 24 h without chilling while in transport, and finally refrigerated at ~4°C until analysis. Samples were analyzed for fluorescence within 2 weeks of collection. DOC measurements were made within 3 weeks at the Southeast Environmental Research Center's water quality lab at Florida International University with a Shimadzu TOC-V CSH TOC analyzer using a high temperature combustion method. UV–vis absorbance

scans were collected on a Varian Cary 50 Bio spectrophotometer and collected over a range of $\lambda=200$ nm to $\lambda=800$ nm in a 1-cm quartz cuvette. A blank scan (Milli-Q water) was subtracted from each sample spectrum and spectra were baseline normalized using the average absorbance between 700 and 800 nm.

Fluorescence EEMs were collected on a Horiba Jobin Yvon SPEX Fluoromax-3 spectrofluorometer using the methods of Maie et al. (2006) and Yamashita et al. (2010). Briefly, EEMs were collected over an excitation wavelength (λ_{ex}) range of 240–455 nm with an increment of 5 nm and an emission range of $\lambda_{ex}+10$ nm to $\lambda_{ex}+250$ nm with an increment of 2 nm in a 1 cm quartz cuvette. The excitation and emission slit widths were set to 5.7 nm and 2 nm, respectively. Fluorescence scans were collected in signal/reference ratio mode with an
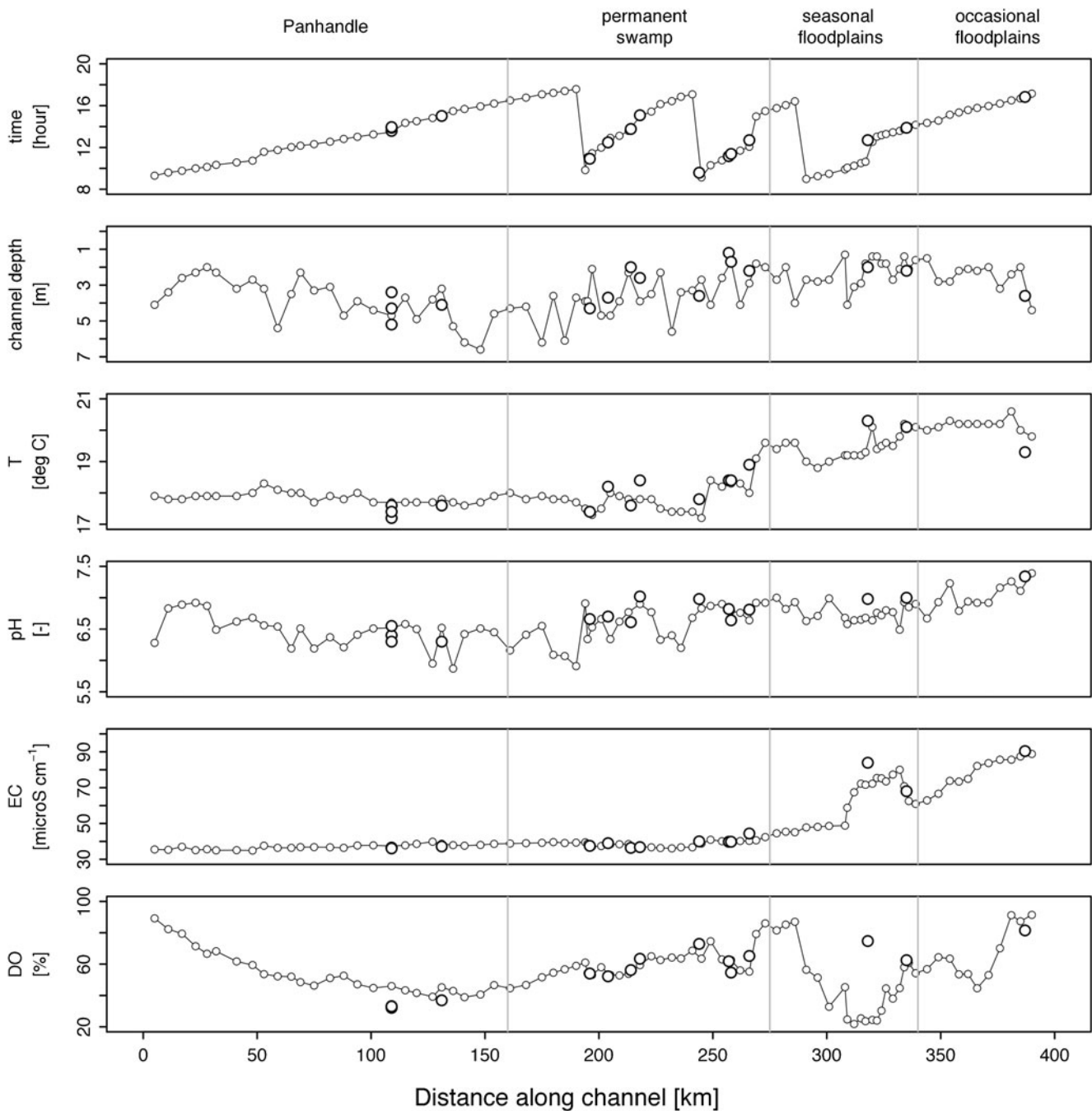
Fig. 2 Stream channel and water chemistry characteristics along the Okavango-Jao-Boro River transect. From top to bottom the panels represent: time of day for each sample collected, channel depth, temperature, pH, conductivity, and % dissolved oxygen. The x-axis is the distance downstream from Mohembo. The large circles represent samples taken adjacent to the main channel

integration time of 0.25 s and reported in quinine sulfate units (QSU). EEMs were corrected for instruments optics and inner-filter effects according to Ohno (2002), Raman normalized, and blank subtracted using Matlab v2009a software. EEMs were modelled using Matlab v2009a and fit to an eight component PARAFAC model described in Chen et al. (2010) and Yamashita et al. (2010) that is comprised of Florida coastal Everglades samples. The Fluorescence Index (FI), which

indicates DOM source (McKnight et al. 2001), was calculated as the ratio of the emission intensities at 470 nm and 520 nm at an excitation wavelength of 370 nm (Jaffé et al. 2008). A higher FI value (e.g., 1.8) indicates a microbial DOM source while a lower value (e.g., 1.2) indicates a terrestrial source; intermediate values indicate a mixed DOM source.

Size exclusion chromatography (SEC) analysis was performed on a Thermo Scientific HPLC system equipped with
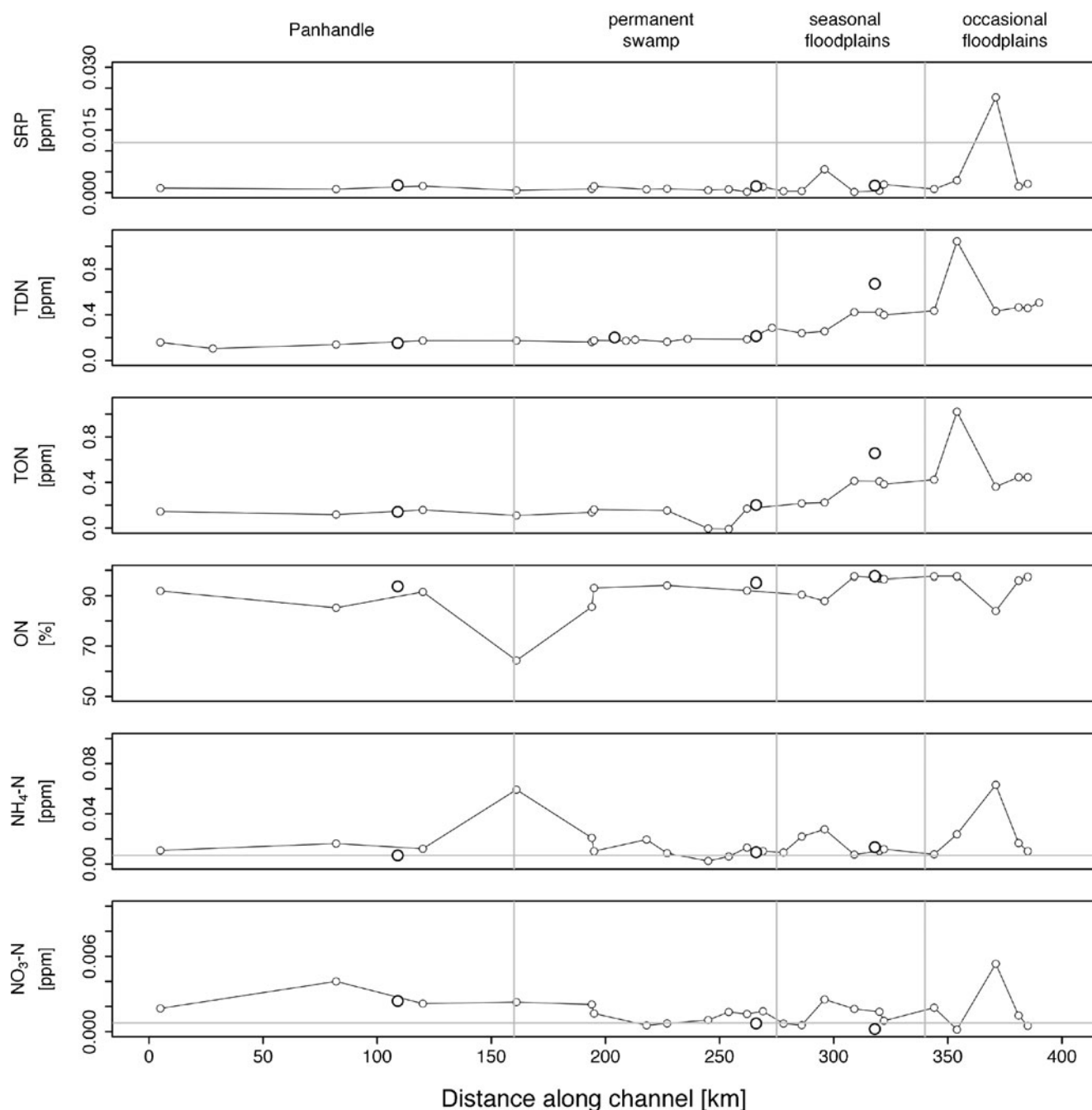
Fig. 3 Nutrient data. From top to bottom the panels show: soluble reactive phosphorus (SRP), total dissolved nitrogen (TDN), total organic nitrogen (TON),% organic nitrogen (ON), ammonia, and nitrate concentrations along the Okavango Delta transect. The x-axis is the distance downstream from Mohembo. The large circles represent samples collected adjacent to the main channel. Horizontal gray lines represent detection limits for nutrient analyses

a photodiode array (PDA Plus detector) using a method similar to Maie et al. (2004). Briefly, 100 μL of filtered water was injected onto an YMC-Pack Diol-120 column. The mobile phase, flow rate 0.7 mL min.$^{-1}$, was comprised of 0.05 M tris(hydroxymethyl)aminomethane (THAM) buffer adjusted to a pH of 7 with concentrated phosphoric acid. The UV–vis detector collected the absorbance at 280 nm. Molecular weight and polydispersity were

calculated according to Maie et al. (2004) from the sample chromatograms and standards of polystyrene (MW=1400, 4300, 6800, 13000, 36000), blue dextran, and glycine.

Statistical analysis, including principal component analysis (PCA) and Pearson correlations were determined using SPSS statistical software. Relative abundances of the PARAFAC components for each sample were entered as the variables for PCA. The PCA analysis was run on the

correlation matrix with a Varimax rotation, and eigenvalues greater than one were retained.

Results & Discussion

Water Chemistry

Electrical conductivity in the upstream permanently flooded Panhandle and permanent swamp hydrotones remained relatively stable at approximately 35 μS cm^{-1} (Fig. 2). The seasonal floodplains had the greatest variability in conductivity values, ranging from 40 to 80 μS cm^{-1} (Fig. 2). In the occasional floodplains EC increased with distance downstream, reaching the highest values measured for the BJO reach near Maun. Water temperature and conductivity increased in the seasonal and occasional floodplains relative to the upstream hydrotones while depth decreased (Fig. 2). In general, the shallower water column of the seasonal and occasional floodplains had more surface area exposed to solar radiation, higher EC, and higher temperatures.

Additionally, lateral inputs of lower (or higher) conductivity water from adjacent floodplains or parallel flow systems (i.e., anabranches with different geomorphology and lithology) can influence the conductivity of water in the channel (Cronberg et al. 1996). An extreme example of this phenomenon can be seen in the seasonal floodplains where a shift to higher conductivity occurs at approximately 307 km and conductivities return to lower values at 340 km. This pattern coincides with a bend in the channel at 300 km where the channel veers eastwards and at ~340 km where the channel comes back southwards to its original course in line with the direction observed upstream of 300 km (Fig. 1, inset). The pattern is not transient, a similar pattern of EC has been observed at this location during peak flood conditions in 1975 and during measurements made in the early 2000s (Wolski unpublished data). While various explanations of the increase in conductivity are possible, such as inflow of high-ionic strength water from an adjacent flow path with higher evaporoconcentration (i.e., greater amount of floodplain), presence of leachable chemicals in the substratum, or input from high salinity groundwater (unlikely in view of the infiltration-dominated nature of surface water-groundwater interactions in the system), the reduction in conductivity is more difficult to explain with these scenarios. The Boro channel maintains its relative coherency in the 300–340 km zone, and no significant changes in channel margin vegetation are observed. Thus, it is not likely that the reduction in EC is caused by unusually high ion uptake by vegetation or other biogeochemical processes, such as sorption to mineral surfaces. The most likely explanation is that the reduction is caused by a return of the channel to its original path, and mixing with that lower conductivity water, originating from upstream of 300 km.

DO percent saturation shows different trends than EC, depth, and temperature. The steady decrease in DO in the Panhandle, from 89% to 37% (Fig. 2), may reflect the conversion from a higher order stream, where photosynthesis exceeds respiration, to a smaller distributary channel, where increased DOM substrate supports greater heterotrophic decomposition and oxygen consumption. The decrease in DO percent saturation in the Panhandle also corresponds to decreasing POM concentrations (Fig. 2), and this shift from POM to DOM may also signal greater microbial processing of DOM with distance downstream. As the Panhandle opens up to the permanent swamp and the water column becomes shallower, light penetration increases and may support greater primary production, reflected in an increase in DO percent saturation from 39% to 75% (Fig. 2). The decrease in water flow along the river-dominated Panhandle to the permanent swamp may result in a higher settling rate of POC, and an increase in light exposure may also contribute to a reduction in POC levels through photo-dissolution (Pisani et al. 2011; Shank et al. 2011).

Downstream, the seasonal floodplains have the greatest variability in DO, with values as low as 22% and as high as 87% with a generally increasing trend along the transect (Fig. 2). Particularly low DO percent saturations were observed between 307 km and 340 km, corresponding to the previously mentioned conductivity shift and input of higher EC flood water from the northern floodplains. The low DO percent saturation in this region may indicate microbial respiration of organic matter and consequential oxygen consumption (Fig. 2).

Nutrients

Nutrient concentrations measured along the BJO provide important information about potential anthropogenic impacts. For the most part, soluble reactive phosphorus, nitrate-N, and ammonia-N concentrations in the Panhandle, permanent swamp, and seasonal floodplains are all low, and many are below the detection limit (Fig. 3). These results are consistent with previous findings for the Delta's oligotrophic to mesotrophic upstream area (Cronberg et al. 1995). At 354 km and 371 km, peaks in nutrient concentrations reveal anthropogenic influences and disturbances to the oligotrophic status of the wetland. At 371 km, peaks in SRP, ammonia-N, and nitrate-N correspond to the location of the "Buffalo fence," which is a veterinary control fence separating wildlife (north) from cattle (south), where anthropogenic activities, such as livestock grazing, may locally impact the nutrient content of the water. These peak nutrient concentrations (Fig. 3) also correspond to minima in the DO profile and a high FI value (Figs. 2 & 4). High FI values are
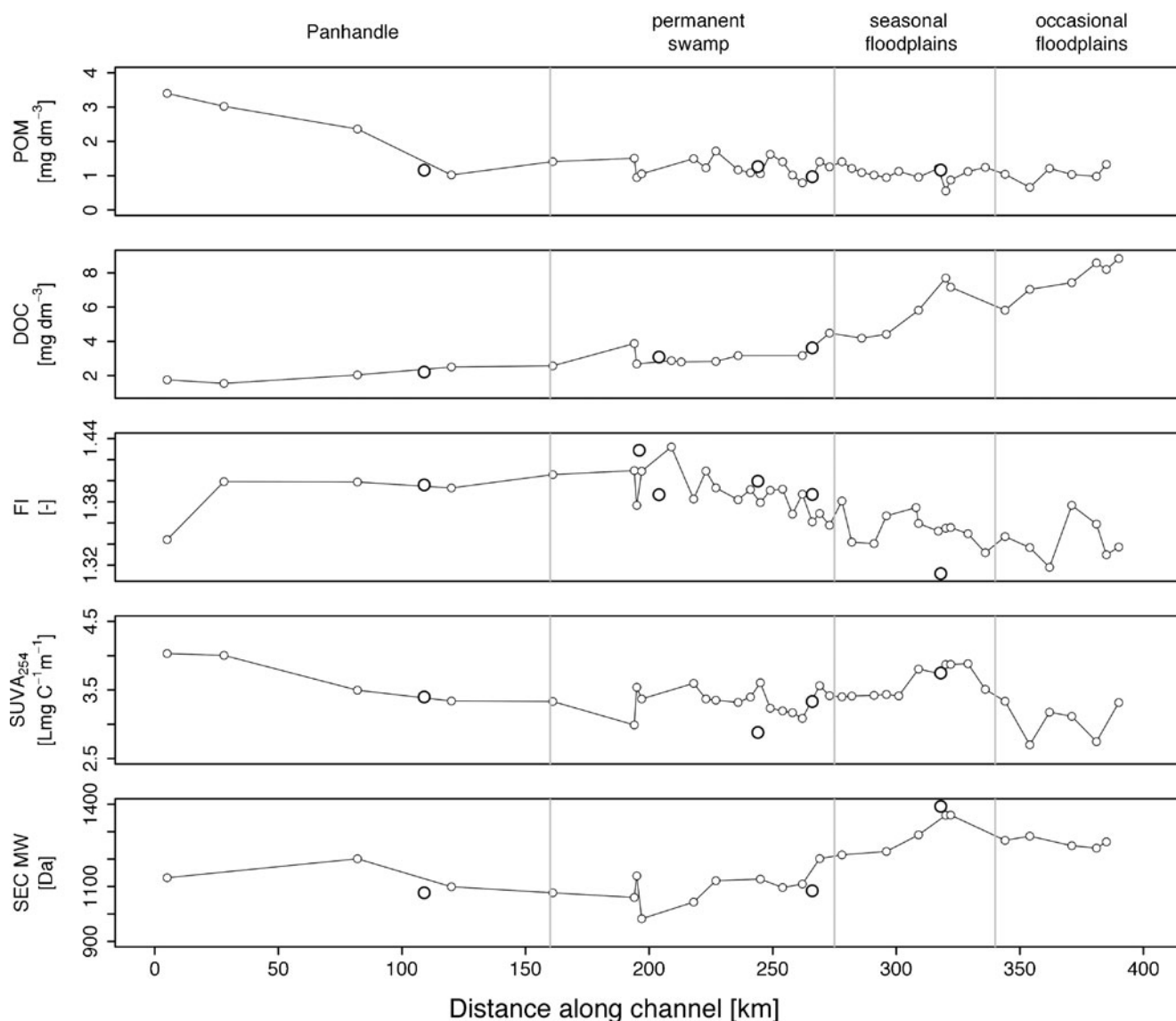
Fig. 4 Organic matter characteristics and concentration. From top to bottom the panels represent: particulate organic matter (POM), dissolved organic carbon (DOC) concentration, fluorescence index, SUVA$_{254}$, and molecular weight along the Delta transect. The x-axis is the distance downstream from Mohembo. The large circles represent samples collected adjacent to the main channel

the result of microbial contributions to the DOM pool and, taken together with the low DO and high inorganic nutrient concentrations, suggest that this point source of anthropogenic influences results in enhanced microbial activity and oxygen consumption. The 354 km sampling point, a location just downstream of a recently burned floodplain (Mosie personal communication), had peaks in TDN and TON concentrations. Nitrogen concentrations are known to be elevated in waters draining burned areas (Battle and Golladay 2003; Mladenov 2004) and are the likely cause of the TDN and TON peaks observed at this location.

Outside of the peaks at 354 km and 371 km, the total dissolved nitrogen (TDN) values measured (Fig. 3) are consistent with those reported by Mladenov et al. (2005), where they

found an increase in TDN from the permanent swamp to the seasonal floodplains. Organic nitrogen content seems to be the dominant driver of the TDN values. Our result of high percent TON, > 80% for most sites (Fig. 3), corroborate Cronberg et al. (1996) who found nutrients in the Delta to be primarily in the organic form. Because of the low inorganic concentrations of nutrients present within the Okavango Delta, photo-degradation may be an important mechanism for nutrient release to more bioavailable forms (Kieber et al. 1999).

DOM Characterization

Within the Panhandle, DOC concentrations increase slightly from 1.5 to 2.2 mg-C L^{-1} (Fig. 4). The highest seasonal DOC

concentrations measured by Mladenov et al. (2005) were at the flood front, followed by a decrease in DOC, and finally the lowest DOC concentration following the peak flood. Our samples were almost all collected following the peak flood, which means that the DOC concentrations presented here are at a seasonal low. Particulate organic matter (POM) concentrations within the Delta are between 1 and 4 mg L^{-1} (Fig. 4), which are consistent with other studies in the Okavango Delta, which suggest the low levels of phytoplankton in the water column are due to nutrient limitation (Cronberg et al. 1996). The fluorescence index values in the Panhandle, but not elsewhere, showed an increase concomitant with a decrease in the SUVA$_{254}$. Together these parameters indicate a low aromaticity, microbial DOM source along the Panhandle. These results are opposite of the trends in SUVA observed by Mladenov et al. (2005) who sampled in the second week of July. The different trends in SUVA between the two studies may be attributed to the rather large seasonal variability in channel and floodplain SUVA values (Mladenov et al. 2005), with our samples being collected in late August after the peak flood had passed and those of Mladenov et al. (2005) collected about 1 month earlier in the season. Supporting the idea that DOM character changes throughout the flood, Cronberg et al. (1996) saw a distinct decrease in DOC concentration just prior to peak flood, which may also indicate a change in DOM source, during expanding and receding flood conditions following peak flood. In the permanent swamp the DOC concentration increased slightly to 3.1 mg-C L^{-1} (Fig. 3). The FI had a decreasing trend after 195 km, indicating more terrestrial inputs at the downstream end of the permanent swamp (Fig. 4).

The seasonal floodplain hydrotone is a region of large variability in water chemistry and DOM character within the Delta. The hydrology in this region is complex with water traveling at different speeds across floodplains and within anabranches, which can have faster flows than within the main channels (Cronberg et al. 1995). The DOC concentration increased approximately three-fold within the seasonal floodplains coinciding with an increase in conductivity (Fig. 4). FI values continued to decrease with distance downstream indicating that there are more terrestrial/soil inputs into the wetland in this zone (Fig. 4). SUVA$_{254}$ values increased in the seasonal floodplains, meaning that the DOM had a more aromatic character, commonly found in more terrestrial DOM sources (Weishaar et al. 2003). This is consistent with the increase in DOM molecular weight, which reflects the presence of larger more lignaceous DOM in this river reach (Fig. 4). However, downstream of 320 km, both SUVA$_{254}$ and SEC MW decrease substantially. These decreases in aromaticity and molecular weight may reflect DOM photobleaching in the most distal reaches of the Okavango Delta.

The peak of DOC and EC between 307 and 340 km may be caused by exchange of water between channel and floodplains around the point where the channel veers eastwards, somewhat perpendicularly to the broad topographic gradient of the system. In that case, the water chemistry and DOM character primarily reflect floodplain inputs rather than the main channel water. Along with DOC and inorganic salts, nutrients, such as nitrate, ammonia, and organic nitrogen, are leached from the floodplains, which may be responsible for an increase in heterotrophic activity, indicated by a decrease in DO between 307 and 340 km (Fig. 4).

The occasional floodplains downstream of 352 km have the highest interannual variation of inundation extent among the hydrotones and are not flooded every year. Within the occasional floodplains the DOC and EC increase to the highest values in the Delta indicating that solutes are most concentrated here. The increase in FI values downstream of the Buffalo Fence (371 km) (Fig. 4) may be influenced by greater anthropogenic and agricultural inputs in this reach downstream of the restricted access area. Inputs of nutrients in this reach (Fig. 3) may fuel microbial activity, which would increase FI values. At the same time, flooding of previously dry land would be expected to contribute terrestrial plant and soil organic matter, which would decrease FI values.

Spatial Distribution of PARAFAC Components

EEM-PARAFAC analysis was carried out using an existing model (Fellman et al. 2009b) developed for the Everglades wetland in Southern Florida (Chen et al. 2010; Yamashita et al. 2010) since they are similar environments and the same instrument was used to collect the fluorescence scans. Application of this 8-component model has enhanced the understanding of DOM source, fate, and transport in the Everglades, which will help predict how land use changes and ecosystem restoration may change DOM dynamics and ecosystem function (Yamashita et al. 2010). This PARAFAC model has also been successfully used to provide information about DOM source, diagenetic state, and transport in coastal Everglades' groundwater samples (Chen et al. 2010). The Okavango Delta EEMs fit well into this model, with a residual (difference between the measured and the modelled EEM) of less than 10% of the original fluorescence intensity. Residuals were predominantly found at low excitation wavelengths, where the signal to noise ratio is lower for the instrument, and near the Raman scatter, which is also a noisy region of the EEM. Otherwise, no other spectral regions contained consistent residuals. Our result that the Everglades' PARAFAC model was able to provide a good fit for EEMs from the

Fig. 5 EEM-PARAFAC relative abundances. C1 & C6 are ubiquitous ▶ humic-like components. C2, C3, & C5 are terrestrial humic-like components. C4 is a microbial humic-like component. C7 & C8 are protein-like components. The x-axis is the distance downstream from Mohembo. The large circles represent samples collected adjacent to the main channel
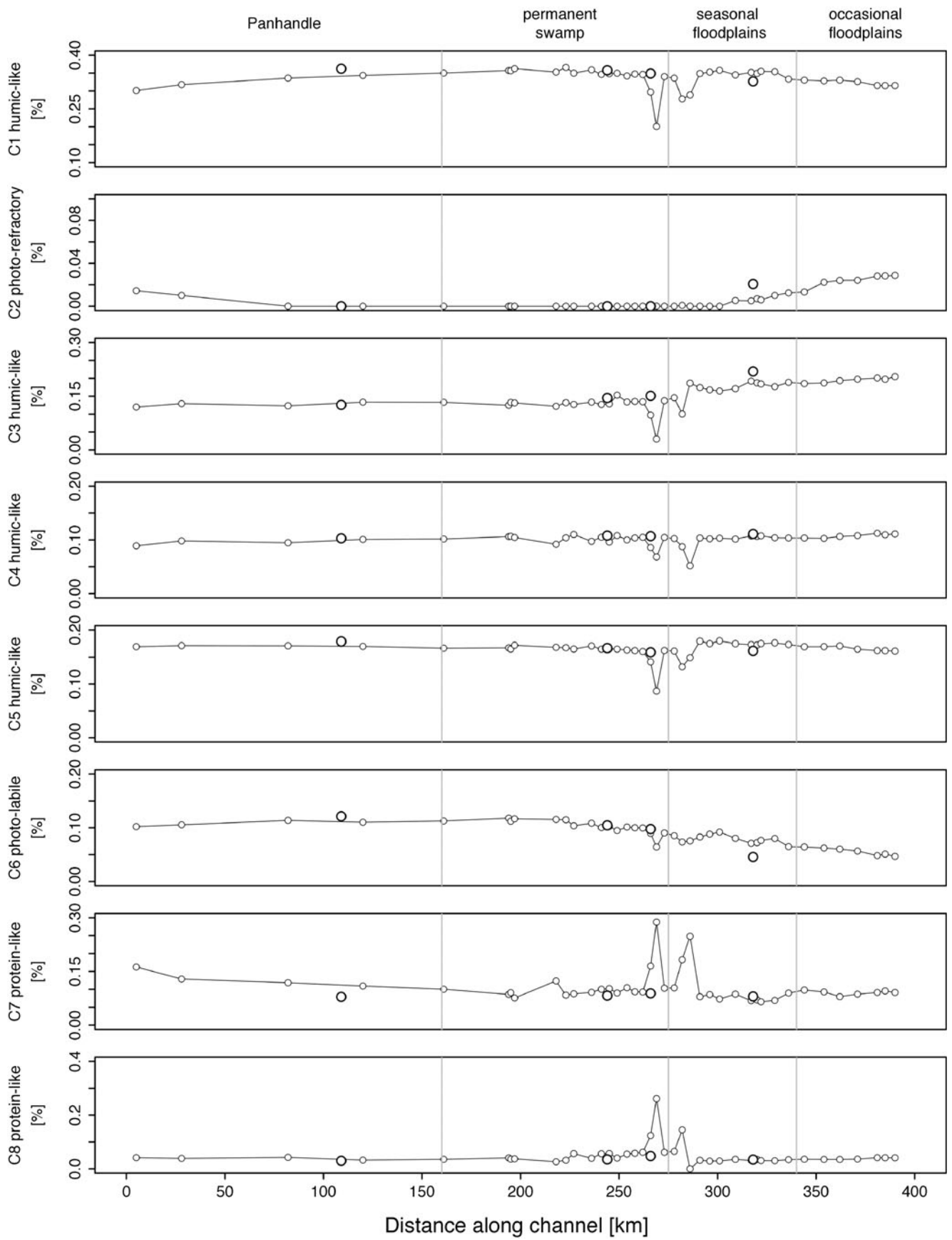
Okavango Delta implies that there is a remarkable degree of consistency between fluorescent components comprising the DOM pool in the two wetland ecosystems.

The PARAFAC components in the model have been identified as humic-like (C1—terrestrial humic-like & C6—microbial humic-like), terrestrial humic-like (C2, C3, C5), microbial humic-like (C4), and protein-like (C7, refractory & C8, bio-available) by Yamashita et al. (2010). C6 is a photo-reactive PARAFAC component, which decreases in intensity following photo-exposure and is found to have a greater intensity in groundwater than light exposed surface water (Chen et al. 2010). C2 has been identified as soil-derived and resistant to photo-degradation (Chen et al. 2010; Yamashita et al. 2010).

PARAFAC modelling of the Okavango Delta samples shows that within the Panhandle, C1, a ubiquitous terrestrial humic-like component, shows the greatest percentage of fluorescence (as in the Everglades) and increases in relative abundance downstream of Mohembo (Fig. 5). The relative abundance of C2 and of C7, the refractory terrestrial and microbial components, decrease along the Panhandle, indicative of dilution with more "fresh" organic matter. The relative abundance of the other PARAFAC components, C3, C4, C5, C6, and C8, do not change appreciably within the Panhandle. Because microbial components C4, C6, C7, and C8, which would be associated with primary productivity (Chen et al. 2010; Yamashita et al. 2010), do not increase, the change to higher percent saturation in DO in this region may be due largely to hydrologic turbulence and equilibration with the atmosphere, rather than primary productivity (Fig. 5). Samples collected outside of the main channel in lagoons and tributaries (large circles, Fig. 5) show similar distributions as those in the main channel.

Starting in the seasonal floodplains and extending into the occasional floodplains, there was an increase in the fluorescence contribution of the soil-derived humic C2 (Fig. 5), most likely due to soil-derived compounds leached from seasonally dry areas. Conversely, the relative abundance of photo-reactive C6 decreases as the wetland becomes shallower (Fig. 5). Chen et al. (2010) showed an inverse relationship between C2 and C6 in the Everglades, suggesting that C2 becomes enriched as a result of the same process by which C6 is degraded. As such, an enrichment in C2 towards the end of the transect, in conjunction with the depletion of C6, suggests enhanced photo-degradation of the DOM in the seasonal and occasional floodplains. Near the beginning of the seasonal floodplains there are two peaks in the relative abundance of protein-like fluorescence that do not coincide with a change in any of the other water quality parameters. Therefore, the reasons for these peaks are not evident, but may be influenced by such localized factors as pockets of enhanced primary productivity or point sources of proteinaceous organic matter from wildlife.

PCA of PARAFAC Component Relative Abundances

Principal Component 1 and Principal Component 2 accounted for 46.8% and 38.8% of the variability, respectively. The loadings plot (Fig. 6, a) shows that the eight PARAFAC components are distributed along Principal Component 1 such that the protein-like components (C7 & C8) are most negative, the humic-like components (C1, C3, C4, & C5) are positive, the photo-reactive humic-like component (C6) is slightly positive, and the photo-recalcitrant humic-like component (C2) is also near zero. The humic and non-humic PARAFAC components have dissimilar distributions along Principal Component 1, suggesting that DOM source controls Principal Component 1.

Along Principal Component 2, the loadings of PARAFAC components are distributed with C2 as the most positive and C6 the most negative (Fig. 6, a). C2 has been identified as a photo-recalcitrant humic-like PARAFAC
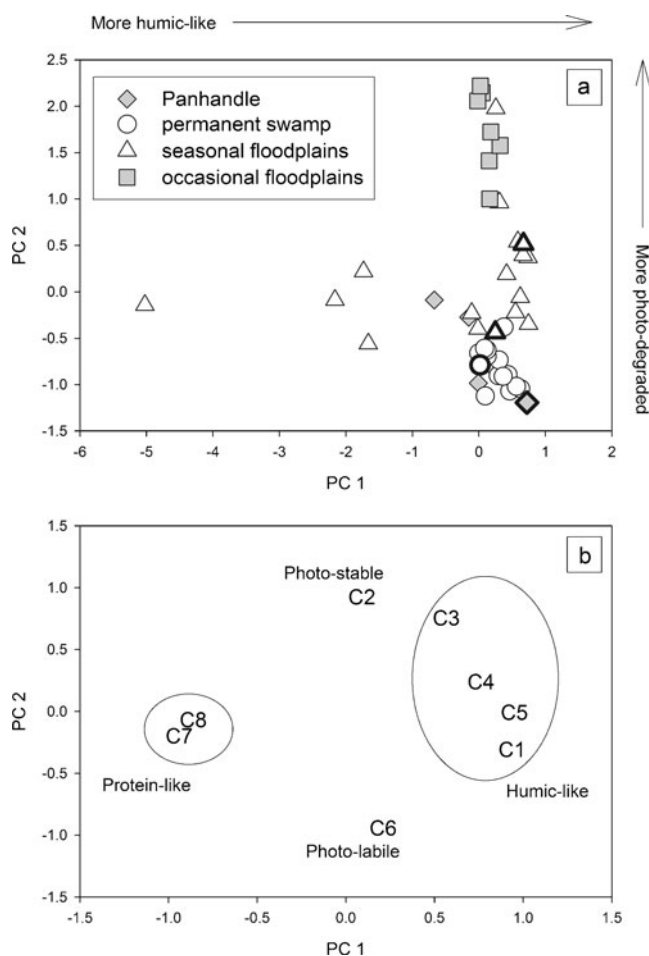

Fig. 6 Graphical representations of principal component analysis of the EEM-PARAFAC relative abundances. (**a**) loadings plot for the 8 PARAFAC components with descriptions of the component identities (**b**) score plot for water samples classified into each hydrotone. Bold symbols are samples collected from lagoons adjacent to the main channel

component derived from oxidation of soil organic matter (SOM) in the Everglades ecosystem (Yamashita et al. 2010). C6 was also characterized as SOM-derived but is considered photo-degradable (Chen et al. 2010). With the high sandy content in soils (> 85%, Bonyongo and Mubyana 2004), SOM contributions to C2 and C6 are probably less important than the effect of photo-degradation on DOM quality in the Delta. Therefore, we interpret positive values of Principal Component 2 as indicative of photo-degradation. Other PARAFAC components, including the protein-like C7 & C8 and the humic-like components are photochemically semi-labile (Yamashita et al. 2010; Chen et al. 2010) and show intermediate Principal Component 2 loadings.

The score plot (Fig. 6, b) shows that source variation, represented by Principal Component 1, and photo-degradation, represented by Principal Component 2, are important drivers of DOM character in the Panhandle. However, the permanent swamp shows less variability along Principal Component 1 meaning that source is less of a driver for DOM character in the permanent swamp than in the Panhandle. The seasonal floodplains show the greatest variability in both Principal Component 1 and 2. Principal Component 1 scores negatively correlate with protein-like fluorescence ($p<0.01$, $r=-0.978$) and DO ($p<0.01$, $r=-0.500$), two indicators of autochthonous DOM inputs. The most negative Principal Component 1 scores are found in sites at the beginning of the seasonal floodplains. Longitudinal variability in DOM character within the wetland is driven by photo-degradation and locally there are changes in DOM source, such as inputs of more microbial DOM that drive sharp decreases in Principal Component 1 in the seasonal floodplains.

DOM character in the occasional floodplains, however, is almost exclusively driven by photo-degradation as seen by the increase in scores for Principal Component 2 and minimal change in Principal Component 1 scores. Principal Component 2 scores positively correlate with EC ($p<0.01$, $r=0.932$) and DOC ($p<0.01$, $r=0.913$), which both increase with distance downstream of Mohembo. PCA results show that, as observed for the PARAFAC component distribution, the samples collected in tributaries and lagoons show similar scores as nearby main channel samples. Overall, the major downstream DOM character control in the Okavango Delta is photo-degradation, as seen by the progressive increase in Principal component 2 with downstream hydrotones. However, there are also localized changes in DOM source material in the Panhandle and seasonal floodplains based on the PCA.

Conclusions

Previously, studies have alluded to the importance of photo-transformations for DOM quality in the Okavango Delta and other large wetlands. Our study of a large tropical wetland,

with substantial homogeneity within its hydrotones and without the confounding influence of human perturbations along most of its length, allows us to incontrovertibly show that even with regular inputs of terrestrially-derived organic matter to the channels, photo-degradation exerts an important control on DOM chemical character. Our PARAFAC and PCA results support this finding and further highlight the two main influences on DOM quantity and character: 1) source: microbial activity, submerged vegetation, and seasonally flooded terrestrial soils/vegetation and 2) processing: in-stream microbial activity, photo-degradation, and evapo-concentration. The pristine nature of the Okavango Delta results in stable nutrient profiles and gradual shifts in DOM concentration and quality profiles that can be explained by controls 1 and 2 above. These predictable changes allow us to identify potential anthropogenic impacts in the reaches downstream of the protected Moremi Game Reserve (delineated by the Buffalo Fence) and possibly in other large wetland systems.

Our findings that C2 and C6, two components reported to be photo-dependent in the Everglades ecosystem, also reflect photo-induced changes in DOM in the Okavango. This consistency may support their use as sensors of UV degradation processes in other large wetland systems. Additionally, the PARAFAC model developed for the Florida Everglades was an excellent fit for the Okavango DOM, suggesting that the same model may be useful for understanding DOM dynamics in different sub-tropical and tropical wetlands.

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