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Linking Organic Matter Dynamics to Management, Restoration, and Climate in the Florida Everglades

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FLORIDA INTERNATIONAL UNIVERSITY

Miami, Florida

LINKING ORGANIC MATTER DYNAMICS TO MANAGEMENT, RESTORATION
AND CLIMATE IN THE FLORIDA EVERGLADES

A dissertation submitted in partial fulfillment of

the requirements for the degree of

DOCTOR OF PHILOSOPHY

in

CHEMISTRY

by

Peter Regier

2017

To: Dean Michael Heithaus
College of Arts, Sciences and Education

This dissertation, written by Peter Regier, and entitled Linking Organic Matter Dynamics to Management, Restoration and Climate in the Florida Everglades, having been approved in respect to style and intellectual merit, is referred to you for judgement.

We have read this dissertation and recommend that it be approved

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Date of Defense: June 30, 2017

The dissertation of Peter Regier is approved.

Dean Michael R. Heithaus
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Andrés G. Gil
Vice President for Research and Economic Development
and Dean of the University Graduate School

Florida International University, 2017

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DEDICATION

I dedicate this dissertation to my family for raising me right, despite my best efforts...

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ABSTRACT OF THE DISSERTATION
LINKING ORGANIC MATTER DYNAMICS TO MANAGEMENT, RESTORATION
AND CLIMATE IN THE FLORIDA EVERGLADES

by

Peter Regier

Florida International University, 2017

Miami, Florida

Professor Rudolf Jaffé, Major Professor

The Florida Everglades is a massive and highly managed subtropical wetland ecosystem, strongly influenced by anthropogenic control of freshwater distribution and highly susceptible to a changing climate, including rising sea-level and changes in temperature and rainfall. Shifting hydrologic regimes impact ecosystem function and biogeochemistry, which in turn control the sources, fate, and transport of organic matter. As a master environmental variable, it is essential to understand how organic matter dynamics will respond to changes in the balance between freshwater and saltwater associated with landscape-scale Everglades restoration efforts and climate change. The research comprising this dissertation improves current understanding of the linkages between organic matter and hydrology in the Everglades across a broad range of temporal and spatial scales. A range of research tools, including stable molecular biomarkers, water quality sensors, data synthesis and multivariate statistics were utilized. Biomarkers were used to track particulate organic matter mobilization in response to experimentally manipulated flows and provided initial evidence that sheet flow restoration can re-

engineer landscape microtopography, influencing both ecosystem structure and organic matter inputs to Everglades National Park (ENP). Short-term and long-term temporal studies indicated the quantity and quality of dissolved organic carbon responds to changes in freshwater flow to marshes and mangrove forests in ENP, and that spatial patterns and trends are driven by a complex mixture of managed and natural surface water inputs (i.e., rainfall and water management inflows) as well as groundwater discharge. Application of climate scenario forecasting to relationships established between organic matter and hydrologic drivers predicted reductions in dissolved organic carbon export from ENP and changes in organic matter molecular composition. Furthermore, high-frequency measurements showed hydrologic connectivity of freshwater and estuarine organic matter pools at sub-monthly time-scales. In summary, the work presented here clearly indicates strong yet spatiotemporally complex relationships between changes in water and the sources and transport of organic carbon through the Everglades.

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CHAPTER I

INTRODUCTION

1.1 Introduction

Organic matter (OM) originates as assimilation of atmospheric carbon into terrestrial or aquatic biomass via photosynthesis. As OM degrades, primarily through heterotrophic activity, it can be sequestered in soils and sediments, mineralized to the atmosphere (Siegenthaler and Sarmiento, 1993) or exported to coastal margins and the open ocean, primarily through rivers (Meybeck, 1982; Hedges et al. 1997; Raymond & Bauer, 2001). It has been estimated that the quantity of carbon in terrestrial OM transported to the ocean may account for more than 79% of total net ecosystem production (Cole et al. 2007).

Organic matter in the water column is classified either as dissolved organic matter (DOM) or particulate organic matter (POM), where DOM is operationally defined by passing through a filter (typical pore sizes range from 0.2-0.7 μm), while POM is retained (Azam & Malfatti, 2007). Dissolved organic matter is generally more prevalent than POM in aquatic systems (Meybeck, 1982; Hope et al. 1994), particularly in North America (Seitzinger et al. 2005), but both components play crucial, often disconnected, environmental roles (Druffel et al. 1992; Raymond and Bauer, 2001; Osburn et al. 2012). Dissolved organic matter influences water quality by regulating nutrient cycles (Boyer et al., 1997; Qualls and Richardson, 2003), transport and complexation of metals (Yamashita & Jaffe, 2008), light availability to benthic communities (Osburn et al. 2009) and microbial activity (Amon and Benner, 1994; Battin et al. 2008; Fellman et al. 2008). Particulate organic matter acts as an additional source of nutrients for aquatic systems and is readily accumulated in coastal sediments (Keil et al. 1994; Kendall et al., 2001; He et al. 2014).

Quantitative and qualitative OM dynamics are influenced by several interrelated ecosystem factors, including hydrology, geomorphology and biogeochemistry (Krause et al. 2015). Hydrology primarily drives OM transport (Raymond & Saiers, 2010; Townsend-Small et al. 2011), but also influences its composition (Fasching et al. 2015). Biologically labile OM can experience non-conservative transport as it is cycled through, or retained in, biota along the flow path (Battin et al. 2008; Edmonds and Grimm, 2011; Hall Jr. et al., 2016). The combination of non-conservative downstream movement and *in situ* processing or retention, known as “spiraling” (Newbold et al. 1982; Webster, 2007), is strongly linked to geomorphological characteristics (Ensign and Doyle, 2005) including benthic surface area to channel volume ratios (Wollheim et al. 2006) and transient storage (Valett et al. 1996; Ensign and Doyle, 2006). Increased residence times and biological interactions of solutes during transport can in turn lead to zones of higher biogeochemical activity (Dahm et al. 1998).

Organic matter behavior is further complicated through mixing of a variety of allochthonous and autochthonous sources along the flow path (e.g., terrestrial plants, soils and microbial byproducts). As specific sources often have different compositional features (Ficken et al. 2000; Hernes and Benner, 2002; He et al. 2014), the origin of OM can regulate susceptibility to processing and degradation via photochemical and biological pathways (Cory et al. 2014; Chen and Jaffe, 2014; Stubbins et al. 2016). The resulting amalgamation of different sources and reactivity yields a highly complex molecular signature consisting of thousands of unique chemical formulae (e.g., Stetson et al. 2003; Roth et al. 2014) spanning degradation time-scales ranging from minutes to millenia (Pollard, 2013; Hansell, 2013).

Furthermore, the environmental conditions controlling OM composition and transport vary spatiotemporally (Rosemond et al., 2015; Sobczak and Raymond, 2015). For instance, recent innovations in the use of *in situ* optical sensors measuring water quality proxies at sub-hourly resolution (Downing et al. 2009; Downing et al. 2012; Lee et al. 2015) demonstrate that standard grab sampling regimes (i.e., weekly or monthly intervals) often miss important, rapid shifts in hydrodynamics and water chemistry, which can strongly influence OM concentration and composition (Kirchner et al. 2004; Pellerin et al. 2011; Wilson et al. 2013). On the opposite side of the temporal spectrum, inter-annual changes in DOM export have been linked to long-term drivers like increasing temperature (Freeman et al. 2001), changes in atmospheric CO₂ concentrations (Freeman et al. 2004), or multi-decadal climatic indices (Mengitsu et al. 2013), although connections between long-term DOM export trends and global climatic drivers remain relatively unclear (Filella and Rodriguez-Murillo, 2014).

In aquatic systems where hydrologic conditions are relatively predictable, like river networks, widely used ecological paradigms including the River Continuum Concept (Vannote et al., 1982), Serial Discontinuity Concept (Ward and Stanford, 1983; Ward and Stanford, 1995), and, more recently, the Pulse-Shunt Concept (Sobczak and Raymond, 2016) provide conceptual starting points to explain complex relationships between OM cycling and environmental drivers. However, extending equivalent unifying frameworks to systems with less predictable hydrodynamics like coastal wetlands and estuaries remains a challenge as a result of the combination of variability in the constantly shifting balance between freshwater, saltwater and groundwater (e.g., Price et al. 2006) and complex biogeochemical processes (Reddy et al., 2010; Troxler et al.,

2013; Maie et al., 2014). Coastal systems play significant, yet poorly quantified roles in the global carbon cycle (Bouillon et al. 2008; Mitsch et al. 2013) and provide valuable ecosystem services (Brauman et al. 2007; Richardson et al. 2014). As such, improving current knowledge of the linkages between water and carbon is essential for constraining global carbon budgets. Such an understanding is urgently needed as coastal and near-shore ecosystems are increasingly threatened by naturally and anthropogenically driven disturbances (Alongi, 2002; Mitsch and Hernandez, 2013).

Research projects presented in the subsequent chapters utilize a range of analytical and statistical techniques to explain how the sources, transport, and fate of organic carbon change through time and space in a complex coastal wetland ecosystem within the context of relevant environmental drivers. All study sites are located within the Florida Everglades (also known as the Greater Everglades Ecosystem, or GEE), a massive landscape mosaic of marshes, wet prairies, tree islands, mangrove forests and seagrass beds (Davis and Ogden, 1994) connected by surface and groundwater flows. The GEE spans much of the South Florida peninsula along a historically connected flow path which originates in the Kissimmee River basin north of Lake Okeechobee and drains into Florida Bay and the Gulf of Mexico (Figure 1).

Prior to settlement of the region, freshwater moved through the system as shallow and slow overland sheet flow promoting strong hydrologic connectivity of upstream and downstream environments. During agricultural and urban development, hydric wetland soils were drained and a vast network of canals and levees was constructed, effectively dissecting the original flow path into discrete impoundments, connected by water control structures rather than natural sheet flow (McVoy et al. 2011). Changes in freshwater

sheetflow led to many negative effects on the Everglades ecosystem (Sklar et al. 2005), including subsidence of organic soils (Davis 1943), enhanced saltwater intrusion into freshwater aquifers (Allison, 1943), loss of characteristic microtopography (Science Coordinating Team 2003) and nutrient enrichment of oligotrophic downstream regions (McCormick et al. 2002).

Figure 1.1 Map of the Greater Everglades Ecosystem (GEE). The region of interest for the present research projects (highlighted by black box encompasses the two primary drainages of Everglades National Park (ENP): Shark River Slough and Taylor Slough, and the boundary between the Water Conservation Areas (WCAs) and ENP. Original figure courtesy of fcelter.fiu.edu.

In response to widespread ecosystem degradation, the Comprehensive Everglades Research Plan (CERP) was implemented to improve water quality, increase freshwater flow to downstream regions, and reestablish seasonal timing for water deliveries (Sklar et al. 2005). The efficacy of Everglades restoration will be judged in part by the impact of management activities on the downstream areas encompassed within Everglades National

Park (ENP), a federally protected region located at the southern terminus of the flow path. Everglades National Park is characterized by low topographic relief with peat and marl soils overlaying highly porous karstic bedrock (DiFrenna et al. 2008). Seasonal hydrologic patterns of Park drainages are strongly influenced by inputs via water control structures (Saha et al., 2012; Sandoval et al. 2016), and changes in freshwater inputs during restoration are expected to impact this region (Obeysekera et al. 2014). In addition, the oligohaline brackish ecotone that joins freshwater marshes to saline mangrove forests in ENP responds to gradients of salinity and nutrients controlled by the balance of freshwater and saltwater (Rivera-Monroy et al. 2011). Changes in flow and salinity associated with rising sea levels throughout the estuarine extent of ENP (Stabenau et al. 2011) and altered freshwater delivery will influence the ecotone, as well as the freshwater and saltwater regions. Shifting surface water flows are predicted to alter landscape topography (USACE, 1999; Science Coordination Team, 2003; Larsen et al. 2009), vegetation communities (Ross et al. 2000), biogeochemical cycling (Reddy et al., 2010; Orem et al. 2015), and carbon sequestration capacity (Jimenez et al. 2012; Breithaupt et al. 2014; Orem et al. 2015). It is therefore essential to understand how OM currently responds to hydrology in order to predict how changes in these factors may affect the carbon cycle in the future, particularly in response to landscape-scale factors like restoration and climate change (Middleton and Souter, 2016).

Within the GEE, a relatively consistent pattern of higher dissolved organic carbon (DOC) concentrations with high aromaticity (associated with terrestrial plants) is present in the north, and both concentration and aromaticity decrease moving southward along the GEE flow path (Yamashita et al. 2010; Chen et al. 2013). Distinct signatures of OM

sources, including terrestrial plants (Saunders et al. 2006; Saunders et al. 2015), flocculent matter (Pisani et al. 2013), mangroves (Cawley et al., 2014; He et al., 2014) and seagrasses (Ya et al., 2015) have been distinguished throughout the GEE using optical properties, stable isotopes and molecular markers. Transport of these components through canals (Yamashita et al., 2010), surface waters (Cawley et al., 2014) and groundwater (Chen et al., 2010) has also been characterized, with components ranging from bio- and photo-refractory to highly labile (Chen & Jaffe, 2014). However, the relationships of OM quantity and quality to hydrology and climate remain poorly understood in the region.

The four chapters of research presented here seek to advance understanding of the linkages between OM and environmental drivers, primarily hydrology (surface water, groundwater and precipitation), in the GEE. In the first project (Chapter 2), specific hypotheses related to the role of flow in restoring landscape patterning are tested. Findings from Chapter 2 have important implications as restoration efforts move to increase flow in areas which have been hydrologically disconnected for decades, including the border between the WCAs and ENP. Chapter 3 continues to examine the relationship between OM and surface water movement, along with other long-term drivers (including climate indices and sea level) through interpretation of monthly DOC export from the estuary of Shark River Slough, the primary drainage of ENP (Saha et al. 2012). Together, Chapter 2 and Chapter 3 establish recent patterns of OM transport, and improve capacity to predict how changes in upstream hydrologic connectivity and flow patterns may impact the estuary. Chapter 4 further advances this understanding through investigation of DOC temporal patterns in the Shark River estuary conducted at fine

temporal resolution (sub-hourly), providing a temporally comprehensive picture of the relationship between the multiple, interrelated drivers of estuarine hydrology and OM. Finally, Chapter 5 builds on previous research exploring compositional patterns and trends of DOM across space (Yamashita et al. 2010) and time (Chen et al. 2013) in ENP by linking long-term patterns and trends in OM quality to hydrodynamics of surface and groundwater. As a whole, the four projects advance current knowledge of interactions between carbon and water in the Everglades, and provide quantitative tools to predict how such relationships will respond to changes in management, restoration and climate.

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CHAPTER II

SHEETFLOW EFFECTS ON SEDIMENT TRANSPORT IN A DEGRADED RIDGE- AND-SLOUGH WETLAND: INSIGHTS USING MOLECULAR MARKERS

(In preparation for Organic Geochemistry)

2.1 Abstract:

Historic freshwater sheetflow in the Florida Everglades distributed sediment to form a landscape patterned by emergent ridges and submerged sloughs. Drainage of wetlands, reduction of overland sheetflow and construction of physical barriers to flow have degraded these corrugated microtopographic features. As part of the Comprehensive Everglades Restoration Plan, the Decompartmentalization Physical Model (DPM) is a landscape-scale pilot test project aiming to reestablish natural sheetflow to the central and southern Everglades by increasing freshwater inputs and redesigning barriers to flow. To validate proof of concept that increased flow will rebuild ridge-slough microtopography by remobilizing slough sediments to ridges, a suite of four molecular markers capable of distinguishing ridge, slough and microbial sources in sediments (in benthic flocculent material or ‘floc’ and in advected sediments in the water column) were determined at the DPM test site during pre-flow, high flow and post-flow conditions over a three-year DPM implementation period. The combined use of the four biomarkers, namely the aquatic proxy (Paq), C₂₀ highly branched isoprenoids (HBIs), kaurenes and botryococcenes, resulted in compositional patterns that clearly distinguished between ridge and slough organic matter, with the sediment traps being mainly slough-like. Of these molecular parameters, the Paq was determined to be the most reliable in distinguishing among organic matter sources. Long-term patterns in the Paq at ridge and slough sites indicate a general increase, indicative of preferential mobilization of slough material. The Paq values for entrained sediments collected from sediment traps are also strongly associated with slough environments, and confirm trends in floc samples. Our results tentatively confirm the hypothesis that increased flow in

degraded ridge-and-slough wetlands is a potentially viable mechanism to restore historic patterns of microtopography.

2.2 Introduction

Landscape patterning in wetlands is driven by an array of interconnected environmental drivers, including hydrology, nutrients, soil type, and vegetation (Eppinga et al., 2008; Larsen et al., 2011). In turn, changes in factors that alter patterning can impact ecosystem function (Rietkirk et al. 2004; Cohen et al. 2011), making understanding drivers of landscape patterns an essential component of wetland restoration efforts.

The Florida Everglades is currently undergoing massive landscape-scale hydrologic restoration to reestablish historic quantity, quality and timing of freshwater deliveries (Davis and Ogden, 1994; Science Coordination Team, 2003; Sklar et al. 2005). Historic water velocities greater than 2 cm s^{-1} controlled distribution of sediments and maintained landscape patterning of ridges and sloughs throughout much of the freshwater Everglades (Larsen et al., 2009; 2011). However, the combination of drainage, flow path impoundment, and dramatically reduced flow velocities have degraded linear patterning (USACE, 1999), resulting in loss of hydrologic connectivity and associated ecosystem function (Ogden, 2005). Current understanding of flow as a mechanism to rebuild landscape microtopography in the Everglades is limited to small spatial-scale experiments or modeling and considerable uncertainty remains regarding response of the ridge and slough to increased flow regimes anticipated with Everglades restoration.

The Decompartmentalization Physical Model (DPM) is a landscape-scale project designed to address this knowledge gap by measuring changes in entrained sediment sources and subsequent transport in response to increased sheetflow. More specifically, DPM seeks to test the hypothesis that higher flow rates through degraded ridge-slough wetlands will entrain sediments originating in slough environments, which are predicted to settle in slower velocity ridge environments, thereby rebuilding elevation differences between ridge and slough sub-environments and restoring historic landscape patterning (Harvey et al. 2009; Larsen et al. 2011).

Biomarkers have frequently been used to assess organic matter sources and transport as well as environmental changes in aquatic environments (e.g., Zhang et al. 2006; Zhou et al. 2010; Tulipani et al. 2014; Zocatelli et al. 2014). The concept has been successfully applied in a variety of ecosystems in the Florida Everglades, including freshwater marshes (Mead et al. 2005; Saunders et al. 2015), mangrove forests (He et al. 2014), and coastal marine environments (Xu et al. 2006; Xu et al. 2007) leading to the development of source-specific molecular markers applicable as proxies for organic matter source, transport and fate. Lipid biomarkers are abundant in plant waxes (Bush and McInerney, 2013) and have proved particularly useful to distinguish organic matter sources of different biomass origins, including terrestrial plants, algae and bacteria (e.g. Seki et al. 2010; Schellekens and Buurman, 2011; Tulipani et al. 2014). Ratios of n-alkanes like the carbon preference index (CPI), average chain length (ACL) and aquatic proxy (Paq) have been widely used to trace historical changes in vegetation (Ficken et al. 2000; Tareq et al. 2005; Zocatelli et al. 2014). Of these ratios, the Paq is specifically designed to discriminate organic matter inputs from emergent and submerged aquatic

plants (Ficken et al. 2000). It has been applied extensively in the Everglades (Mead et al. 2005; Saunders et al. 2006; Saunders et al. 2015), making it an ideal metric for distinguishing ridge and slough contributions to floc and sediment in the DPM test-plot.

The applicability of the Paq or any other biomarker as a proxy for environmental change depends on its environmental stability. Some studies warn that ignoring degradation effects when interpreting observed changes in n-alkane distributions through time may limit the accurate interpretation of organic matter source variations (e.g., Nguyen Tu et al. 2011; Schellekens and Buurman, 2011). However, ratios like the Paq, CPI, and ACL appear to be quite robust to changes induced by degradation processes, even when bulk carbon concentrations decrease dramatically (e.g., Wang et al. 2014; Li et al. 2017).

Along with the Paq, we selected three additional biomarkers to distinguish and characterize sources of organic matter present in floc and sediment samples in Everglades marsh environments. Kaurenes, a class of diterpenoids found in abundance in higher plants (e.g., Xiang et al. 2004), have been reported as particularly enriched in Everglades sawgrass (Saunders et al. 2006), and are suggested as a good proxy for organic matter from ridges in the Everglades where such emergent plants are most abundant. In addition to emergent and submerged plants, periphyton is highly abundant in the Everglades, and organic matter inputs to floc have previously been assessed using C₂₀ highly branched isoprenoids (C₂₀ HBIs) and botryococcenes (Neto et al. 2006; Pisani et al., 2013; Gao et al., 2007). While the most likely source of the C₂₀ HBIs is cyanobacteria (Kenig et al. 1995; Neto et al. 2006), the botryococcenes are likely associated with filamentous green algae, specifically *Botriococcus braunii* (Maxwell et al. 1968; Gao et al. 2007; Xu and

Jaffe, 2010). The four abovementioned organic matter source proxies for the Everglades have been previously successfully calibrated for a ridge and slough environment (Saunders et al., 2006) and applied (Saunders et al., 2015) in Everglades National Park. The current study applied the suite of four biomarkers to assess the sources and transport of sediments/floc under low and increased sheetflow conditions as part of the DPM implementation study. Ridge-to-slough transects were used to confirm validation for the specific study region, including the capacity of the Paq to differentiate ridge and slough organic matter sources, the applicability of kaurenes as an indicator of ridge vegetation sources, and HBIs and botryococcenes as indicators of sediments and floc sourced from sloughs where periphyton is usually more abundant. Using a spatial gradient sampling design to monitor sites along a broad flow path during three years of high flow events and the preceding and intervening low flow periods, we assessed slough contributions of organic matter to ridges, and longitudinal sediment transport dynamics along the flow path. On the basis of our results, we present initial evidence supporting the hypothesis that increased water discharge in Everglades marsh environments can potentially lead to the reestablishment of the historic ridge-and-slough microtopography in this ecosystem.

2.3 Methods:

2.3.1 Site description

The DPM study area is located in Water Conservation Area 3 (WCA-3), approximately 26 miles to the WNW of Miami, Florida in an area between the L67A and L67C levees, known as “The Pocket” (Figure 2.1). A gated culvert structure, the S-152, was constructed on the L67A levee to generate experimental sheetflow conditions

(velocities typically range from 2-5 cm s⁻¹), and a 3000-foot section of the L67C levee was degraded approximately 4.5 km south of the S-152 to allow water to flow freely over the levee. The culverts were opened between the months of November and January (2013 through 2016) when TP levels in the L67A are at or below 10 µg L⁻¹, to avoid artificially enriching the ecosystem. Due to Everglades-wide, emergency high water conditions from January through May, 2016, the S-152 was also operated for 4 days in February and from early March through early May of that year. While the culverts were open, water flowed from WCA-3A through the DPM footprint south to the L67C levee degrade and into WCA-3B.

Across the study area, slough vegetation is primarily *Utricularia* spp. (bladderworts), *Eleocharis* spp. (spike rush), *Nymphaea odorata* (white water lily), and floating or benthic periphyton, while ridges are dominated by *Cladium jamaicense* (sawgrass). Prior to the first flow event samples of the leaves and roots of dominant vegetation species present in the DPM footprint were collected. Although the Paq is well established to distinguish plant inputs from ridges and sloughs (Saunders et al. 2006; Saunders et al. 2015), site-specific samples were used as additional validation of the Paq using results presented in supplementary information (Appendix 2.1).

Figure 2.1 Map of DPM footprint. (Left) Site map showing sampling locations where floc and sediment samples were collected for this study. Inflow to the test-plot occurs through culverts at the S-152 control structure. The anticipated flow path is shaded, with sheetflow moving from the L67-A to the L67-C. (Right) Close-up map of site Z5-1, exemplifying sampling locations of paired floc collection and horizontal traps along a slough-to-ridge transect. Approximate orientation of horizontal traps (arrow head indicates location of trap inlet), parallel to water flow, is shown for a high-flow period.

2.3.2 Sampling design

Two sampling designs were implemented, including a BACI design aimed at evaluating temporal variability in sediment biomarkers, and a spatial gradient design to evaluate spatial variability across the study area, including gradients related to distance from the flow structure (S-152) or built features (e.g., canals, levees, or levee gap). Both of these designs sampled ridge and slough environments. For the BACI design, floc samples from adjacent ridge and slough habitats were collected at three-week intervals during periods of September to January and at six week intervals in the period from February to June, or until water depths decreased to < 20 cm. Sampling included one pre-flow year, starting September 2012, and the three following years with flow events. Sampling sites included the high-flow (impact) site RS1, a control (C1) and a moderate-flow site RS2. Both C1 and RS2 were located approximately one kilometer from the S-152.

For the spatial gradient design, all sites were due south of S-152, except for Z6-1 (due east, near site C1), and were located at approximately 150-m, 300-m, 700-m, 1000-m, and 2200-m from the S-152. At two sites, Z5-1 and Z6-1, floc and advected sediments were also collected along 30-m transects, perpendicular to a ridge-slough border, and spanning the slough interior, slough edge, ridge edge and ridge interior (Figure 2.1). Edge plots were within 3 m of the border, and interior plots 10-15 m from the border. Floc collections in the spatial gradient sites were also made before flow events (September through October), immediately after the flow window (typically January or February), and at six week intervals after January. Advected sediment from horizontal traps (described below) was collected at the spatial sites and, when sufficient

sample permitted, analyzed for biomarkers. A total of 393 floc and advected sediment samples were collected for marsh sites during this study between September 2012 and May 2016. The current study will focus on temporal and ridge-slough transect trends and patterns. Analysis of samples in the context of a BACI sampling design was outside the scope of this initial analysis but will be reported in subsequent publications.

2.3.3 Sampling floc and advected sediments

Floc was collected by pushing a 10-cm diameter soil corer through the floc layer and into the soil approximately 10 cm (see also Pisani et al., 2013). A cap was placed on top to ensure a vacuum seal then the corer was lifted out of the soil and floc was extruded from the top and collected in Ziploc bags. The height of the floc above the soil surface was measured while extruding the floc from the corer. Floc was collected in representative slough or ridge portions of each habitat, and care was taken to avoid collecting in previously sampled areas or established trails.

Horizontal sediment traps were paired with floc sampling sites and collected advected sediments during the time intervals between floc sampling events. The traps, deployed at mid-water column, utilized a design adapted from Phillips et al. (2000), previously used to quantify sediment exchange in estuarine systems. Only traps deployed under high-flow at the impact sites (Z5-1, RS1, and Z5-3; all within 700 m of S-152) collected sufficient material for biomarker analyses. Floc and sediment samples were kept on ice and transported to the South Florida Water Management District (SFWMD) Field Operations Center laboratory, stored at 4°C and homogenized within 24 hours. Homogenized samples were frozen and transported to Florida International University (FIU) for biomarker analysis.

2.3.4 Sample preparation and extraction

Upon arrival at FIU, excess water was decanted and samples were refrozen, then freeze-dried at -40 C and 0.133 mBar (Labconco Freezone) for 24 hours or until completely dewatered. Freeze-dried samples were passed through a 35 mesh sieve to remove larger vegetation and root debris and homogenized to <35 mesh with a mortar and pestle. Extraction methods followed procedures outlined by Folch et al., (1957) with modifications. First, 0.8 g of homogenized sample were weighed into cellulose thimbles cleaned by pre-rinsing with methylene chloride (DCM; Fisher Scientific). Samples were then extracted thrice with DCM and transferred to round-bottom flasks to remove excess solvent via rotary evaporation. The remaining sample was transferred to hexane for fractionation. Blanks of 0.8 g combusted sand spiked with two n-alkane standards were extracted in tandem with samples to assess recovery rates and identify potential contamination during the extraction and fractionation processes. One blank was run for every nine biomarker samples. All solvents used for extraction and fractionation procedures were Optima™ grade.

2.3.5 Fractionation of lipid classes

Eight and a half grams of silica gel deactivated by 5% deionized water was mixed with hexane to form a slurry and loaded into a glass column and then topped with sodium sulfate to trap remnant water. Next, the extracted sample in hexane was loaded at the top of the column. Fraction 1 (F1), containing non-polar aliphatic hydrocarbons, was eluted using 25 ml of hexane. Following F1, fraction 2 (F2), containing polyunsaturated and aromatic hydrocarbons, was eluted using 25 ml of a 3:1 hexane:toluene solvent mixture.

Fractions were collected in pear flasks and excess solvent was again removed using rotary evaporation. Samples were then transferred using DCM to 300 µl GC inserts and spiked with squalane as an internal standard.

2.3.6 Gas-chromatography mass-spectrometry

Separation and quantification of molecular biomarkers was conducted using an Agilent 6890 Gas Chromatograph (GC) coupled to an Agilent 5973 Mass Spectrometer (MS) in electron ionization mode at 70 eV. The GC was fitted with an RTX-1 (Restek) 30 m capillary column with an internal diameter of 0.25 mm receiving He carrier gas flowing at 1.2 mL/min. The injection temperature was set at 280 °C and the GC oven was programmed to ramp from 60 to 300 °C at a rate of 6 °C/min followed an isothermal hold for 15 min.

2.3.7 Biomarker identification and quantification

Biomarkers were identified by comparing chromatographic retentions times and mass spectra with authentic standards and literature reports as well as through mass spectral interpretation using Agilent ChemStation software. The n-alkanes in F1 used to calculate the Paq were identified based on retention time using a mass chromatogram restricted to compounds containing the ion $m/z = 57$. Peaks were checked for interferences including co-eluting compounds by comparison with typical n-alkane mass spectral characteristics performed after background subtraction. The Paq is based on the C_{23} , C_{25} , C_{29} and C_{31} n-alkane peaks, according to the formula provided by Ficken et al. (2000): $P_{aq} = C_{23} + C_{25}/C_{23} + C_{25} + C_{29} + C_{31}$. The HBIs present in F1 consisted of two compounds: the C_{20-0} HBI and the less abundant C_{20-1} HBI. The former (significantly more abundant) peak, was well resolved chromatographically, while the latter appears as

a shoulder peak on the C₁₇ n-alkane, and was integrated accordingly. Spectral confirmation of HBI peaks used the m/z doublet found at 168/169 (Yon et al., 1982; Requejo and Quinn, 1983; Jaffe et al., 2001). The kaurenes consist of two peaks in F1 with characteristic MS spectra of m/z = 272, 257, 123 and 274, 259, 123, respectively. Botryococcenes in F1 and F2 consist of a group of isomers that elute in the range of C₂₇ to C₂₉ n-alkanes (F1). A total of 26 isomers were identified by Gao et al., (2007) but do not consistently appear in all samples. Compound identification was based on mass spectral characteristics and was performed on a peak-by-peak basis within established retention time ranges. The peak area of squalene spiked immediately prior to injection was used to calculate concentration values for the HBIs, kaurenes and botryococcenes.

2.3.8 Statistics

Statistical analyses were conducted using the JMP® Version 12 statistical package (SAS Institute Inc., Cary, NC, 1989-2007). Comparison tests for multiple sample groups was performed using the Tukey-Kramer honest significant difference test to account for unequal sample sizes (Kramer, 1956). The results of Tukey-Kramer tests are presented in Figures 2.4 and 2.5 as letters, where groups with no common letters are significantly different ($p > 0.05$). Principal component analysis (PCA) was conducted on normalized data and plotted as site averages of PC1 and PC2 loadings.

2.4 Results and Discussion

2.4.1 Ridge-slough spatial transects

Biomarker validation for differentiating between ridge and slough organic matter sources was performed along ridge-slough gradient for two transects (Z5-1 and Z6-1, see

Figure 2.1), where floc samples were collected during low and high flow periods (Figure 2.2). For both sites, the Paq increased from ridge to slough, with the largest change occurring between ridge edge and slough edge. Highest variability at ridge-edge sites likely stems from increased mixing of slough and ridge organic matter sources, where emergent vegetation reduces flow velocities and suspended particulates settle out of the water column on the edge of the ridge (Larsen et al., 2009; Larsen et al., 2011). As for the Paq, a general trend of increasing average HBI concentration values is also observed from ridge to slough. However, dramatic differences in HBI concentration between Z5-1 and Z6-1 were observed, indicating higher spatial heterogeneity throughout the DPM plot in comparison to the Paq, which may be a function of the high seasonally and spatial heterogeneity of HBIs, observed elsewhere in the Everglades (Pisani et al. 2013).

In contrast to the Paq and HBIs, kaurenes were highly enriched at ridge and ridge edge sites but generally absent or present only at very low concentrations for the slough and slough edge. Kaurene patterns are in agreement with sawgrass being the primary source of kaurenes in this environment, and sawgrass being most abundant on the ridges (Saunders et al. 2015). Furthermore, the clear divide between ridge edge and slough edge for both sites indicates minimal movement of ridge-derived materials into the sloughs. While spatial patterns for the botryococcenes generally followed an increasing trend from ridge to slough, similar to the Paq and HBIs, botryococcenes had considerably higher variability at Z6-1 slough sites compared to Z5-1 slough sites (in contrast to the HBIs), although this variability appears to be driven by a few very high botryococcene values

Figure 2.2 Boxplots showing samples collected along ridge-to-slough spatial gradients at Z5-1 and Z6-1 sampling sites. Outliers are represented by black dots.

associated with sampling dates after the second high flow. Dissimilar patterns in algal-derived HBI and botryococcene patterns may result from differences in flow between the two sites, as previously mentioned. Additionally, the difference between the two algal markers may be related to periphyton and variations in species-specific primary productivity patterns, although both parameters exhibit correlations to periphyton

coverage (Saunders et al. 2015). Ridge-slough spatial gradients confirm that the Paq is a robust biomarker proxy capable of distinguishing between ridge and slough sources of organic matter, while kaurenes are a strong indicator of ridge vegetation and both the HBIs and botryococcenes exhibit considerable variability between sampling sites. The consistency in the Paq between sites is attributed to it being ratio rather than a concentration-dependent measurement like the other three biomarkers, rendering the Paq as more robust to changes in organic matter concentrations associated with fluctuating water depths and related ecological processes.

2.4.2 Principal component analysis

To summarize the spatial and temporal patterns present within the almost 400 samples collected during the study, biomarker data were subjected to principal component analysis (PCA), a multivariate statistical technique useful for dimensional reduction of large and complex environmental datasets. First, all four biomarkers were plotted using two principal components, which explained 62.6% of variability present in the dataset (Appendix 2.2). Since the data presented in Figure 2.2 demonstrate the high spatial variability present in the botryococcene measurements, PCA was performed again excluding botryococcenes to improve the statistical power of this analysis. The resulting PCA improved separation between sample types and explained 78.0% of variability, and was therefore selected to represent the dataset (Figure 2.3). Average loadings for each of the three biomarkers and for each sample type (ridge, slough and marsh traps) are also plotted in Figure 2.3 for reference. One site (CC2) was removed from the PCA as an outlier (PC1: -6.35; PC2: 5.15). This site was removed as there was only one sample and

Figure 2.3 Principal component analysis of samples collected throughout the study (n=393). Three biomarkers (Paq, HBIs and Kaurenes) were reduced to two principal components (PC1 and PC2). PC loadings for ridge, slough and marsh sites are shown as average values for each site (ridge sites are green triangles, slough sites are blue dots and marsh trap sites are brown open diamonds). The average of ridge, slough and marsh trap sites are shown for reference.

it is located in a degraded tree island dominated by invasive cattail and does not represent the ridge-slough landscape of interest well.

As shown in Figure 2.3, the ridge and slough samples cluster separately, with ridge samples featuring more negative PC1 values, while slough samples generally clustered closer to zero or positive PC1, driven primarily by the Paq. Marsh trap samples clustered more closely with slough than ridge sites, indicating enrichment in slough-like material in entrained sediments. As PC1 divides general ridge and slough clusters, and is strongly associated with the loading for Paq, it is clearly indicative of organic matter

source (slough versus ridge). Overlap between slough sites and ridge sites along PC1 is attributed to mixing of ridge and slough sources via entrainment of ridge floc into sloughs and settling of slough sediments on ridges. Furthermore, the majority of marsh traps exhibit PC1 loadings consistent with sloughs as the primary source of organic material entrained in the water column.

The boundary between ridge and slough sub-ecosystems is a gradient rather than a clear delineation, and so some overlap of these environments is expected. Both Figure 2.2 and PC1 in Figure 2.3 demonstrate the power of source-specific biomarkers, particularly the Paq, for distinguishing between ridge and slough organic matter, even in heterogeneous landscapes. In contrast to the Paq, both the HBIs and kaurenes have weaker loadings along PC1, but exhibit stronger PC2 values. Because there is no clear distinction between ridge and slough sources along PC2, we suggest that PC2 is driven by seasonality relating either to primary productivity patterns or inputs from periphyton-derived organic matter. Since HBIs are known to vary seasonally in the Everglades (Pisani et al. 2013), the similar distributions of ridge and slough sites along PC2 can be attributed to seasonal patterns in HBI production rather than the influence of sheetflow. Kaurenes sourced from sawgrass are not related to seasonal patterns in algae or periphyton, so the positive loading of kaurenes along PC2 is likely driven simply by the division between ridge and slough sites, as kaurenes are mostly absent in slough environments (Figure 2.2). Therefore, Figure 2.3 clearly shows the applicability of the Paq as a strong proxy for differentiating ridge and slough sources of organic matter, while kaurenes are only indicative of ridges and patterns in HBI concentrations are likely a function of seasonality rather than changes in flow. As such, the remainder of this

study focuses on the Paq patterns to interpret the spatiotemporal dynamics of floc and sediments in response to experimentally increased sheetflow.

2.4.3 Temporal trends

To assess temporal trends in Paq values, data were divided by sample type, and separated by sampling year (Figure 2.4). Ridge sites for all years except 2016 were statistically lower than all years for slough sites. A similar temporal trend is present for slough sites, where sampling year 2016 is significantly higher than the previous three years of samples. The Paq values of the marsh traps were all significantly higher than ridge samples from 2013 to 2016, and much more closely related to slough than ridge Paq values. A significant increase in ridge samples between 2013 and 2016 suggests that more slough-derived organic matter is being retained on the ridges over time. Following the increasing temporal trends observed for both ridges and sloughs, 2016 marsh trap samples exhibit a considerably higher average Paq, indicating the entrainment of slough-like sediments. These temporal trends may reflect the tendency for high flows to increase water levels (by 11-12 cm maximum at the high flow sites; Dreschel & Sklar, 2017), and longer hydroperiods associated with increased flow may shift towards a higher Paq signature (Saunders et al. 2015), although the associated changes in vegetation expected with a Paq shift are not yet evident in the test-plot. The increase in Paq during 2016 may also reflect greater redistribution of organic matter due to the emergency flows, which effectively increased the high flow period by 2.5 months. Regardless of drivers, the clear distinction in Paq values between ridge and slough sources along with general increasing temporal trends in floc and sediment samples provide evidence that, through consecutive

years of increased flow, the sediments sampled in the DPM footprint are increasingly slough-derived compared to baseline pre-flow samples.

To further investigate the effects of flow on mobilization of sediments from the ridge-and-slough landscape, the dataset was again classified by sample type, but this time was divided into groups based on flow conditions (Figure 2.5). “BEFORE” indicates low flow samples collected prior to the first high flow event. “HIGH” samples were collected during the three flow events, and “AFTER” samples were collected during low-flow conditions after the three flow events. In addition, “CONTROL” sites are separated out for comparison with samples collected along the southern flowpath (see shaded area in Figure 2.1). As marsh sediment traps were unable to collect sufficient quantities of sediment for analysis during low flow periods, all marsh values in Figure 2.5 correspond to high flow and are therefore divided into ridge and slough for interpretation. As observed in Figure 2.4, ridge samples have lower Paq values, where BEFORE, HIGH and CONTROL groups are all statistically lower than both slough and marsh trap groups. Also consistent with Figure 2.4, increasing Paq trends are evident for ridge and slough floc samples from BEFORE to AFTER. It is interesting to note that both ridge and slough floc exhibit a continued increasing trend in Paq after flow rates were reduced back to low-flow conditions. Such a delayed response may suggest either continued settling of sediments trapped in vegetation or that sediments with a strong slough signature continue to mobilize for some time after flow disturbance. Of the two mechanisms, the former seems more likely, as during the AFTER period, mid-water column velocities were <1 cm/s at all sites (C. Saunders, unpubl. data), including impact sites, below the typical entrainment threshold of Everglades sediments (Larsen et al., 2009).

Figure 2.4 Boxplots for Paq values for all samples divided by sample site type and sub-divided by year to show temporal patterns. Statistical differences between sub-groupings are indicated by letters, where different letters indicate significant differences ($p < 0.05$).

Figure 2.5 Boxplots for Paq values for all samples divided by sample site type and sub-divided by flow conditions. Statistical differences between sub-groupings are indicated by letters, where different letters indicate significant differences ($p < 0.05$).

The study site (Pocket) has been cut off from sheetflow for decades, resulting in ponding and loss of ridge-slough microtopography (Ogden et al. 2005), converting the landscape to a flatter, more drained region isolated from seasonal inundation. When impoundment occurs, the standard bimodal distribution of elevation in ridge-and-slough wetlands can shift towards a more homogenous, unimodal distribution (Watts et al. 2010). With these drier conditions, increased intrusion of marsh plants like sawgrass into slough areas may occur (Bernhardt and Willard, 2009; Saunders et al., 2015). Based on this, the increasing Paq trends at ridge and slough sites from BEFORE to AFTER may initially reflect scouring of older, more ridge-like material deposited during impoundment of the Pocket. Although measurable accretion occurs at inter-annual time-scales (<5 mm/year (Craft & Richardson, 1993)), and is therefore outside the temporal scope of the current study, our data suggest that mobilized sediments are becoming increasingly slough-like, and the consistency of this pattern at ridge sites suggests that these sediments may be settling in ridge regions.

The CONTROL group for ridge sites is not statistically different from BEFORE, HIGH, or AFTER, which is consistent with sites relatively unaffected by flow. In contrast, CONTROL samples from slough sites are significantly more enriched in slough-like material (or depleted in ridge-like material) relative to BEFORE and HIGH groups. This likely reflects the fact that water depths at the C1 control site (both ridge and slough) were on average 6 cm deeper than at RS1 (C. Saunders, unpubl. data). Potential explanations for the unexpected behavior of the slough CONTROL site include flow direction and site topography. Dye experiments to track flow from the S-152 structure during increased flow conditions indicate that, contrary to expectations based on

microtopography, much of the flow moved to the east in the direction of C1 rather than to the south (Eric Cline, SFWMD, pers. communication;).

If influence of increased flow at C1 is partially responsible for the Paq patterns at the slough CONTROL site, it would follow that similar patterns would be present for ridge CONTROL sites, the majority of which were collected near the C1 slough site. This is not evident in Figure 2.5, which could be explained by the large change in elevation between C1 ridge and slough sampling sites, where the ridge topography may attenuate local flow velocities (Larsen et al. 2009; Choi & Harvey, 2014). For context, Watts et al. 2010 reported that conserved (i.e. relatively undisturbed) ridge-slough landscapes show an average difference between ridge and slough elevations of 20 cm or more, while impacted sites showed considerably smaller differences in the range of 0-15 cm. The elevation difference measured at C1 is 18.2 cm, falling nearer to a conserved ridge-slough environmental, while the nearby Z6-1 site has an average elevation difference of 8.6 cm (C.Saunders, unpubl. data).

Figures 2.4 and 2.5 clearly indicate mobilization of slough-like organic matter, which agrees with the high Paq values present in advected sediment, collected from traps. Consistent with the hypothesized role of flow in restoring corrugated ridge/slough patterning, there is a clear temporal trend of increased Paq values in ridges, which can be attributed to settling of mobilized slough materials on the edges of ridges due to decreased flow velocities (Harvey et al. 2009; Larsen et al. 2011). However, a concurrent increasing trend in the slough sites is somewhat unexpected, and may be an artifact of decades of peat accretion in degraded sloughs that are more dominated by ridge environments (Bernhardt and Willard, 2009), or possibly changes in the types of slough

vegetation (Saunders et al., 2015) driven by flow. Given the short duration of flow events and the slow pace of wetland soil accretion in general (2-4 mm/year in ideal accretion conditions (Craft & Richardson, 1993)), the accretion in ridges or deepening of sloughs cannot be assessed in the study at this time. This notwithstanding, the Paq provides a robust metric to define relatively discrete ridge and slough sources of organic matter, and temporal patterns support a general increase in the amount of slough material being mobilized and entrained during increased flows.

2.5 Conclusions:

We applied a four-component suite of organic biomarkers to test the hypothesis that increased sheetflow is a viable mechanism for restoring ridge-slough microtopography in Everglades wetlands. Our data indicate that the Paq is the most applicable biomarker of the four selected, because, as a ratio, it is impervious to variability in concentration, and it clearly delineates ridge and slough sources of floc and sediments. Data collected along ridge-to-slough transects and in the greater DPM footprint throughout three consecutive periods of increased sheetflow clearly and consistently indicate that the Paq, and, by proxy, the amount of slough-derived material relative to ridge material, is increasing over time. Increasing trends suggest a shift from more ridge-like material to more slough-like material being mobilized, which is confirmed by high Paq values for entrained sediments collected by traps located in the marsh. The results presented provide initial validation of the hypothesis that sheetflow can rebuild ridge-and-slough microtopography. Testing hypotheses underpinning core tenets of hydrologic function in ridge-and-slough wetlands at the landscape scale is an essential step towards implementation and adaptive

management of Everglades restoration. The biomarker data presented here contribute to a more comprehensive picture of how sheetflow impacts Everglades ridge-and-slough landscape through sediment redistribution, a critical target for restoration.

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CHAPTER III

LONG-TERM ENVIRONMENTAL DRIVERS OF DOC FLUXES: LINKAGES BETWEEN MANAGEMENT, HYDROLOGY AND CLIMATE IN A SUBTROPICAL COASTAL ESTUARY

(Modified from *Regier et al., 2016; Estuarine, Coastal and Shelf Science*)

3.1 Abstract:

Urban and agricultural development of the South Florida peninsula has disrupted historic freshwater flow in the Everglades, a hydrologically connected ecosystem stretching from central Florida to the Gulf of Mexico, USA. Current system-scale restoration efforts aim to restore natural hydrologic regimes to reestablish pre-drainage ecosystem functioning through increased water availability, quality and timing. Aquatic transport of carbon in this ecosystem, primarily as dissolved organic carbon (DOC), plays a critical role in biogeochemical cycling and food-web dynamics, and will be affected both by water management policies and climate change. To better understand DOC behavior in South Florida estuaries and how hydrology, climate and water management may affect them, 14 years of monthly data collected in the Shark River estuary were used to examine DOC flux dynamics in a broader environmental context. Multivariate statistical methods were applied to long-term datasets for hydrology, water quality and climate to untangle the interconnected environmental drivers that control DOC export at monthly and annual scales. DOC fluxes were determined to be primarily controlled by hydrology but also by seasonality and long-term climate patterns and episodic weather events. A 4-component model (salinity, rainfall, inflow, Atlantic Multidecadal Oscillation) capable of predicting DOC fluxes ($R^2=0.84$, $p<0.0001$, $n=155$) was established and applied to potential climate change scenarios for the Everglades to assess DOC flux response to climate and restoration variables. The majority of scenario runs indicated that DOC export from the Everglades is expected to decrease due to future changes in rainfall, water management and salinity.

3.2 Introduction

Organic matter (OM) is an important biogeochemical component in coastal wetlands. Optically active fractions attenuate sunlight (Osburn et al. 2009), controlling *in situ* and benthic primary production. OM regulates metal speciation and mobilization (Yamashita & Jaffe 2008; Bergamaschi et al. 2012) and fuels microbial communities (Tranvik 1998). Significant portions of organic nitrogen (N) and phosphorus (P) are associated with dissolved OM (DOM) (Boyer et al. 1997; Boyer, 2006), controlling nutrient availability and transport (Qualls & Richardson 2003). Recently, carbon (C) cycling in coastal wetlands has attracted attention as an important global C sink (Bridgham et al. 2006) through accretion of peat and mangrove soils (Breithaupt et al. 2012; Grimsditch et al. 2013). In addition, aquatic OM transport from wetlands to coastal ocean margins, primarily as dissolved organic carbon (DOC), comprises a significant component of global oceanic C budgets (Hedges et al. 1997). Annual to decadal patterns and controls of DOC export have received significant attention in northern latitudes where long-term increases in DOC concentration have been observed in surface waters (Freeman et al. 2001; Worrall et al. 2004; Filella & Rodríguez-Murillo 2014). While hydrology is generally the primary control on DOC flux magnitudes, a wide range of factors have been identified as potential drivers of long-term patterns and changes in DOC export. For example, climate-controlled parameters including temperature (Evans et al. 2005) and precipitation (Pumpanen et al. 2014), seasonal cycles (Clark et al. 2005; Sánchez-Carrillo et al. 2009), land-use factors like drainage and water management (Krupa et al. 2012) and nutrients (Dittmar & Lara 2001) have all been linked to long-term trends and patterns of DOC transport. However, equivalent

understanding of DOC flux in lower latitude systems is lacking (Filella & Rodriguez 2014) with little to no information on annual to decadal C export trends in many areas, including the Florida Everglades. As these regions contain some of the most productive ecosystems on earth and face mounting pressures from anthropogenic and climatic forces (Erwin 2009; Mitsch & Hernandez 2013), closing this knowledge gap is crucial to constrain global C export estimates.

Along with global ramifications, the environmental controls of DOC transport have important system-scale implications for environmental management and restoration projects like the Comprehensive Everglades Restoration Plan (CERP). Historic drainage and development of the Florida Everglades has compartmentalized the previously hydraulically connected flow path, isolating downstream regions including Everglades National Park (ENP) from natural freshwater delivery patterns (McVoy et al. 2011). Restoration efforts guided by CERP are focused on “getting the water right” by increasing freshwater delivery to ENP while maintaining water quality standards (Sklar et al. 2005). However, progress is hindered by uncertainty regarding ecosystem response to altered freshwater flow regimes and the potential impacts of climate change, specifically sea-level rise (SLR) (Estenoz & Bush, 2015). This is particularly important in the estuarine region of ENP which is highly susceptible to saltwater intrusion due to low-lying topography and karstified bedrock but simultaneously dependent on freshwater inflows controlled by water management infrastructure (Price et al. 2006; Saha et al. 2012). While significant efforts to constrain C budgets in ENP have refined our understanding of how C moves through the Everglades (Romigh et al. 2006, Bergamaschi et al. 2012, Troxler et al. 2013, Cawley et al. 2014,), a critical knowledge gap regarding

the patterns, magnitudes and drivers of DOC fluxes at annual to decadal temporal scales remains. This is important information for adaptive management of Everglades restoration (Nungesser et al. 2014) since current studies of OM fate and transport rarely span more than a year or two, limiting our understanding of the impact that drivers acting at annual timescales (e.g. land use, water management and climate) may have. Due to the lack of long-term DOC flux information in the Everglades (Childers, 2006), the drivers of annual to decadal DOC export are not well understood for this system. This study seeks to address this knowledge gap through interpretation of long-term DOC flux data along the primary drainage of ENP, Shark River Slough by addressing two questions:

1. What drives monthly and yearly variation of DOC fluxes in the Shark River?
2. What changes in DOC fluxes are predicted by these drivers based on climate change scenarios for the region?

3.3 Methods:

3.3.1 Site description

Shark River Slough (SRS), located at the northern border of ENP, is a low-lying marshy area whose channels deliver the majority of fresh water flowing through the Everglades. This slough spans salinity and vegetation gradients, with freshwater wetlands in the northern slough dominated by sawgrass and 0.3-1.5 m of organic-rich peat soils on top of karstified carbonate bedrock draining into the Shark River estuary, the largest contiguous mangrove forest in the continental USA (Lodge 2010). The estuary empties into Ponce de Leon Bay, a shallow embayment connected to the Gulf of Mexico. This

study focuses on data collected at or near SRS-5 (Figure 3.1), a long-term sampling site for the Florida Coastal Everglades Long-Term Ecological Research project (FCE-LTER, fcelter.fiu.edu). SRS-5 was selected for its mid-estuarine location adjacent to USGS hydrologic gage #252230081021300. The Everglades has distinct seasonality, with a dry season from November-April and a wet season from May-October. Since seasonal transition periods make defining the start and end of the wet season ambiguous, a threshold of 70 mm for average monthly rainfall during 2001-2014 was used to confirm the seasonal division of months for this study. The wet season receives more than 60% of annual rainfall (Duever 1994) with lower salinities throughout the tidal region, and increased temperatures leading to higher evapotranspiration (ET) rates. Inflows from water management structures to ENP also follow seasonal hydrologic patterns but generally lag behind rainfall patterns by 1-2 months.

3.3.2 Data collection

The selection of variables for multivariate analysis and modeling was guided in part by a conceptual ecological model for the South Florida water column presented in Wingard and Lorenz (2014). The model provides a general framework of drivers, pressures and ecological processes linked to a range of measureable attributes and ecosystem services (Appendix 3.4) and “Hydrology and water quality” was selected as the measureable attribute most representative of DOC fluxes. Variables identified as potentially relevant to DOC fluxes based on the linkages in the conceptual model were included in the study only if available data covered the entire time-period for the study and minimal gap-filling (<10%) was required. As indicated by the conceptual model, variables selected to explain DOC fluxes cover a broad spectrum of processes from

Figure 3.1 Map of Everglades National Park (ENP) showing the location of SRS-5 in Shark River Slough. The ENP boundary is marked by a dashed line. Inflow structures are marked as arrows along the northern border of ENP.

system drivers to ecosystem services. While this approach allows for assessment of potential drivers across a broad range of temporal and spatial scales, it is likely that feedback loops and/or redundant variables exist within the selected dataset.

Data collection focused on FCE-LTER data products, which provide continuous monthly coverage of water quality parameters from May 2001 to September 2014, with additional inputs from USGS hydrology and NOAA climate data resources (Table 3.1). When multiple datasets for the same parameter were available, preference was given to higher frequency measurements that are more likely to accurately capture rapid fluctuations that represent key ecological events in temporally variable ecosystems (Kirchner et al. 2004; Krause et al. 2015). All variables were binned (averages or sums) to monthly and yearly resolutions for monthly and annual analysis. Multiple parameters

were collected from a common dataset when possible since sampling at different points in the tidal cycle, even on the same day, can produce varied results (e.g. Twilley 1985). Measurements of a particular unit type (e.g. units of distance) were normalized to common units (e.g. mm). DOC fluxes were calculated as the product of monthly DOC concentrations and monthly sums of tidally filtered discharge (m^3/month). Gap-filling of missing values via multiple imputation using the ‘Amelia’ package in R (Honaker et al. 2011). Each missing value was filled with the average of five imputation runs, with no gaps longer than 2 consecutive entries were filled (53 imputed values filled, less than 2% of total data-set). For detailed information on data collected for multivariate statistics, see Appendix 3.1.

3.3.3 Statistics

The Seasonal Mann-Kendall test was used to determine if significant long-term trends were present for each variable (Hirsch et al. 1982), using the “Kendall” package in R (McLeod, 2011). Multivariate analyses of z-score normalized data were conducted using Principal Component Analysis (PCA) performed with all variables in Table 3.1 using the JMP® Version 12 statistical package (SAS Institute Inc., Cary, NC, 1989-2007). Since DOC flux is calculated from DOC concentration and discharge and is therefore dependently related to these variables, PCA plots for monthly and annual data were first plotted with DOC flux removed from the variable pool and then with DOC concentration and discharge removed but keeping DOC flux. Wilcoxon rank sums tests indicated that PC loadings including and excluding DOC concentration and discharge were not statistically different for monthly ($Z=0.19$, $p=0.84$) or annual ($Z=0.08$, $p=0.93$) datasets. Thus, although a dependent relationship is present, it does not affect the

interpretations made in the following sections and DOC flux is plotted for PCAs as a convenient reference point.

3.3.4 Modeling DOC fluxes

Modelling of DOC fluxes was conducted using all the variables from multivariate analysis (excluding DOC concentration and discharge) as independent variables, with model selection and validation conducted in JMP. To avoid over-fitting, parameters were selected via backwards stepwise regression using the lowest Akaike Information Criterion (AIC) and Bayesian Information Criterion (BIC) values as cutoffs (Akaike, 1974; Schwarz, 1978). Four independent variables were selected via stepwise regression for modelling DOC fluxes: salinity, rainfall, inflow and AMO. It is noted that salinity correlates to discharge, and was used to calculate DOC fluxes. However, salinity represents an important parameter for interpreting estuarine processes, particularly in the Shark River due both to unique “upside-down estuary” characteristics where salinity mediates primary productivity in the mangrove ecotone (Childers et al. 2006) and high vulnerability saltwater intrusion due to topography. For this reason, salinity remained in the model, though it is important to consider this relationship when interpreting model results. The four-component model yielded AIC and BIC values of 6910.26 and 6927.56, respectively, and was selected over a three component model excluding AMO (AIC=6920.35, BIC=6934.84) and a five component model including SL (AIC=6909.87, BIC=6929.94). Components selected as predictors were tested for normality using the Shapiro-Wilk test (Shapiro & Wilk, 1965) and non-parametric components were transformed via Box-Cox transform methods (Box & Cox, 1964). Next, DOC fluxes were modeled with both transformed and untransformed predictor variables using

multiple linear regression with a standard least squares model personality. The final model was selected from all possible configurations of transformed and untransformed predictors by the highest R^2 value. Model components were validated by t-ratios and the overall model was statistically validated by the ANOVA-derived F-ratio, with model error determined by the individual 95% confidence intervals for each point and the standard error for the model as a whole (see Appendix 3.2).

3.3.5 Modeling DOC flux response to climate change

After model construction, a range of climate change scenarios based on recent downscaled climate modeling of ENP over a 50-year time window (Obeysekera et al. 2014) were used to manipulate model predictor variables (Table 3.3). For all scenarios, a 1.5°C increase in temperature with an associated increase in evapotranspiration, and sea-level rise (SLR) of 0.46 m is assumed (Obeysekera et al. 2014). Downscaled global climate models (GCMs) for the Greater Everglades Ecosystem (GEE) do not have sufficient resolution to determine if long-term precipitation trends will increase or decrease so both +10% rainfall (+RF) and -10% rainfall (-RF) conditions were considered. The accompanying changes for inflows were an increase of 22% for +RF or a reduction for -RF of 58% (Obeysekera et al. 2014). For consistency with previous nomenclature, +ET was added to +RF and -RF giving two basic scenarios: +RF+ET and -RF+ET (Obeysekera et al. 2014). Other parameters selected as model predictors that weren't explicitly quantified by Obeysekera et al. 2014 were adjusted based on best available estimates (see Section 3.4.4).

Figure 3.2 DOC concentrations, discharge rates and DOC fluxes are presented for SRS-5 for 2001-2014. Wet season months are shown as black line segments with gray line segments representing dry season months. Vertical lines indicate tropical storm events: hurricanes (solid black), tropical storms (dashed black) and tropical depressions (dashed gray). The two periods of extreme drought during the study period are shaded in gray.

Table 3.1: Multivariate data abbreviations, units, gap-filling, 2001-2014 means and SD, data sources and measurement frequency

Variable	Abbr.	Units	% gap-fill	Mean±SD	Data Source	Frequency
Dissolved Organic Carbon	DOC	µM	4%	1097.2 (233.2)	FCE-LTER	Monthly
Tidally Filtered Discharge	Disc	m³ s⁻¹	1%	9.2 (9.0)	USGS	Hourly
DOC Flux	Flux	mg C d⁻¹	0%	1.1E+10 (1.0E+10)	This study	Monthly
Total Nitrogen	TN	µM	1%	40.2 (16.6)	FCE-LTER	Monthly
Total Phosphorus	TP	µM	4%	0.51 (0.31)	FCE-LTER	Monthly
Salinity	Sal	N/A*	7%	15.1 (6.8)	USGS	Daily
Water Level	WL	cm	0%	854.5 (158.0)	EDEN	Daily
Water Management Inflows	Inflow	m³ s⁻¹	0%	22.1 (27.9)	USGS	Daily
Sea Level**	SL	mm	0%	1703.9 (90.1)	NOAA***	Daily
Temperature	Temp	°C	1%	24.4 (3.6)	NOAA***	Daily
Rainfall	RF	mm	1%	105.5 (89.9)	EDEN	Hourly
Evapotranspiration	ET	mm	0%	119.7 (39.3)	EDEN	Hourly
Drought	Drght	%	0%	0.38 (0.36)	UNL	Weekly
El Niño	ENSO	N/A	0%	0.04 (0.77)	NOAA	Monthly
Atlantic Multidecadal Oscillation	AMO	N/A	0%	N/A	NOAA	Monthly

SD - standard deviation; Abbr. - abbreviation

EDEN - Everglades Depth Estimation Network (<http://sofia.usgs.gov/eden/>)

FCE-LTER - Florida Coastal Everglades Long-term Ecological Research Project (<http://fcelter.fiu.edu/data/core/>)

NOAA - National Oceanographic and Atmospheric Administration (<http://www.esrl.noaa.gov/>)

UNL - University of Nebraska - Lincoln (droughtmonitor.unl.edu)

USGS - Gages 252230081021300; 254543080491101; 2289019; 2289041; 254543080405401 (waterdata.usgs.gov/)

* salinity reported in PSU (unitless)

** measured at Key West (~120 km from SRS-5)

*** data accessed via <http://fcelter.fiu.edu/data/core/>

3.4 Results:

3.4.1 DOC concentration, discharge and DOC flux patterns

DOC fluxes were calculated from DOC concentration and discharge (Figure 3.2). DOC concentrations are significantly lower ($p < 0.05$) in the wet season which is attributed to dilution from increased freshwater delivery to the estuary, though clear seasonal patterns were not observed. The periods of lowest DOC concentration correspond to the two periods of extended drought (2007 and 2010-2011), followed by increased concentrations post-drought.

In contrast to DOC concentration, discharge has a clear seasonal signature with onset of the wet season corresponding to increasing discharge following approximately a one-month lag. Decreased rainfall and inflows translate to the lowest discharge year during 2007, the period of most pronounced drought during this study. In 2010-2011, drought is also associated with low discharge, although not as pronounced as 2007. Tropical storms also appear to influence discharge regimes, with the highest discharge for a full year in 2005 corresponding to the only two hurricanes (Katrina and Wilma) during this time-period. Tropical storms Ernesto (2006) and Fay (2008) are also associated with increased discharge, while tropical depressions Ivan (2004) and Bonnie (2010) do not have apparent impacts on discharge.

DOC flux patterns combine the influences of DOC concentration and discharge, but are primarily driven by discharge ($R^2 = 0.96$) compared to DOC ($R^2 = 0.03$) (coefficients of determination for all variables in Table 3.1 at monthly and annual temporal resolution are located in Appendix 3.6 and Appendix 3.7, respectively). As with

discharge, DOC fluxes increase with tropical storms and decrease during periods of extreme drought.

3.4.2 Principal component analysis

PCA techniques were applied at monthly and yearly temporal resolution (Figures 3a and 3b, respectively) for dimensional reduction of the wide range of environmental variables to find the primary sources of variability within the dataset. The number of principal components selected was based on the knee of the scree plot of eigenvalues with only eigenvalues explaining 15% or more of variability in the dataset allowed (two components were selected for each PCA). Rotation of principal components did not improve variability explained for monthly or yearly data (monthly PC1+PC2 variability explained: 53.6% (un-rotated) versus 53.5% (rotated); yearly PC1+PC2 variability explained: 59.9% (un-rotated) versus 59.9% (rotated)). The strength of association between variables and each of the principal components is presented in loading plots (Figure 3.3a and 3.3c) and the relationships between principal components and each observation are shown as score plots (Figure 3.3b and 3.3d).

Figure 3.3 Principal component analysis (PCA) for Table 3.1 variables. Axes are labeled with the percent variability explained by each principal component. Loading plots (a and c) and score plots (b and d) display PCA results for monthly (a and b) and annual (c and d) temporal resolutions. For 3.3b, black dots are wet-season months and gray dots are dry-season months. For 3.3d, dashed black ovals divide years with below average flux values (Low Flux) from years with above average fluxes (High Flux).

3.4.2.1 Monthly principal component analysis

The monthly loading plot (Figure 3.3a) clearly shows that DOC fluxes are closely associated with PC1 (loadings presented in Appendix 3.5). PC1 also couples with discharge, inflow and water level (loadings of 0.91, 0.85 and 0.91, respectively) all of which link to freshwater hydrology. Negative PC1 correlates most strongly with salinity (loading of -0.84), a further indication that PC1 relates to freshwater discharge to the estuary. PC2 exhibits a weak relationship to DOC flux (loading of -0.16), but strong positive correlations with temperature, ET and RF (loadings of 0.82, 0.90 and 0.72, respectively), indicating a link to seasonal climatic patterning. As rainfall is the largest freshwater input to the Shark River (Saha et al. 2012), RF patterns would be expected strongly correlate to freshwater delivery and therefore DOC fluxes. However, only a weak correlation between RF and flux exists ($R^2=0.11$, Appendix 3.6) while flux and inflow more closely co-vary ($R^2=0.48$, Appendix 3.6). This is likely due to the spatially distributed nature of rainfall versus point-source inputs from inflow structures. Furthermore, rainfall is highly variable from day to day while inflow magnitudes exhibit a less variable hydrograph (see inflow data, <http://waterdata.usgs.gov/> and precipitation data, <http://sofia.usgs.gov/eden/>). The score plot for monthly data (Figure 3.3b) reaffirms the association of PC1 with hydrology and PC2 with seasonal climate. Wet season and dry season points clearly separate along PC2 with high flux months positioned at positive PC1 and low flux months at negative PC1 values.

3.4.2.2 Annual principal component analysis

The annual loading plot (Figure 3.3c) gives a similar explanation for PC1 as observed in Figure 3.3a (2001 and 2014 are excluded as incomplete years). DOC fluxes

correlate strongly with PC1 which again is primarily associated with freshwater hydrology, represented by discharge, inflow and WL (loadings of 0.78, 0.81 and 0.82, respectively). However, seasonality does not explain PC2 even though temperature and RF are still the primary separator variables. Unlike Figure 3.3a, temperature and RF in Figure 3.3c act as end-members along the yearly PC2 axis (loadings of 0.93 and -0.91, respectively), indicating a decoupling of seasonally correlated variables. In addition, ET is no longer strongly associated with PC2. The third strongest PC2 correlation is AMO, a decadal climatic index associated with long-term RF and temperature patterns (Knight et al. 2006), although a much weaker relationship is observed (loading = -0.56). Both AMO and RF are negatively correlated to PC2, suggesting annual trends in climate that influence temperature and rainfall patterns are likely primary drivers of PC2.

Figure 3.4 Monthly DOC fluxes predicted via multiple linear regression plotted against actual monthly flux values. Figure 3.4a shows the initial model using untransformed salinity ($R^2=0.78$, $p<0.0001$, $n=155$). Figure 3.4b is the final model predicted using log-transformed salinity ($R^2=0.84$, $p<0.0001$, $n=155$). Confidence intervals (95%) are shown in dark gray dashed lines.

In the annual score plot (Figure 3.3d), a division between high and low flux years (relative to the average annual flux of 1.06×10^{10} mg C d⁻¹) separates the dataset with high flux years clustering at positive PC1 values and low flux years clustered at negative PC1.

This division aligns directly with AMO and perpendicular to ENSO, the two long-term climatic indices included in multi-variate statistics. The influence of each index in separating years can be understood by its axis which runs orthogonally to its loading vector. AMO, which correlates to RF at monthly and annual scales, divides drought and hurricanes with all storm years located at negative PC2 values. In contrast, ENSO's axis separates low flux years from high flux years.

3.4.2.3 Nutrients and DOC dynamics

As the majority of nitrogen and phosphorus pools in the Everglades are associated with DOM, it is assumed that TN and TP co-vary in some manner with DOC. Nutrients play critical roles in the oligotrophic coastal estuaries of ENP, particularly P, which is the limiting nutrient of primary productivity in the mangrove ecotone (Childers et al. 2006). However, only weak associations for TN and TP are observed with DOC concentrations or fluxes for this data-set (see Figure 3.3 and Appendices 3.6 and 3.7). These relationships will not be discussed further in this study, but readers are directed towards an array of publications focused on N and P dynamics in ENP (e.g. Price et al. 2006, Briceño & Boyer, 2014, Orem et al. 2015).

3.4.3 Modeling long-term DOC fluxes

Multiple linear regression modeling of four independent variables (salinity, rainfall, inflow and AMO) explained 78% of the variance in DOC fluxes during the 14 years of the study (Figure 3.4a) with salinity contributing the most predictive power to the model followed by inflow, rainfall and AMO (see Appendix 3.8). As non-normality was observed in predictor variables, transformed variables were remodeled as described in Methods section 3.3.4. A four-component model was again selected (AIC=6866.99,

BIC=6884.29) and performed better than either the three-component model (AIC=6880.65, BIC=6894.14) or five-component model (AIC=6866.42, BIC=6886.49). The final model (Figure 3.4b) contained transformed salinity (power of 0.1) along with untransformed rainfall, inflow and AMO and predict 84% of DOC flux variability. Of the four predictors, log-transformed salinity provided the most modelling power (60.4%), followed by rainfall, inflow and AMO (20.8%, 11.1% and 7.7% of total model power, respectively) as shown in Table 3.2. The root mean square error for the final model was $3.79\text{E}+9 \text{ mg C d}^{-1}$ (or $\pm 37.1\%$). Although techniques like Monte Carlo resampling may be beneficial for reducing this uncertainty, they were beyond the modelling scope of the present study.

Table 3.2: DOC flux model predictor variables

Initial Model		
Source	% model power*	p-value
Sal	52.5%	<0.0001
Inflow	20.2%	<0.0001
RF	20.0%	<0.0001
AMO	7.4%	0.0004
Final Model		
Source	% model power*	p-value
LogSal**	60.4%	<0.0001
RF	20.8%	<0.0001
Inflow	11.1%	<0.0001
AMO	7.7%	<0.0001

* percent of total model predictive power provided by individual predictor variables

** log-transformed salinity

It is noted that the change between normal salinity and log-transformed salinity as a model predictor altered the power distribution for model components, with salinity,

rainfall and AMO each increasing in modeling power (+17.3%, +4.2% and +1.7%, respectively) while inflow decreased by 5.3%. While this is an important reminder of how data transformation of independent variables can strongly alter model outputs, it is noted that the general drivers stayed the same between models. In both, salinity is the strongest independent variable (more than double the modeling power of any other parameter) while the influence of freshwater (RF and inflow) does not change appreciably between the two model runs (31.9% of predictive power for the original model vs. 33.0% for the log-transformed salinity model). Thus, while the results of modeling are sensitive to changes in parameters, it is observed that the general implications of the original model are not considerably changed in the final model. As an additional check of model sensitivity, 10 random noise variables of different magnitudes were inserted into the candidate pool of predictors and stepwise regression was rerun. The four original model components were selected, providing evidence that the model is not sensitive to random noise. For additional model validation, see Appendix 3.2.

3.4.4 Predicting DOC flux response to climate change forecasts

For the four components selected for the DOC flux model, rainfall and inflows were both explicitly modeled (see Section 3.3.5), while salinity and climate impacts from AMO were not (Obeysekera et al. 2014). Salinity and sea-level are not strongly correlated during this study, likely due in part to the strongly skewed distribution of salinity (Shapiro-Wilk test: $W=0.95$, $p<0.0001$) compared to normally distributed sea level (Shapiro-Wilk test: $W=0.99$, $p=0.43$). Several treatments were applied to +RF+ET and -RF+ET scenarios to represent the broad range of potential salinity changes over 50 years of SLR. The treatments were no increase (+0), a conservative increase (+1), a

moderate increase (+5) and a large increase (+10), equivalent to +76% of the median salinity (13.1) at SRS-5 during the study period. The final model parameter, AMO, varies on a 60-year oscillation following the North Atlantic Oscillation (Sun et al. 2015), making it difficult to predict changes over a 50-year window. As such, AMO was treated as static for all forecasting scenarios.

Table 3.3 Changes in predictor variables for modeling DOC flux response to climate change scenarios

Scenario	RF	Inflow	Salinity	% Change*
+RF+ET	+10%	+22%	0	+7%
+RF+ET+1	+10%	+22%	+1	-5%
+RF+ET+3	+10%	+22%	+5	-42%
+RF+ET+5	+10%	+22%	+10	-77%
-RF+ET	-10%	-58%	0	-13%
-RF+ET+1	-10%	-58%	+1	-24%
-RF+ET+3	-10%	-58%	+5	-61%
-RF+ET+5	-10%	-58%	+10	-96%

+RF+ET: 10% increased RF; -RF+ET: 10% decreased RF

* % change in average DOC flux compared to 2001-2014 average

DOC fluxes were calculated for each scenario by manipulating predictor variables according to Table 3.3, with the average change for DOC fluxes throughout the study period reported as % change (Table 3.3). For +RF+ET with increased inflows and static AMO, baseline salinity (+0) resulted in the only increased DOC flux prediction (+7%) of all modeled scenarios, while for -RF+ET, baseline salinity conditions resulted in a -13% change in DOC fluxes over the study time-period. A conservative +1 increase in salinity yields 5% and 24% decreases in average DOC fluxes for +RF+ET and -RF+ET scenarios respectively, while +5 and +10 salinity scenarios forecasted significant decreases in DOC

fluxes greater than the 37.1% average model error. Thus, only dramatically increased freshwater inflows combined with a very conservative estimate for SLR will maintain current DOC flux regimes, while either a decrease in rainfall or increase in SLR suggest considerable reductions in export of DOC from the region.

3.5 Discussion:

3.5.1 Long-term DOC flux drivers

3.5.1.1 Hydrology controls monthly DOC fluxes

As would be expected in an estuarine system, freshwater and saltwater inputs act as endmembers along the hydrologically controlled monthly PC1 axis, with DOC flux correlated more strongly to inflows than RF (Figure 3.3a). Similar patterns for annual data confirm the crucial role water management plays across time-scales in hydrology-mediated transport of DOC through ENP (Figure 3.3b). These results match previous findings by Saha et al. 2012 indicating that, while RF provides the majority of freshwater to the Shark River, inflows control freshwater delivery patterns, maintaining ecosystem function and hydrologic connectivity along the Everglades flow-path. The strength of this relationship indicates that variables associated with PC1 are useful proxies for freshwater inputs (variables positively correlated to monthly PC1) and saltwater influence (variables negatively correlated to monthly PC1). These proxies are seasonally robust, with PC1 strongly correlating to both wet season and dry season DOC fluxes ($R^2=0.77$ and 0.79, respectively).

3.5.1.2 Climatic control of DOC fluxes

Linkages between ENSO and DOC export have been reported elsewhere (Mengitsu et al. 2013; Ovalle et al. 2013) and ENSO is already identified as a strong predictor of discharge patterns across time-scales ranging from years (Ovalle et al. 2013) to centuries (Wanders & Wada, 2015). However, modelling results determined that AMO, not ENSO, is the better climatic index for predicting monthly DOC fluxes for this dataset (Table 3.2). As AMO varies on an oscillation of approximately 60 years that follows the North Atlantic Oscillation (Enfield et al. 2001; Sun et al. 2015), it is interesting that a study covering just 14 years identifies AMO co-varying with DOC fluxes at annual resolution. Furthermore, AMO is currently two decades into a positive phase, suggesting a transition to a negative phase within the next several decades is likely (Drinkwater et al. 2014). Historical data for the region indicated that inflows to Lake Okeechobee in the headwaters of the GEE were cut in half between consecutive positive (1930-1964) and negative (1965-1990) AMO phases (Enfield et al. 2001). Thus, it is expected that as AMO transitions from positive to negative in the coming decades, freshwater delivery to the region via RF will decrease dramatically.

Results from this study suggests that, while RF and temperature are seasonally correlated (Figure 3.3a), annual patterns are diverging (Figure 3.3c). Multi-decadal trends in RF and temperature data collected at the Flamingo Ranger Station (28 km from study site, data retrieved from fcelter.fiu.edu/data/core/) show a significant increasing trend for temperature ($\tau=0.07$, $p<0.05$, Appendix 3.9) and a non-significant decreasing trend for RF ($\tau=-0.02$, $p=0.50$, Appendix 3.9). RF trends during the wet season have already been reported for Florida using century time-scale data (Irizarry-Ortiz et al.

2013). Together, increasing temperature (and subsequently increasing ET) combined with decreasing RF and a potential negative shift in AMO (see section 3.5.1.2) all point towards climate-induced reductions in freshwater availability to the estuary.

3.5.1.3 Drought and DOC fluxes

The relationship between PC2 and extreme weather events (Figure 3.3d) indicates the influence of episodic (tropical storm) and persistent (drought) events on annual DOC export regimes. Drought years are associated with below average DOC fluxes due to reduced rainfall and associated reductions in discharge to the Shark River (Figure 3.3c). For upstream wetland regions, higher drought means lower water levels, disrupting anoxic conditions favorable for peat accretion. While several studies support increased DOC loss from wetlands under enhanced drought conditions (Freeman et al. 2001; Ise et al. 2008; Fenner & Freeman, 2011), evidence has emerged that does not support the correlation between drought and DOC loss (Laiho 2006; Muhr et al. 2010), with some studies suggesting enhanced accumulation based on environmental feedbacks like phenolic inhibition of soil respiration (Wang et al. 2015). As such, the negative relationship between drought and DOC fluxes observed anecdotally for 2007 and 2010 (Figure 3.2) may represent the relationship between discharge and flux. However, it does not account for potentially contradictory drought impacts on the balance between accumulation and decomposition of peatlands upstream which contribute a large portion of DOC exported by the Shark River (Cawley et al. 2014) and could therefore dramatically alter DOC concentrations entering the estuarine ecotone.

3.5.1.4 Storms and DOC fluxes

The influence of episodic storm events on DOC flux magnitudes is observed for each of the 6 months associated with storms (vertical lines in Figure 3.1), each of which surpasses the 90th percentile for monthly DOC fluxes for this study. As a group, these 6 months have significantly higher DOC flux values than either the average wet season or dry season fluxes (Wilcoxon test, $p=0.023$ and $p=0.0003$ respectively). Immediate and delayed storm impacts on DOC fluxes are most evident for Hurricane Wilma, the strongest storm to hit the estuary during the study period. Following the storm, DOC flux values spiked above the 97.5% percentile, the highest flux rate between 2003 and 2014 (Figure 3.1). Deposition of up to 4.5 cm of calcareous sediment and a 3 m storm surge associated with Wilma destroyed large portions of the coastal mangrove (Castañeda-Moya et al. 2010). These changes have since altered sediment composition along the estuary (Breithaupt et al. 2012) and primary production as mangrove forests recover (Castañeda-Moya et al. 2010), processes that continue to influence long-term DOC production and transport. With intensity of tropical storms predicted to increase due to future changes in climate (IPCC, 2014), it is anticipated that DOC export will be increasingly affected by these events.

3.5.2 Modelling long-term DOC fluxes

Of the four model predictors identified for the final model, the three most powerful predictors relate to the estuarine salinity gradient which is controlled by freshwater inputs, tidal influence and long-term SLR trends (estimated at 2.61 mm yr⁻¹ for ENP by Stabenau et al. 2011). Accelerating SLR rate projections along with uncertainty surrounding future freshwater availability to the coastal ecotone highlight the

increasingly important function of the salinity gradient in regulating C export in the coastal Everglades (SFRCC, 2011; Obeysekera et al. 2014). Future changes in inflow will be based on water management decisions which will, in turn, be based on availability of freshwater supplies as increasing urban demand is fed from the same freshwater stocks used for water management inflows to ENP. While AMO is not directly related to the balance of freshwater and saltwater here, it has been linked to long-term rainfall, temperature and freshwater flow changes. As such, it constitutes a key climatic driver of water budgets and wet/dry year patterning (Enfield et al. 2001; Moses et al. 2013) and potentially long-term DOC trends (Mengitsu et al. 2013). Thus, all four model components seem to be inter-related, with the three most powerful predictor variables possibly driven at annual time-scales by AMO.

3.5.3 Predicting the effects of climate change scenarios on DOC fluxes

The +RF+ET run with no salinity change is the only scenario that predicts higher DOC fluxes, with more rainfall driving higher freshwater inflows to the coastal mangrove fringe (Table 3.3). More freshwater delivery will maintain stage in peat wetlands, minimizing oxidative loss of sequestered peat reserves while promoting C storage through primary production. In the estuarine zone, increased rainfall is expected to maintain the brackish ecotone, minimizing DOC loss from salinity-induced peat collapse and subsequent coastal erosion of organic-rich mangrove soils. However, the +RF+ET scenario with no change in salinity implies negligible impacts from sea-level rise, a highly unlikely scenario based on GCM predictions (IPCC, 2014). Under the +RF+ET +1 scenario (Table 3.3), freshwater inputs will mostly keep pace with rising seas, preserving the current salinity gradient and flux regimes. However, moderate or strong

salinity increases associated with SLR could shift the balance between decomposition and accretion of carbon (Larsen et al. 2010a). Potential die-offs of salt-intolerant communities due to enhanced saltwater intrusion could destabilize sequestered organic-rich sediments, leading to significant losses of current below-ground C stores (Orem et al. 2015) and altering the quality and quantity of DOC produced (Maie et al. 2006).

All decreased rainfall (-RF+ET) scenarios predict a net reduction in DOC flux due to diminished freshwater delivery to the estuary (Table 3.3). Reduced precipitation regimes are predicted to lower water levels across ENP by 0.1-0.2 m (Obeysekera et al. 2014), with a potential drop of up to 0.3 m in ridge-and-slough wetlands (van der Valk et al. 2015). This could increase hydrologic exchange with deeper pore water which exhibits higher DOC concentrations than surface water in both ridge and slough sub-ecosystems (Larsen et al. 2010b). Historically dry years will become the new average, accompanied by a narrowing of the SRS flow-path resulting in exposure of submerged peat deposits which could trigger oxidative peat loss (Orem et al. 2015). As submerged C stocks are exposed to dry-down conditions during prolonged drought, they will be more prone to wildfires which export OC from the system primarily through oxidation to CO₂ rather than aquatic transport as DOC (Page et al. 2002). Decreased freshwater pressure may also enhance saltwater intrusion via coastal groundwater discharge (Price et al. 2006) with consequent pulses of saltwater into freshwater wetlands anticipated to decrease DOC export from marshes (Morris et al. 2002; Chambers et al. 2013).

With enhanced saltwater intrusion based on higher salinity -RF+ET scenarios, both inundation and salinity are expected to increase in coastal regions. The combination of these factors has been shown to raise DOC concentrations in pore water, estimated at

+23% based on an 8 cm rise in water level for the Shark River (Chambers et al. 2014). Since soils farther upstream in the Shark River estuary have higher %OC content than downstream soils (Krauss et al. 2006), it is predicted that increased tidal action in the upper estuary due to decreased freshwater pressure may mobilize organic-rich sediments into the Shark River channel, increasing DOC concentrations. These potential changes support earlier evidence that larger tidal ranges due to enhanced saltwater intrusion are connected to greater C losses to the coastal ocean (Twilley et al. 1992). In general, -RF+ET conditions appear to indicate that DOC concentrations are expected to increase. However, the potential impact of increased DOC concentrations is overwhelmed by dramatic decreases in discharge associated with decreased RF, driving reduced DOC export regimes.

3.5.4 Long-term DOC flux trends in the Shark River

Linear regression of the monthly DOC flux time-series indicates an average annual flux rate decrease of 4.41×10^8 mg C d⁻¹, equivalent to -4% annual. While the regression slope is significant (t-ratio=-2.17, p=0.03), the line fits the data poorly ($R^2=0.03$) and no significant trend is detected using the Seasonal Mann-Kendall test (tau=-0.0548, p=0.302, Appendix 3.9). Although these statistics may limit confidence in this trend, total organic carbon (TOC) concentration records indicate consistent declines throughout South Florida from 1993-2008 and TOC is still declining in the Florida Keys at a rate of -2% to -4% annually (Briceño & Boyer 2014). Furthermore, these findings closely match predictions of global riverine DOC export trends, estimated at -1.5% by 2030 and -2.1% by 2050 (Seitzinger et al. 2010). Based on model scenario forecasts, it is expected that these trends will strengthen as climate and management drivers limit

discharge to the Shark River. DOC concentration declined significantly during the study period by <1% ($p=0.04$) while the decreasing trend observed for discharge was not significant (-3%, $p=0.12$). This contrasts with long-term increasing DOC concentration trends across a range of higher latitude systems (Filella & Rodríguez-Murillo 2014) and may be related to long-term increases in latitudinal decoupling of AMO altering RF and temperature patterns (Enfield et al. 2001).

3.5.5 Regional and global implications

The primary challenge for Everglades restoration is "getting the water right", meaning a return to historic quality, quantity and timing of freshwater flows delivered to ENP (Sklar et al. 2005). Water management inflows are identified as a key driver of DOC fluxes in this study, meaning feedback from hydrologic restoration on C export is expected. Additionally, long-term climatic patterns (observed here through AMO and ENSO) and episodic climate events (storms and droughts) play significant roles in regulating long-term DOC fluxes in the Everglades, and scenario modeling forecasts a dramatic drop in DOC fluxes in response to reduced rainfall and increased saltwater intrusion from sea-level rise. Although increased inflows associated with hydrologic restoration will likely help offset decreased DOC flux rates, reduced rainfall scenarios suggest limited freshwater available for water management in ENP. Changes in freshwater stage and estuarine discharge due to inflow reductions may affect ENP C sequestration capacity, an ecosystem service currently valued at over \$1 billion (Richardson et al. 2014).

From a global perspective, smaller watersheds like the Shark River have generally been excluded from C export assessments due to insufficient data coverage for modeling

(Laurelle et al. 2013). However, tidal wetlands and estuaries like the Everglades that occupy a small percentage of coastal areas worldwide are estimated to sequester up to one third of all the organic C buried in coastal oceans (Bauer et al. 2013). Furthermore, area-normalized flux rates for this study (see Appendix 3.3) are more than three times larger than average export rates reported for global rivers (Harrison et al. 2005). The potential of smaller rivers, particularly those draining carbon rich coastal ecosystems, to influence global carbon budgets highlights the importance of characterizing these systems and incorporating them into existing export models to more accurately constrain global C budgets and better model the impacts of climate change on coastal and ocean biogeochemistry.

3.6 Conclusions

This study utilized long-term datasets to assess drivers of DOC fluxes over decadal temporal scales (2001-2014) for the Shark River estuary. Through multivariate analysis and modeling in the context of climate change predictions for the region, several important drivers were identified and the implications of predicted climatic shifts discussed. Important findings from this study include:

- Freshwater discharge, controlled by natural and managed freshwater sources, regulates DOC fluxes
- DOC fluxes were altered by drought (decreased fluxes) and tropical storms (increased fluxes)
- Salinity, rainfall, water management inflows and AMO are important predictors of DOC fluxes, modeling 84% of all DOC flux variability during the study period

- Modeling based on climate change scenarios generally predicts decreased DOC fluxes, with increased rainfall and minimal sea-level rise required to maintain current flux magnitudes

The data presented in this study only represents a small portion of the complex interactions between climate, management, hydrology and biogeochemistry (e.g. Appendix 3.4). Additional studies, both long-term and short-term, that incorporate interdisciplinary (hydrological, biogeochemical, climatic) datasets are needed to continue untangling the response of coastal ecosystems like the Everglades to changes in management and climate.

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CHAPTER IV

SHORT-TERM DISSOLVED ORGANIC CARBON DYNAMICS REFLECT TIDAL, WATER MANAGEMENT, AND PRECIPITATION PATTERNS IN A SUBTROPICAL ESTUARY

(Modified from *Regier & Jaffe, 2016; Frontiers in Marine Science*)

4.1 Abstract

Estuaries significantly impact the global carbon cycle by regulating the exchange of organic matter, primarily in the form of dissolved organic carbon (DOC), between terrestrial and marine carbon pools. Estuarine DOC patterns are complex as tides and other hydrological and climatic drivers can affect carbon fluxes on short and long time scales. While estuarine and coastal DOC dynamics have been well studied, variations on short time scales are less well constrained. Recent advancements in sonde technology enable autonomous *in situ* collection of high frequency DOC data using fluorescent dissolved organic matter (FDOM) as a proxy, dramatically improving our capacity to characterize rapid changes in DOC, even in remote ecosystems. This study utilizes high-frequency FDOM measurements to untangle rapid and complex hydrologic drivers of DOC in the Shark River estuary, the main drainage of Everglades National Park, Florida. Non-conservative mixing of FDOM along the salinity gradient suggested mangrove inputs accounted for 6% of the total DOC pool. Average changes in FDOM concentrations through individual tidal cycles ranged from less than 10% to greater than 50% and multi-day trends greater than 100% change in FDOM concentration were observed. Salinity and water level both inversely correlated to FDOM at sub-hourly and daily resolutions, while freshwater controls via precipitation and water management were observed at diel to monthly time-scales. In particular, the role of water management in rapidly shifting estuarine salinity gradients and DOC export regimes at sub-weekly time-scales was evident. Additionally, sub-hourly spikes in ebb tide FDOM indicated rapid exchange of DOC between mangrove sediments and the river channel. DOC fluxes calculated from high-resolution FDOM measurements were compared to monthly DOC

measurements with high-resolution fluxes considerably improving accuracy of fluxes (thereby constraining carbon budgets). This study provides a better understanding of short-term DOC behavior and associated hydrological drivers and indicates the importance of high-frequency measurements to accurately constraining coastal carbon processes and budgets, particularly in coastal systems increasingly altered by hydrologic restoration and climate change.

4.2 Introduction

Estuaries are the continental-oceanic interface of the global aquatic carbon (C) cycle. Terrestrially derived organic C is transported to coastal margins through these systems, primarily as dissolved organic carbon (DOC) (Hedges et al. 1997). Tidal wetlands and estuaries, which occupy a small portion of world coastlines, account for an estimated third of all organic C buried in coastal sediments (Bauer et al. 2013), serving as a globally relevant C sink (Chmura et al. 2003, Bridgham et al. 2006). DOC also influences biogeochemical cycling within estuaries, including regulating the transport of nutrients and metals (Boyer et al. 1997, Qualls & Richardson 2003, Yamashita & Jaffé 2008) and impacts microbial communities (Tranvik 1998, Fellman et al. 2010). Components of the DOC pool which absorb UV light, known as chromophoric dissolved organic matter (CDOM), control benthic productivity through light attenuation in the water column (Osburn et al. 2009, Ganju et al. 2014).

DOC dynamics vary dramatically across temporal scales (Spencer et al. 2007, Jollymore et al. 2012), from sub-hourly changes in tidal systems (e.g. Bergamaschi et al. 2012) to inter-annual trends (e.g. Evans et al. 2005). Characterizing the patterns and

drivers of DOC variability to understand ecological impacts and constrain coastal C budgets thus requires information spanning a wide range of temporal resolutions. Although long-term investigations of coastal DOC patterns are relatively common (e.g. Chen et al. 2013, Regier et al. 2016), equivalent studies at high temporal resolution are lacking due to the complex logistics and laboratory costs associated with DOC sampling in remote estuarine environments. However, high-resolution measurements are critical for temporally dynamic systems like estuaries, where rapid water quality changes observable in high-frequency measurements may not accurately represented by weekly or monthly sampling intervals (Kirchner et al. 2004, Jollymore et al. 2012, Sobczak & Raymond, 2015).

The solution to this dearth of high-frequency DOC information lies in recent technological advances in multi-parameter sondes coupled with sensors measuring fluorescent dissolved organic matter (FDOM), a proxy for DOC (Downing et al. 2009). Sondes combine sensors, data-logging and internal power sources into a single water-proof instrument to achieve high-frequency sampling intervals *in situ*, eliminating the need laboratory analysis except to calibrate proxy relationships. These sensors have been applied in a range of environments, including lakes (Watras et al. 2015), streams and rivers (Pellerin et al. 2012, Wilson et al. 2013), wetlands (Ryder et al. 2014) and coastal systems (Downing et al. 2009, Bergamaschi et al. 2012). High-frequency FDOM data provide the resolution necessary to fill in knowledge gaps beyond the scope of conventional monthly sampling frequencies. For instance, high-frequency FDOM measurements have facilitated the development of ecosystem-specific proxies for mercury (Bergamaschi et al. 2012), nutrients (Wilson et al. 2013, Etheridge et al. 2014)

and DOC lability (Wilson et al. 2013). Likewise, high-resolution characterization of DOC proxies have provided new insight into processes controlling diel carbon cycles (Watras et al. 2015), rapid changes in hydrologic export of DOC (Bergamaschi et al. 2012, Wilson et al. 2013) and the role of DOC in light attenuation within optically complex waters (Ganju et al. 2014). As such, the application of instruments capable of high-frequency DOC data collection holds great potential for advancing our understanding of temporally variable aquatic ecosystems.

In the present study, high-resolution measurements were collected to examine patterns and trends in DOC at sub-hourly time-scales in the coastal estuaries of Everglades National Park (ENP). Landscape-scale restoration efforts underway to re-establish hydrologic connectivity along the Everglades flow-path are expected to alter seasonal timing, quantity and quality of freshwater inflows to ENP (Sklar et al. 2005), but the potential effects on ecosystem function remain uncertain (Estenoz & Bush 2015). Since hydrology controls DOC patterns in this system, it is expected that changes in the balance between freshwater (due to changes in management and rainfall) and saltwater intrusion (due to sea-level rise) will alter DOC cycling and export patterns (Orem et al. 2015, Regier et al. 2016). To this end, significant efforts have been placed into understanding the spatial and temporal patterns of DOC quality and quantity across the Everglades landscape (Maie et al. 2006a, Yamashita et al. 2010, Chen et al. 2013). In addition, DOC export patterns and drivers have been investigated at low and high temporal resolutions (Bergamaschi et al. 2012, Cawley et al. 2014, Regier et al. 2016). However, the relationship between rapidly changing and complex estuarine hydrology and high-resolution DOC patterns for this system remains mostly undetermined. This

study applies high-frequency measurements of FDOM to this knowledge gap, to better understand the hydrologic drivers of short-term DOC patterns in the Shark River, located in the mangrove forests of the coastal Everglades. In addition, this study builds on previous characterization of long-term DOC flux drivers (Regier et al. 2016) by linking short-term (daily) to long-term (monthly) DOC export regimes.

4.3 Methods

4.3.1 Site Description

Data for this study was collected in the Shark River estuary, located in the coastal ecotone of southwest ENP (Figure 4.1). The Shark River connects vast upstream freshwater wetlands to coastal margins and is situated within the largest contiguous mangrove forest in the United States. Data was collected at SRS-5 (Figure 4.1), a monitoring site maintained by the Florida Coastal Everglades Long Term Ecological Research (FCE-LTER) project. The site is subject to semi-diurnal tides and experiences distinct wet and dry seasons, where the wet season delivers the majority of annual freshwater inflows to the estuary via rainfall and inputs through water management structures (Duever 1994, Saha et al. 2012).

Figure 4.1 Map of the study area, including long-term monitoring station and USGS gage station locations, where GI stands for Gunboat Island (#252230081021300) and RB stands for Rookery Branch (#022908295). S12A-D water management structures are marked on the northern border of Everglades National Park. PDB stands for Ponce de Leon Bay, the marine endmember for Shark River transects

4.3.2 Instrument calibration and setup

High-frequency data were collected *in situ* (measured directly in the water column) using an EXO-2 water quality sonde (Yellow Springs Instrument Company (YSI), Ohio). The sensor measuring FDOM had excitation and emission wavelength ranges of 365 ± 5 nm and 480 ± 40 nm, respectively, with a range of 0 to 300 ppb quinine sulfate equivalents (QSE) and resolution of 0.01 ppb QSE reported by the manufacturer. The sonde was calibrated prior to deployment according to manufacturer protocols and again immediately after instrument retrieval. Calibration solutions for FDOM

fluorescence were made from quinine sulfate dihydrate diluted with 0.05 M H₂SO₄, with calibration errors lower than 5% for all deployments. Fluorescence of FDOM is reported in quinine sulfate units (QSU). Prior to deployment, sensors were wrapped in copper tape and surrounded by an anti-fouling sensor guard to minimize impacts of biofouling. Additionally, a wiper was programmed to clean sensor heads every three hours. In spite of these precautions, sensor drift was detected in two time-series, which were not included in this study. For the data presented here, no drift was detected based on pre and post-calibration. Evidence of erratic turbidity spikes during preliminary deployments indicated interference due to crab activity, known to alter particulate and nutrient behavior in mangrove sediments (Kristensen & Alongi, 2006). In order to protect against this, mesh was installed over openings in the sensor guard so that water flowed through uninhibited but crabs were unable to interfere with data collection.

4.3.3 Data collection

A total of five time-series were collected between November 2014 and November 2015 averaging 27 days in duration (Table 4.1). Two time-series were collected during the wet-dry seasonal transition (T1 and T2), two during the dry season (D1 and D2) and one during the wet season (W1). The sonde was equipped with six external sensors (temperature/conductivity, pH, dissolved oxygen (DO), turbidity, FDOM and chlorophyll) and one internal pressure sensor for measuring depth. The sonde was secured to the boardwalk at SRS-5 and situated adjacent to the riverbank with sensor heads located approximately 0.5 meters below the lowest low tide mark. Ancillary hydrologic data was retrieved from the USGS gage at Gunboat Island (#252230081021300), located less than one kilometer upstream from SRS-5 (Figure 4.1).

As the sonde was not deployed relative to a standard vertical datum, stage values collected by the sonde were not directly comparable between time-series. Therefore, stage data from the USGS gage at Gunboat Island was matched to sonde stage using time-lagged correlations. After matching, sonde stage and USGS stage showed strong linear relationships ($r > 0.93$, $p < 0.0001$ for all time-series).

Table 4.1 Average values of selected hydrologic variables for each time-series

<i>Time-series</i>	<i>Start Date</i>	<i>End Date</i>	<i>GI Stage (mm)*</i>	<i>Discharge (m³/s)*</i>	<i>Filtered discharge (m³/s)*</i>	<i>Rainfall (mm)</i>	<i>S12A-D inflows (m³/s)</i>	<i>Stage at Key West (mm)</i>
T1	11/4/2014	11/20/2014	-0.22	6.20	4.64	1.78	8.18	-0.72
D1	1/8/2015	2/9/2015	-0.17	-6.11	-5.07	0.51	1.70	-2.23
D2	3/16/2015	4/6/2015	-0.13	-4.46	-4.43	0.76	0.00	-2.99
W1	6/2/2015	7/1/2015	-0.20	-4.13	-4.89	4.32	0.00	-2.43
T2	10/1/2015	11/1/2015	0.07	-0.17	0.84	2.03	10.17	0.72

* Stage and discharge calculated from 15-minute data, filtered discharge calculated from hourly data, all other variables calculated from daily data (first and last day of each time-series are clipped)

Table 4.2 Averages and standard deviations for water quality variables by time-series

<i>Time-series</i>	<i># of data</i>	<i>Temperature (°C)</i>	<i>Salinity</i>	<i>pH</i>
T1	1517	22.75 (1.03)	14.69 (6.06)	7.46 (0.04)
D1	3054	21.18 (1.34)	17.91 (6.28)	7.47 (0.06)
D2	1998	26.13 (1.08)	27.02 (4.27)	7.51 (0.05)
W1	2767	29.7 (1.21)	22.81 (5.21)	7.5 (0.06)
T2	2933	27.25 (1.03)	21.6 (6.92)	7.42 (0.1)

<i>Time-series</i>	<i>DO (mg/L)</i>	<i>FDOM (QSU)</i>	<i>Turbidity (FNU)</i>	<i>Chlorophyll (µg/L)</i>
T1	4.27 (0.43)	132.89 (22.27)	6.43 (5.02)	2.93 (0.44)
D1	4.22 (0.59)	146.67 (32.5)	9.61 (26.47)	5.53 (5.85)
D2	3.03 (0.48)	116.68 (30.27)	7.25 (7)	6.07 (3.32)
W1	1.99 (0.41)	139.55 (24.3)	6.33 (23.82)	5.53 (1.21)
T2	2.74 (0.72)	114.52 (22.42)	9.96 (19.08)	7.68 (18.5)

Data collected at 15-minute intervals from sonde and USGS sources are denoted as 15-minute. Tidally filtered discharge was reported at hourly resolution after applying the PL33 low-pass filter for removal of tidal fluctuations (Flagg et al. 1976). Daily averages of high temporal resolution measurements were also reported, with the first and

last day of each time-series excluded since these dates did not capture 24 hours of continuous data. Long-term daily salinity data for calculations of δ -salinity was retrieved from the Gulf of Mexico Coastal Ocean Observing System (GCOOS) station GBIF1 (<http://data.gcoos.org/index.php>) as hourly data and binned to daily averages, where days with less than 12 measurements were excluded. Rainfall data was collected at the Shark River station of the Everglades Depth Estimation Network (EDEN, <http://sofia.usgs.gov/eden/>). Water management inflows were calculated as the sum of daily average discharge for S12A-D structures (USGS gages, <http://waterdata.usgs.gov/>).

4.3.4 Fluorescence interference and corrections

Corrections for thermal quenching of fluorescence were conducted following methods of Watras et al. (2011). Briefly, temperature and FDOM fluorescence were measured simultaneously for water samples collected at SRS-4, SRS-5 and SRS-6 (Figure 4.1) over a broad temperature range (5-30 °C) exceeding the expected seasonal temperature range for SRS-5. Based on linear regression, a correction factor ($\rho = -0.0064 \pm 0.0004$) was established. A reference temperature (T_r) of 25 °C was used instead of 20 °C to reflect sub-tropical temperature regimes.

Interference from dissolved and suspended materials that absorb or scatter light can alter *in situ* fluorescence measurements, and impact instruments differently based on geometry of the sensor optics (Downing et al. 2012). For dissolved materials, absorbance of UV radiation by CDOM can be presented as absorbance at 254 nm (A_{254} , unitless) or absorption coefficients (a_{254}) (Hu et al. 2002, Kowalczyk et al. 2010). As a quantitative measurement, a_{254} is preferred to A_{254} as a_{254} values are comparable between studies regardless of path length. However, A_{254} values are also reported here to facilitate

comparison with values presented by Downing et al. (2012) and Cawley et al. (2014). Conversion of A_{254} to a_{254} was performed using Equation 2 in Kowalczyk et al. (2010) where path length was 1 cm for both Downing et al. (2012) and Cawley et al. (2014).

The Shark River is characterized by relatively high CDOM absorbance (A_{254}) ranging from 0.1-0.6 (a_{254} : 23-138 m^{-1}) based on Cawley et al. (2014). Figure 4.1 in Downing et al. (2012) indicates this range of absorbance values equates to FDOM attenuation up to ~15%. Monthly absorbance data collected upstream (SRS-4) and downstream (SRS-6) of the study site (Figure 4.1) spanning 11/2014 to 05/2015 were used to estimate SRS-5 absorbance as the average of SRS-4 and SRS-6 (Appendix 4.1). Estimated A_{254} values for SRS-5 (average A_{254} : 0.44, average a_{254} : 101 m^{-1}) indicated that, at least for the portion of the study period, attenuation due to dissolved materials accounted of less than 10% of the FDOM signal based on a closed path sensor with optics at 90° (Downing et al. 2012).

To assess fluorescence interference due to suspended solids (measured as turbidity), a turbid solution containing 15g of mangrove sediment collected at SRS-5 (dried, ground and sieved through a 30-mesh screen) and ~4 L of filtered low-absorbance (A_{254} : 0.09, a_{254} : 21 m^{-1}) mangrove creek water was mixed (filtered using combusted 0.7 μm GF/F filters). The solution was equilibrated for 48 hours to negate potential FDOM inputs leached from the sediments (Downing et al. 2012, Lee et al. 2015). The solution was then placed in a constantly stirred vessel connected to a YSI flow-cell containing the FDOM and turbidity sensors with previously acid-washed tubing and a peristaltic pump. Sequential removal of turbidity was achieved by siphoning 250 mL aliquots from the stirred vessel, filtering and then returning the filtrate to solution (Appendix 4.2). As

previously observed, highly turbid waters attenuated FDOM fluorescence considerably (Downing et al. 2012, Lee et al. 2015). Less turbid conditions (values less than 100 FNU) showed a strong linear relationship ($r = 0.99$, $p < 0.0001$, $n = 216$) to FDOM (Appendix 4.2, values less than 100 FNU). For this study, turbidity values were generally low with 0.5% of turbidity values exceeding 100 FNU and 1.9% exceeding 25 FNU. Based on linear regression of turbidity values lower than 100 FNU in Appendix 4.2, it is estimated that 25 FNU attenuated less than 5% of the total FDOM fluorescence signal. Furthermore, spikes in turbidity did not appear to elicit anomalous FDOM signals (e.g. Appendix 4.3). This suggests that, while attenuation of fluorescence by suspended solids likely influences FDOM signals, a simple correction for the effects of turbidity on FDOM signals may not be appropriate (Lee et al. 2015). As such, turbidity corrections were not applied to FDOM measurements (see Section 4.3.6 for estimates of error).

4.3.5 Establishing the FDOM-DOC relationship

The relationship between FDOM and DOC was calibrated by collecting grab samples concurrent with *in situ* FDOM measurements. Due to high seasonal and spatial variability of DOC optical properties in the Shark River (Cawley et al. 2014), the FDOM:DOC relationship was established both with spatial transects and temporal sampling. Four seven-point spatial transects were collected from the marine end member (Ponce De Leon Bay) to the freshwater end member at SRS-4 (Figure 4.1). Transects were collected during wet and dry seasons and seasonal transitions and temporal data were collected through portions of two consecutive tidal cycles. DOC samples were filtered through 0.7 μm GF/F filters and quantified on a Shimadzu TOC analyzer after acidification and purging to remove inorganic C. A total of 53 paired measurements of

DOC and FDOM collected from 02/2015 to 04/2016 exhibited strong linear correlation ($r = 0.96$, $p < 0.0001$, Appendix 4.4) yielding a conversion equation of FDOM (QSU) = $0.11 * \text{DOC } (\mu\text{M}) + 19.06$. The root mean square error (RMSE) for this regression was ± 9.8 QSU or $\pm 7.5\%$ of the average FDOM value (see Section 4.3.6). Due to the error component associated with converting FDOM fluorescence to DOC concentrations, FDOM measurements were primarily reported in QSU throughout the manuscript while DOC concentrations were reported in μM or ppm for comparison with literature values and to facilitate calculating DOC fluxes. DOC fluxes were calculated as the product of DOC concentration and discharge.

4.3.6 Statistics and FDOM errors

All statistical analyses were performed using the JMP® Version 12 statistical package (SAS Institute Inc., Cary, NC, 1989-2007). Results of linear regressions are reported as correlations (r). Changes in FDOM presented as percent were calculated using the average FDOM value for the study (130.8 QSU) for consistency. Non-conservative mixing lines were calculated for regression plots of FDOM versus salinity (e.g. Figure 4.3), based on previously published methods (Cawley et al. 2014).

Mangrove inputs during FDOM spikes were quantified for three consecutive tidal cycles in T2 with clear ebb tide spikes (Figure 4.5). For each tidal cycle, consecutive data points were connected with lines. Next, a baseline was drawn by connecting the lowest FDOM value at the start of the tidal cycle to the lowest value at the end of the tidal cycle. The baseline was then set to zero, so integrations only included the change in FDOM during the tidal cycle rather than the entire FDOM signature. Next, spikes were removed by connecting the points immediately preceding and following the spike.

Finally, each tidal cycle was integrated with and without FDOM spikes using the “AUC” package in R (Ballings & Van den Poel, 2013). The integration process is represented graphically in Appendix 4.5. FDOM contributions from the three tidal cycles ranged from 5.7% to 14.8% and were estimated to account for up to 24% in other tidal cycles.

Error terms associated with each of the three potential interferences to *in situ* FDOM measurements are identified in Section 4.3.4. The correction factor for temperature was based on linear regression of $r > 0.99$ ($p < 0.0001$) with and RMSE less than 1 QSU. For dissolved materials, attenuation was estimated at less than 10% based on A_{254} values for the site. For suspended solids, attenuation/scattering effects on FDOM were estimated at less than 5% for >98% of the data-set. Assuming attenuation of dissolved and suspended solids is additive, FDOM measurements may be ~15% lower than actual FDOM values. These conditions represent the upper limits of FDOM attenuation based on high levels of dissolved matter (A_{254} : 0.44, a_{254} : 101 m^{-1}) and high turbidity (25.0 FNU). As attenuation from dissolved and suspended solids is not corrected for in FDOM values reported in this study, it is important to remember these potential sources of under-linearity when interpreting QSU values.

4.4 Results

4.4.1 Environmental conditions

This study covers a period of limited freshwater delivery to the Shark River estuary due to below-average rainfall and consequent reductions in water management inputs across the northern border of ENP into Shark River Slough (Table 4.1). This limited rainfall led to moderate to severe drought for the region stretching from the early

dry season through the early wet season (droughtmonitor.unl.edu). The combination of these factors resulted in lower than normal discharge rates from the Shark River, with net negative flows (marine inflows to the estuary) from 12/2014 to 09/2015, the longest period of negative discharge for the 2002-2015 data record (USGS gage #252230081021300, tidally filtered discharge). As such, time-series D1, D2 and W1 (early dry, late dry and early wet seasons, respectively) all received minimal freshwater inputs from water management (although W1 received increased rainfall). In contrast, T1 and T2 time-periods exhibited high discharge rates for the estuary linked to high inflows from the S12A-D structures (Figure 4.1). Sea level acted as an additional hydrologic control and increased from D2 through T2, with the highest daily mean sea level value recorded at Key West between 1913-2013 occurring on 10/01/2015, the start-date for T2 (CO-OPS). Basic statistics for *in situ* water quality data collected for this study are displayed in Table 4.2, by time-series. Salinity and freshwater hydrology were inversely related, with lowest salinity during periods of high freshwater discharge and low sea-level (T1). Salinity increased through D1 and peaked during D2 due to minimal freshwater inputs. Salinity values decreased throughout W1 due to increased rainfall and during T2 due to increased water management inflows (Table 4.1). Dissolved oxygen (DO) inversely co-varied with seasonal patterns in temperature and on diel time-scales, with higher values during the day. In general, turbidity increased with channel velocity (both positive and negative), suggesting control by tidal or wind-induced erosion rather than allochthonous delivery to the estuary, matching previously reported decoupling of particulate and dissolved carbon pools for this system (He et al. 2014).

Figure 4.2 FDOM, salinity, stage and tidally filtered discharge for the 5 time-series. Gray dots are 15-minute interval measurements for FDOM, salinity and stage. Black lines for FDOM, salinity and stage are smoothing lines to highlight multi-day trends. For filtered discharge, black lines is hourly tidally filtered discharge measured at Gunboat Island. Gray filtered discharge lines represent data from the adjacent Harney River drainage to serve as reference for gaps in the Gunboat discharge record.

Figure 4.3 The fDOM:salinity relationship. Figure 4.3A shows all data together, while 4.3B and 4.3C divide the data-set into D&W and T sub-groups, respectively. The dark gray dots for Figure 4.3A are T time-series. The dark gray dots for Figure 4.3C are discussed in Section 4.3.

Values for FDOM ranged from 55.2 QSU to 208.6 QSU, matching previously reported QSU values for maximum fluorescence intensity in coastal mangrove rivers of the Everglades (Jaffé et al. 2004). High tidal variability was clearly evident for the high resolution data, with variation of the FDOM signal in excess of 100% between consecutive low and high tides (e.g. 1/26/15 and 3/27/15, Figure 4.2). Highest FDOM values occurred during the beginning of the dry season, similar to previously observed longer-term seasonal trends upstream of SRS-5, which have been attributed to a combination of evaporation-mediated concentration and water management inputs (Chen et al. 2013). In contrast, FDOM values were considerably lower during the late dry season (D2) when DOC concentrations are historically higher in the upstream freshwater marshes (Chen et al. 2013).

4.4.2 Relationships between FDOM, water quality and hydrology

To quantitatively assess the relationships between water quality, hydrology and FDOM, linear regression of FDOM versus parameters in Table 4.2 is presented in Table 4.3 as correlations, both for 15-minute data and daily averages. Of these parameters, salinity had the strongest relationship to FDOM at both temporal scales. The relationship between FDOM and stage had the second highest r values, with a higher correlation for daily data. At daily resolution, filtered discharge exhibited the third strongest correlation (though weak: $r = 0.28$). Temperature, pH and filtered discharge showed weak correlations to FDOM for the high-resolution data ($r = -0.20$, -0.24 and 0.24 , respectively) as did temperature, discharge and turbidity for daily resolution ($r = -0.22$, 0.17 and -0.22 , respectively). Based on the above (see Table 4.3), salinity, stage and

tidally filtered discharge (at daily resolution) were investigated as potential drivers of high-frequency FDOM dynamics.

4.4.2.1 Salinity and FDOM

Measurements of FDOM at 15-minute intervals showed distinct semi-diurnal patterns related to tidal influence and inversely tracked salinity patterns where highest FDOM values corresponded to lowest salinity for each tidal cycle (Figure 4.2), as observed in other mangrove systems (Dittmar & Lara, 2001). Correlations to FDOM

Table 4.3 Correlations of FDOM to water quality and hydrology variables

<i>Parameter</i>	<i>15-minute</i>	<i>Daily</i>
Temperature (°C)	-0.20	-0.22
Salinity	-0.83	-0.78
pH	-0.24	-0.14
DO (mg/L)	0.00	0.00
Turbidity (FNU)	0.00	-0.22
Chlorophyll (µg/L)	0.00	0.10
Stage (m)	-0.60	-0.73
Discharge (m ³ /s)	0.00	0.17
Filtered Discharge (m ³ /s)	0.24	0.28

15-minute data measured at 15-minute increments except filtered discharge (hourly); daily data averages of 15-minute data

were higher for 15-minute than daily measurements (Table 4.3), indicating tidal control.

The relationship between salinity and FDOM was examined using the ratio of the two variables (FDOM:salinity) shown in Figure 4.3A. A clear divide in the data-set was observed through this relationship, where T1 and T2 had lower FDOM:salinity ratios compared to the remaining three time-series. This divide matched closely with management-driven inflows as well as tidally filtered discharge (both considerably higher for T1 and T2, see Table 4.1). A similar divide in the DOC:salinity ratio observed by Cawley et al. 2014 indicated that T1 and T2 most closely resembled wet season

characteristics while the remaining time-series matched the dry season. As outlined in Section 4.4.1, the study period experienced abnormal hydrology, and the divide in FDOM: salinity confirmed that conventional seasonal wet/dry timing did not fit this data-set. Rather, seasonal transition time-series (T1 and T2) resembled classic wet season hydrology and salinity gradients while the remaining three time-series resembled dry season conditions due to reduced rainfall and consequent drought. Based on this observation, the data-set was divided into two sub-groups: the first for time-series during periods of low freshwater inflow (D1, D2 and W1, Figure 4.3B), the second for time-series during periods of high freshwater inflow (T1 and T2, Figure 4.3C). Dividing the data-set in this manner dramatically improved linear regression fits ($r = 0.94$ for D&W, $r = 0.93$ for T) in comparison to the full data-set ($r = 0.83$). An additional split in Figure 4.3C during T2 was observed, where FDOM: salinity ratios transitioned from high salinity and low freshwater inputs to dramatically increased freshwater inflows and low salinity. To examine this, T2 was sub-divided into two sections: before and during the start of high outflows (positive discharge from the estuary, Figure 4.2) and during and after high outflows. The first sub-group clustered more with D&W time-series due to enhanced saltwater presence, higher stage and low or negative filtered discharge (Figure 4.3C, dark gray points). The second sub-grouping fell in the same FDOM: salinity region as T1: characteristic of high water management inflows in spite of high sea levels.

The data presented in Figure 4.3 suggest a non-conservative relationship between FDOM and salinity, where FDOM values were higher at the mid-estuary than would be expected for conservative (linear) mixing behavior of freshwater and marine endmembers. A similar relationship was previously reported for this location by Cawley

et al. (2014), who determined that non-conservative inputs were primarily due to DOC contributions from the riparian mangrove forests. Following this hypothesis, FDOM: salinity plots were fitted with quadratic regression lines which improved fits over linear regression (full data-set: $r = 0.85$, D&W: $r = 0.94$, T: $r = 0.94$). Non-conservative inputs were calculated for individual neap and spring tide for each time-series ($n=20$) as the difference between integrations of quadratic and linear fits (Cawley et al. 2014). An average non-conservative input percentage of $6 \pm 2\%$ was estimated with a maximum of 9% (neap tide, D2) and a minimum of 3% for the consecutive spring tide.

4.4.2.2 FDOM and tidal dynamics

Tidal FDOM patterns were inversely related to stage with a temporal lag component, where highest tidal values for FDOM lagged lowest stage (low tide) by 1-2 hours. Stage correlations to FDOM (FDOM:stage) were considerably higher for daily data (Table 4.3), likely due to the temporal lag observed at tidal time-scales. When tidal FDOM patterns were time-matched to stage (lowest FDOM values time-lagged to coincide with peak stage), a much stronger regression was achieved ($r = 0.77$), similar to FDOM: salinity. As with salinity, the FDOM:stage data was divided into T and D&W groupings, with a better fit for D&W ($r = 0.79$) than T ($r = 0.72$), indicating stronger tidal control of FDOM:stage during periods of low freshwater inflows. Values of FDOM were consistently higher for neap tides (average 136.4 QSU) compared to spring tides (average 124.6 QSU). Neap tides also exhibited lower salinity, lower stage and higher tidally filtered discharge, indicating reduced tidal influence. The difference in FDOM between neap and spring tides was considerably larger for T time-series (+17.1 QSU, average of spring and neap: 119.8 QSU) compared to D&W time-series (+10.2 QSU, average of

spring and neap: 136.5 QSU). In general, decreasing FDOM trends were observed during spring tides, while increasing trends accompanied neap tides. Differences in neap/spring FDOM patterns provided proof that greater freshwater influence during neap tides led to higher allochthonous DOC inputs to the estuary. In addition, this suggested a temporal decoupling between weekly (spring/neap tides) and monthly (time-series) resolutions for the relationship between freshwater discharge and FDOM where neap tides increased both filtered discharge rates and FDOM signals while Figure 4.3 indicated dilution of FDOM (lower signal) during periods of increased freshwater delivery.

Rapid changes in FDOM during ebb tides were consistently observed near the tidal FDOM minimum which did not fit the semi-diurnal sinusoidal tidal signature. Examples of these FDOM patterns along with additional parameters are shown in Figure 4.4, with the unexpected spikes highlighted in black. These FDOM spikes consistently coincided with a knee observed in ebb tide stage patterns which could not be fully explained by tidal flow asymmetry typically observed in mangrove channels (Mazda et al. 1995). The knee denoted a deceleration of falling water levels attributed to geomorphological control of tidal hydrodynamics by riparian mangrove forests. Specifically, it was hypothesized that these patterns correspond to tidally regulated porewater exchange between mangrove sediments and the river channel. The location where the sonde was deployed is immediately adjacent to mangrove sediments perforated with crab burrows, a feature shown to enhance hydraulic connectivity of mangrove sediments to the water column (up to 20% in some systems, Stieglitz et al. (2013)). Reduced dissolved oxygen (DO) levels, often associated with porewater hypoxia in mangrove ecosystems (Bouillon et al. 2007), were generally present during FDOM spikes

supporting the hypothesis of porewater contributions. However, these patterns were somewhat variable, with examples in Figure 4.4 showing consistently depleted DO concurrent with FDOM spikes during T2 but not T1.

Figure 4.4 Time-series comparing mangrove inputs during T1 (left) and T2 (right). Black points highlight FDOM spikes during ebb tide. Note that lower salinities during T1 show no FDOM spike. In contrast, T2 has very pronounced spikes.

4.4.2.3 Daily FDOM patterns

Multi-day patterns in FDOM (see smoothing lines in Figure 4.2) corresponded to freshwater input patterns observed as tidally filtered discharge. Correlation of daily FDOM values to filtered discharge was relatively weak for the whole data set ($r = 0.30$, $n=145$, $p=0.0009$) and for D&W ($r = 0.29$, $n=77$, $p=0.0083$) but stronger for T ($r = 0.60$, $n=45$, $p<0.0001$), likely due to substantial water management inputs during T1 and T2. To quantify the impact of filtered discharge on changes in FDOM, the difference in FDOM between consecutive days was calculated as $\delta\text{-FDOM} = \text{FDOM}_{(x+1)} - \text{FDOM}_{(x)}$

where x is the date. Based on δ -FDOM calculations for time-series, daily changes in FDOM of +40.0 QSU to -28.6 QSU indicate equivalent shifts of +377.4 μM (+31%) to -274.7 μM (-22%) for DOC concentrations. The regression of δ -FDOM:filtered discharge ($r = 0.65$, $n=115$, $p<0.0001$) showed a much stronger relationship than FDOM:filtered discharge ($r = 0.30$, $n=120$, $p=0.0009$). Interestingly, correlations between filtered discharge and δ -FDOM were stronger for D&W ($r = 0.74$, $n=72$, $p<0.0001$) than T ($r = 0.71$, $n=43$, $p<0.0001$), which was unexpected since T time-series were more strongly linked to filtered discharge patterns. Regression slopes for T and D&W (0.01 and 0.03, respectively) indicated that equivalent changes in filtered discharge yielded a change in the FDOM signal three times greater for dry season time-series compared to wet season. This was attributed to lower stage during D&W time-series (Table 4.1), leading to smaller volume in the Shark River. The corresponding evapo-concentration of the Shark River DOC pool would be more sensitive to dilution from changes in freshwater flow.

4.4.3 DOC fluxes

Previously, long-term DOC fluxes were calculated for this site based on monthly DOC concentrations and tidally filtered discharge (Regier et al. 2016), with modeling of monthly flux values predicted by salinity, rainfall, water management inflows and the Atlantic Multidecadal Oscillation (AMO), a long-term climatic index. Short-term fluxes based on DOC (using FDOM as a proxy) and hourly tidally filtered discharge were calculated for this study to compare and contrast patterns and drivers of DOC fluxes in the Shark River across temporal scales. Both T time-series exhibited net positive flux values (DOC exported from the estuary), averaging $3.4 \times 10^9 \text{ mg C d}^{-1}$. In contrast, all D&W time-series had negative flux values averaging $3.4 \times 10^9 \text{ mg C d}^{-1}$, indicating

considerably longer DOC residence times between periods of positive filtered discharge (average movement calculated from velocities of 2432 m d^{-1} for D&W in comparison to 8843 m d^{-1} for T time-series in relation to approximately 9,500 m from the study site to the river mouth). For hourly flux values, no correlations for water quality or hydrology variables (except discharge) were observed, including salinity and stage, which both correlated to long-term fluxes (Regier et al. 2016). As discharge was higher during neap tides, DOC fluxes were also considerably higher, with averages of $2.8 \times 10^9 \text{ mg C d}^{-1}$ and $5.9 \times 10^9 \text{ mg C d}^{-1}$ for neap and spring respectively. This pattern held true when fluxes were sub-divided into D&W and T groupings with neap tide fluxes $6.2 \times 10^9 \text{ mg C d}^{-1}$ and $1.2 \times 10^{10} \text{ mg C d}^{-1}$ higher than spring tide fluxes for D&W and T subsets respectively.

To validate the extrapolation of high-frequency FDOM measurements to DOC values and improve the accuracy of DOC flux determinations, flux values were calculated from daily DOC data (based on FDOM as a proxy) and monthly grab samples where the DOC value at the beginning of each time-series was extrapolated to all days in the time-series (Gaiser & Childers 2016). As the two sets of fluxes were determined for the same days using the same filtered discharge data, the only difference was the application of low-resolution versus high-resolution DOC concentrations in the estimates. The resulting flux calculations were compared using linear regression (Figure 4.6), with stronger correlations for D&W time-series ($r = 0.95$, $n=73$, $p<0.0001$) in comparison to T time-series ($r = 0.93$, $n=43$, $p<0.0001$). To interpret if fluxes based on monthly grab samples were over-estimated or under-estimated in comparison to high-frequency flux calculations, a 1:1 line was included. In general, linear regression for D&W fell slightly below the 1:1 line (slope = 0.80), indicating monthly fluxes were under-estimated

(Figure 4.6A) while T time-series were on or above the line (slope = 1.25), particularly for high fluxes during T2 (Figure 4.6B).

4.5 Discussion

4.5.1 Tidal-scale FDOM dynamics

High-resolution measurements of FDOM showed highly variable DOC behavior controlled at tidal and daily time-scales by a mixture of tidal influence, freshwater inputs and exchange with mangrove forests. Whereas tidal control was consistent for all time-series, freshwater control of FDOM was more sporadic and varied seasonally. The study period was unique as the two major sources of freshwater to the Shark River (rainfall and water management inflows), which are usually coupled (though time-lagged, Saha et al. 2012) were separated, allowing for a comparison of the influence of each freshwater source on high-resolution FDOM patterns. In addition, previously unobserved spikes during ebb tide were identified as likely originating from porewater exchange within the mangrove forests. While tidal control is evident at hourly resolution and freshwater influence is well characterized at daily resolution, the abovementioned mangrove-derived spikes would not be observable, even at hourly resolution.

Figure 4.5 Quantification of rapid spikes in FDOM during ebb-tide attributed to mangrove porewater inputs were calculated for three consecutive tidal cycles during T2. Dark gray areas outlined in black represent FDOM spikes associated with ebb tide mangrove porewater inputs. Light gray areas outlined in gray represent the rest of the change in FDOM during each tidal cycle, where change is defined as FDOM above a baseline running from the lowest FDOM value at the start of the tidal cycle to the lowest FDOM value at the end of the tidal cycle. Percentages indicate the percent of FDOM change attributed to ebb tide mangrove porewater inputs.

Figure 4.6 Comparison of DOC fluxes calculated using the same discharge data but different data sources of DOC (different sampling resolutions). Fluxes calculated from monthly grab samples are on the y-axis, fluxes calculated from daily averages of high-resolution fDOM measurements are on the x-axis. Figure 4.6A plots D&W time-series (D1: open squares, D2: solid triangles, W1: crosses). Figure 4.6B plots T time-series (T1: solid diamonds, T2: open circles). Black lines represent best-fit regression lines and gray lines show a 1:1 line.

A recent mesocosm study of C response to salinity and inundation in mangrove peat soils from the region, found that higher salinity decreased porewater DOC by 2.8 ± 3.3 ppm ($23 \pm 27\%$ of average DOC for this study), while increased inundation enhanced DOC concentrations by 3.6 ± 4.5 ppm ($30 \pm 37\%$) (based on a 8 cm increase in stage; Chambers et al. 2014). Findings from the current study of an inverse relationship between DOC and salinity at tidal time-scales match findings from the mesocosm study (Chambers et al. 2014). However, increased salinity conditions equivalent to those reported by Chambers et al. (2014) yielded a much larger decrease in DOC (-7.5 ppm or -62% for D&W time-series in Figure 4.3B, -5.0 ppm or -41% for T time-series in Figure 4.3C).

Increased salinity conditions equivalent to those reported by Chambers et al. (2014) yielded a much larger decrease in DOC (-7.5 ppm or -62% for D&W time-series in Figure 4.3B, -5.0 ppm or -41% for T time-series in Figure 4.3C). In contrast, the inverse relationship between tidal stage and DOC (attributed to dilution) does not match with higher DOC in inundated mesocosm experiments (Chambers et al. 2014). In the latter, an equivalent increase in stage of 8 cm yields decreased DOC of considerably smaller magnitudes (-0.7 ppm or -6% for D&W time-series, -0.5 ppm or -4% for T time-series).

Decoupled response of DOC to inundation between mesocosm and *in situ* measurements may stem from the estimated small contributions of mangrove-derived DOC at this location (approximately 6% of the DOC pool), whereas the mesocosm results present changes in DOC exclusively from mangrove peats. Based on Chambers et al. (2014), increased inundation is expected to decrease the concentration of the overall

DOC pool through dilution while simultaneously enhancing mangrove inputs. As sea level rise drives higher saltwater intrusion and increased inundation in this region, higher C loss from the mangrove forest (see also Section 4.5.2) is expected to account for a larger portion of the Shark River DOC pool and increase outwelling of mangrove-derived DOC (Dittmar & Lara, 2001). Such processes are expected to increase light attenuation in the water column (Ganju et al. 2014) of adjacent light-sensitive seagrass and coral reef communities (McPherson et al. 2011, Shank et al. 2010) through long-range DOC transport (Maie et al. 2012; Yamashita et al. 2013). However, DOC export from this region in general is predicted to decrease in the future due to shifting hydrology due to climate change (Regier et al., 2016), and thus, the potential balance between enhanced mangrove forest inundation and predictions based on long-term DOC datasets remains to be determined. Better understanding of the potentially complex relationship between inundation and DOC export is therefore crucial for low-relief coastal systems like mangrove forests, where ecosystem sustainability is based on accretion keeping pace with sea-level rise (McKee, 2011). Mangrove accretion is primarily dependent on primary productivity (Cahoon & Lynch, 1997) and correlates to organic C burial rates, which are below global averages for the Shark River (Breithaupt et al. 2014). Thus, potential DOC losses from mangrove peats due to the combined effects of increased salinity and inundation could increase the vulnerability of the coastal mangrove fringe to submergence.

4.5.2 Mangrove contributions to the DOC pool

The DOC pool in the Shark River is strongly influenced by upper watershed freshwater wetland sources, combined with mangrove inputs (Yamashita et al. 2010,

Bergamaschi et al. 2012, Cawley et al. 2014). However, it is not clear from previous studies if this mangrove contribution is related to porewater inputs, litter leachates, or combinations of these. As such, these contributions could respond differently to inundation patterns, tidal action, changes in primary productivity and associated litter-fall. Bouillon et al. (2007) reported considerable porewater contributions of DOC (estimated at 30% of the total DOC pool) draining a mangrove forest in Tanzania during ebb tide, with porewaters exhibiting considerably higher salinity than the creek water column. In contrast, the notably lower percentage of DOC attributed to mangrove inputs in the Shark River indicates that porewater DOC may not account for a considerable component of the DOC pool. However, this is likely due to the large allochthonous DOC inputs received from upstream freshwater marshes in the Everglades, whereas the Tanzania creek system received minimal freshwater inputs (Bouillon et al. 2007).

However, the abovementioned spikes in FDOM during ebb tide provide new information on the role of mangrove inputs to this system. Although non-conservative mixing calculations indicate that mangrove DOC comprises a relatively minor component of the total DOC pool, FDOM spikes indicate seasonally variable contributions exceeding the 6% mangrove input estimation. For three consecutive tidal cycles, FDOM signals were compared by including or excluding the FDOM spikes (Figure 4.5). Based on this comparison, between 8 and 16% of the total change in FDOM during these tidal cycles was attributed to mangrove porewater inputs. The percent contribution of FDOM spikes varied with season, with higher and more consistent mangrove DOC contributions observed during the T time-series compared to D&W time-series. This supports previous research reporting higher CDOM production during wet periods compared to dry periods

(Shank et al. 2010). However, the magnitude of these FDOM spikes infer that the majority of mangrove DOC export into the river during ebb tide (estimated at 65% for SRS-6, Romigh et al. 2006)) occurs at rapid time-scales (1-2 hours). Thus, accurately characterizing this highly dynamic exchange process to constrain aquatic C fluxes in mangrove forests requires high-frequency measurements.

Seasonal variation in FDOM spikes also gives insight into the potential role of mangrove porewaters and primary production in DOC exchange between mangrove forests and the river channel. If primary production preferentially dictated mangrove DOC inputs over hydrology, it would be expected that the highest inputs (largest spikes) would coincide with peak primary productivity during the wet-season (Castañeda-Moya et al. 2013). However, spikes are smaller and less consistent during W1 than T1 or T2, suggesting that the extent and duration of tidal inundation rather than patterns in primary productivity controls the magnitude of DOC porewater exchange. Furthermore, this may indicate that DOC spikes are more strongly associated with leaching from mangrove sediments and porewater exchange, rather than direct leaching from mangrove leaves and stems (Maie et al. 2006b, Romigh et al. 2006).

4.5.3 Water management and rainfall control daily FDOM patterns

Daily and multi-day patterns in FDOM showed clear links to freshwater inputs (Figure 4.2, Section 4.4.2.3), indicating the essential role of upstream hydrology in regulating DOC concentrations in the Shark River. In particular, inflows from water management structures drive a division in FDOM:salinity ratios between time-series (Figure 4.3). Of the hydrologic parameters influencing the estuarine salinity gradient, water management structures are the only means of directly regulating freshwater inflows

to this system, with natural delivery of freshwater from rainfall and potential groundwater inputs and seepage through barriers to flow (Saha et al. 2012). A comparison of T1 and T2 time-series demonstrates the control of FDOM temporal patterns exerted by managed freshwater inputs. Both T1 and T2 exhibit similar FDOM:salinity ratios (Figure 4.3), suggesting similar DOC source and mixing dynamics. However, neither the salinity gradient (dramatically different sea levels, Table 4.1, and salinity, Table 4.2, between the two time-series) nor rainfall (similar for all time-series except W1) can explain the similar FDOM:salinity distributions for T1 and T2 in contrast to the other three time-series. Instead, freshwater control by water management inflows appears to link these time-series (high for T1 and T2, low or absent for the other time-series). This is evident in the shift of FDOM:salinity observed for T2 (Figure 4.3C and Section 4.4.2.1) from ratios characteristic of the dry-season to wet-season which occurred in less than a day. Based on this rapid change along with the divide in Figure 4.2, it is clear that water management inflows (either directly or indirectly) control Shark River hydrology and DOC concentration and export at short time-scales.

Both rainfall and water management inputs were identified as significant freshwater drivers of long-term DOC fluxes in this system, with rainfall contributing almost double the modeling power as managed inflows (Regier et al. 2016). For the high-frequency data collected during this study, the influence of rainfall is less obvious than water management, likely due to unusually low precipitation rates for all time-series except for W1 (Table 4.1). The clearest evidence of rainfall driving changes in DOC occurred with onset of the rainy season (between D2 and W1). Low FDOM values for D2 (relative to D1) were attributed to enhanced saltwater intrusion into upstream

freshwater marshes observed through semi-diurnal tidal signatures in stage data the Rookery Branch gage 20 km upstream of SRS-5 (#022908295, <http://waterdata.usgs.gov/>). Subsequently increased FDOM during W1 was attributed to the enhanced hydrologic connectivity of the estuary to upstream marsh regions as a result of increased rainfall. Decreased DOC concentration and exports due to drought conditions (e.g. D2) have been reported for other coastal wetland systems (e.g. Ardón et al. 2016). Likewise, rainfall events have been linked to increased DOC concentrations in both marsh and mangrove systems (Bergamaschi et al. 2012, Ryder et al. 2014), although shifts in other drivers between D2 and W1 like soil temperature may be partially responsible for the changes in DOC concentration (Davidson & Janssens 2006; Ryder et al. 2014).

During the study period, the influences of water management and rainfall on daily FDOM patterns were evident. However, whereas water management inflows dramatically shifted estuarine hydrology from negative to positive discharge, rainfall did not. The importance of water management to maintain seasonal freshwater delivery has been well-established for this region (Sklar et al. 2005, Obeysekera et al. 2014). High-frequency measurements presented here indicate that, particularly during periods of below-average freshwater flow (e.g. drought), water management inputs are capable of rapidly altering salinity and associated water quality gradients in the coastal Everglades. Based on this, corrective actions by water management (e.g. emergency water releases to slow saltwater intrusion during periods of high drought) guided by high-frequency monitoring provides managers with new tools to rapidly respond to observed or predicted environmental problems. Likewise, as this region is clearly sensitive to managed

inflows, high-frequency measurements are increasingly critical in the monitoring of estuarine response to changes in freshwater inputs.

4.5.4 Linking short-term and long-term fluxes

Hydrology is the primary driver of DOC fluxes, and the strong linear fits in Figure 4.6 confirm this. However, differences in fluxes based on monitoring frequency of DOC concentrations are evident through the deviations of fluxes from the 1:1 line (Figure 4.6A). In general, D&W time-series cluster together close to 1:1, suggesting that during periods of lower freshwater inflows and therefore less variable filtered discharge, (Figure 4.2), interpolating daily DOC fluxes from monthly DOC values is relatively accurate. In contrast, T time-series show more variability (Figure 4.6B), where T1 flux calculations closely follow the 1:1 line but T2 does not. In particular, high flux values during T2 are dramatically over-estimated (up to 180%) by interpolation of monthly DOC to daily resolution. This is likely due to large and rapid fluctuations in discharge (Figure 4.2) driving rapid changes in DOC concentrations. As such, interpolation of daily fluxes from monthly DOC sampling frequencies may be applicable during periods of relatively static discharge, but is not sufficiently accurate to constrain DOC export rates during periods of variable freshwater flows. This supports previous findings that weekly grab sampling was temporally inadequate to characterize DOC fluxes during rapid shifts in hydrology (Jollymore et al. 2012, Pellerin et al. 2012). Thus, current long-term monitoring projects seeking to better constrain C budgets in temporally variable aquatic systems like estuaries could greatly benefit from the simultaneous application of high-frequency measurements.

4.6 Conclusions

A suite of environmental drivers, including salinity, stage and tidally filtered discharge, were identified as regulators of high-frequency FDOM patterns in the Shark River estuary. Values for FDOM changed considerably at tidal time-scales, changing in excess of 100% between consecutive low and high tides during periods of high freshwater discharge. The drivers of FDOM manifested in multiple distinct patterns, with salinity and stage varying semi-diurnally with tides, and knees in ebb tide stage corresponding to spikes in FDOM potentially attributed to mangrove porewater inputs accounting for up to 24% the tidal FDOM signal, particularly during periods of higher inundation. Freshwater discharge also controlled daily and multi-day changes in FDOM (up to $\pm 25\%$), indicating hydrologically driven shifts in DOC concentration, and potentially source. The influence of water management on DOC behavior in the mangrove estuary demonstrated the capability of managed inflows to restore the salinity gradient and accompanying estuarine C dynamics following pronounced drought and elevated sea levels. Rainfall was observed to alter DOC concentrations but had less influence over salinity and FDOM than water management (potentially related to drought conditions during much of this study). In general, managed inflows most strongly affected FDOM characteristics during seasonal transitions while precipitation preferentially and expectedly, controlled FDOM during the onset of the wet season. While management strategies currently focus on longer term hydrologic response (e.g. seasonal to inter-annual) in the context of Everglades restoration, rapid response of the coastal zone to freshwater inflows suggests the ability of water management to control hydrology in the mangrove ecotone at much shorter time-scales. Since response of DOC

mixing and source dynamics to environmental drivers changes vary across temporal scales, integration of high-frequency data into current long-term monitoring programs is essential to understand temporally complex relationships between water quality and hydrology.

Hydrology, climate and management have all been identified as drivers of long-term DOC export in the Shark River (Regier et al. 2016), and findings here generally support that these drivers apply to short-term (hours to days) variations in DOC (based on FDOM as a proxy). Adaptive restoration management relies on constantly improving our understanding of ecosystem function and response to climatic and management factors. Further investigating key ecological indicators like biogeochemistry and nutrient transport spanning spatial and temporal scales will advance modeling capabilities and inform management decision-making. High-resolution measurements of FDOM provide new insights into organic matter cycling in coastal systems and indicate the potential value of high-frequency data to complement and expand existing long-term monitoring programs through a temporally integrated understanding of biogeochemical processes and nutrient budgets in variable coastal ecosystems.

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CHAPTER V

LINKING HYDROLOGY TO LONG TERM DISSOLVED ORGANIC MATTER COMPOSITION IN THE FLORIDA EVERGLADES

(In preparation for Limnology and Oceanography)

5.1 Abstract

Dissolved organic matter (DOM) acts as a master variable in aquatic ecosystems by controlling biogeochemical cycles, influencing water quality and linking terrestrial and oceanic carbon pools. However, water flows can strongly alter the sources, transport and fate of DOM, controlling changes in quantity and composition. In this study, we investigate the relationships between DOM composition based on EEM fluorescence and hydrologic parameters in the subtropical coastal wetlands of Everglades National Park (ENP), the southern portion of the Florida Everglades. Study sites span the two major drainages of ENP: Shark River Slough (SRS) and Taylor Slough (TS) using monthly data collected over 10 years. We found that SRS DOM patterns were more associated with water management inflows while DOM in TS showed a stronger connection to rainfall. The influence of groundwater discharge on DOM composition was observed through the seasonality of the ratio of photo-labile to photo-refractory components, and was most clearly evident for freshwater sites in TS. Furthermore, long-term decreasing trends of one of the fluorescent components, primarily attributed to upstream agricultural areas, suggest the influence of upstream inputs to the ENP DOM pool has been steadily decreasing over the past decade. Relationships developed between water depth and DOM compositional features were then used to predicted changes in response to shifting environmental conditions (temperature and rainfall). Increased rainfall is not predicted to dramatically alter compositional dynamics in freshwater wetland sites, while decreased rainfall predictions indicate dramatic changes to both the quantity and quality of organic carbon in SRS and TS. Findings from the present study clearly show the complex

interplay between Everglades hydrology and DOM patterns, and indicate DOM composition is expected to shift in response to climate change.

5.2 Introduction

Dissolved organic matter (DOM) is an integral component of the aquatic carbon cycle (Battin et al. 2009), accounting for the majority of terrestrial organic carbon inputs from rivers to the ocean (Meybeck, 1982; Hedges et al. 1997). During transit, DOM controls biogeochemistry and water quality by regulating nutrient availability (Boyer et al., 1997; Qualls and Richardson, 2003, Boyer, 2006), transport and complexation of metals (Yamashita & Jaffe, 2008), light availability to benthic communities (Ganju et al. 2014) and the microbial loop (Amon and Benner, 1996; Fellman et al. 2010). The role of DOM in these processes is a function of its molecular composition, controlled by mixing of allochthonous and autochthonous sources including terrestrial plants, soils and microbial inputs (Roth et al. 2014), and can consist of thousands of unique chemical formulae (e.g., Stetson et al. 2003). DOM composition also dictates susceptibility to biological and photochemical degradation (Cory et al. 2014; Chen and Jaffé 2014; Stubbins et al. 2016), processes that can affect molecular complexity.

Because the molecular composition of DOM determines its reactivity in natural waters, understanding the processes that drive changes in composition is essential for defining ecosystem function and predicting response to shifting environmental conditions (Medeiros et al. 2017; Gonsior et al. 2017). However, high molecular diversity and gradients of reactivity, from ephemeral to refractory (Ide et al. 2017), make characterizing the DOM pool a significant challenge. As a result, a variety of analytical

approaches have been used to describe the composition of natural DOM, ranging from determination of individual molecules using mass spectrometry and nuclear magnetic resonance to classifying general compositional features via fluorescence spectroscopy (Minor et al. 2014 and references therein). While molecular-scale studies are essential to fully understand DOM compositional relationships to the natural environment (Nebbioso & Piccolo, 2013; Roth et al. 2014), such measurements require expensive and complex instrumentation, and a high level of statistical interpretation, making them impractical for large sample sizes. Measuring the optical properties of DOM via fluorescence spectroscopy offers a simple alternative to quickly analyze general compositional features, and has long been recognized for its value in this capacity (Stewart and Wetzel, 1980; Kieber et al. 1990), particularly synchronous fluorescence, which simultaneously measures absorbance and fluorescence spectra (Coble, 1996; Jaffe et al. 2004). More recently, fluorescence spectroscopy data collected in the form of excitation-emission matrices (EEMs) have been combined with parallel factor analysis (EEM-PARAFAC) to decompose the complex mixture of fluorescence signatures present in DOM into discrete components indicative of different compositional features (Stedmon et al. 2003; Fellman et al. 2010).

EEM-PARAFAC has been used to trace changes in DOM source and reactivity (Cory & McKnight, 2005; Stedmon & Markager, 2005; Yamashita et al. 2008), biological and photochemical processing (Fellman et al. 2008; Chen and Jaffé 2014), impacts of land use (Williams et al. 2010; Yamashita et al. 2010) and anthropogenic influence in natural systems (Cawley et al. 2012; Shutova et al. 2014; Graeber et al. 2015). Use of EEM-PARAFAC from the Arctic (Gueguen et al. 2013; Walker et al.

2013; Mann et al. 2016) to the tropics (Cao et al. 2016; Lambert et al. 2016), and in headwater streams (Yamashita et al. 2011; Burrows et al. 2013; Hosen et al. 2014), major rivers (Walker et al. 2013; Cao et al. 2016; Lambert et al. 2016), wetlands (Fellman et al. 2008; Yamashita et al. 2010; Cawley et al. 2012; Chen et al., 2013), estuaries (Stedmon & Markager, 2005; Osburn et al. 2012; Cawley et al. 2014), and coastal and open oceans (Jorgensen et al. 2011; Gueguen et al. 2013; Kowalczyk et al. 2013) demonstrates the universal applicability of the technique. Furthermore, increased standardization of data collection and processing allows for direct comparison of PARAFAC components observed in different environments or regions, paving the way for open-source databases like OpenFluor (Murphy et al., 2014).

Due to its broad applicability in a variety of environments, minimal sample preparation and quick analysis, EEM-PARAFAC is an optimal technique for characterizing the optical signatures of DOM sources and reactivity for studies requiring very large sample-sets. As such, EEM-PARAFAC has been applied across broad spatial (Guo et al. 2011; Jaffe et al. 2012; Spencer et al. 2012; Kothawala et al. 2014) and temporal scales (Kowalczyk et al. 2009; Chen et al. 2013). Such studies are of growing relevance, as long-term (inter-annual to decadal) changes in DOC export have been widely observed, but the drivers of these trends remain unclear (Filella & Rodriguez, 2014), with suggested mechanisms ranging from changes in temperature (Evans et al. 2005), precipitation (Pumpanen et al. 2014) and nutrients (Dittmar & Lara, 2001) to land management practices (Krupa et al. 2012).

In this study, we present ten years of monthly EEM-PARAFAC data collected at seven stations in the Florida Everglades that is, to the best of our knowledge, the most

comprehensive record of its kind for a coastal wetland. Historically, the Greater Everglades Ecosystem (GEE), which occupies much of the Southern Florida peninsula, was hydrologically connected via slow and shallow overland sheetflow of freshwater moving from the Kissimmee River basin in the north to the Gulf of Mexico in the south. Drainage, dredging, and construction of canals and barriers to flow disrupted this hydrologic connectivity, and resulted in dramatic loss of organic soils (McVoy et al. 2011), declining water table depths and changes in direction of sheetflow (Sklar et al. 2005). Current landscape-scale efforts are underway to restore sheetflow connectivity along the GEE flowpath (Science Coordination Team, 2003), but the impacts of altered hydrologic regimes on ecosystem function, including carbon cycling, remain uncertain (Estenoz & Bush, 2015, Orem et al. 2015). Coincident with anticipated changes in hydrology related to restoration activities, climate models for the region predict changes in rainfall patterns, evapotranspiration rates, and relative sea-level, influencing salinity gradients and freshwater availability (Obeysekera et al. 2014; Koch et al. 2015). Improved understanding of historic and current linkages between Everglades hydrology and DOM dynamics is therefore essential to inform adaptive management strategies guiding Everglades restoration and climate change resiliency (Orem et al. 2015).

Previous DOM research in the Everglades indicates a clear latitudinal gradient in DOC, with highest concentrations found in the northern freshwater wetlands, especially in agricultural areas, and lowest concentrations in the coastal estuaries and bays south of Everglades National Park (Qualls & Richardson, 2003; Yamashita et al. 2010; Chen et al. 2013). This gradient in carbon concentration is accompanied by similar changes in DOM quality, with a decrease in humic-like components and increase in protein-like materials

moving north to south (Yamashita et al. 2010; Chen et al. 2013). Temporal patterns observed for DOC and DOM suggest seasonal differences in transport along major flowpaths are related to seasonal hydrodynamics (Chen et al. 2013; Cawley et al. 2014; Regier et al., 2016). In addition, while both photochemical and biological degradation pathways play important roles in DOM composition, where photochemical appears to have a greater impact on the humic-rich Everglades DOM pool (Qualls & Richardson, 2003; Chen and Jaffe, 2014), Everglades DOM seems to be relatively refractory on time scales relevant to its residence time in the system (Chen and Jaffe, 2016). Moreover, multiple hydrologic pathways, including groundwater (e.g., Chen et al. 2010) and tidal mixing (e.g., Cawley et al. 2014; Regier & Jaffe, 2016) further affect spatial and temporal patterns of DOM. While there is a reasonably clear understanding of the temporal and spatial patterns and trends of DOM, the connections between hydrology and DOM quantity and composition remain elusive. As hydrologic regimes are anticipated to shift dramatically with ongoing restoration activities and the impacts of a changing climate, it is essential to understand how DOM responds to changes in hydrology in order to predict ecosystem response. The current study interprets long-term trends and patterns of DOM composition measured as EEM-PARAFAC fluorescence components in relation to hydrology. Established relationships are then manipulated based on climate change scenarios set forth by Obeysekera et al. (2014) to predict how DOM composition will respond to shifting hydrologic conditions.

5.3 Methods

5.3.1 Site Description:

The GEE is a large subtropical coastal wetland ecosystem characterized by north-

south gradients of vegetation and nutrients controlled by the balance between freshwater and saltwater (Boyer et al. 1997; Ross et al. 2000). Samples for this study were collected at sites in freshwater marshes, estuarine mangroves and seagrass beds along the two major drainages of Everglades National Park (ENP): Shark River Slough (SRS) and Taylor Slough (TS). ENP is located at the southern terminus of the GEE flow path and encompasses an oligotrophic ecotone at the nexus of marsh and mangroves that is highly sensitive to changes in salinity and nutrients (Michot et al., 2011; Rivera-Monroy et al. 2011, Briceño et al., 2014). SRS covers 1700 km² (Saha et al. 2012) and is the primary drainage of ENP, while TS is considerably smaller, with the southern portion covering just 446 km² (Sandoval et al. 2016). SRS is characterized by deep organic-rich peat soils and longer hydro-periods, while TS sites are located in wet prairies with shallow, less organic-rich marl soils and much shorter hydro-periods (Saha et al. 2012; Obeysekera et al., 2014; Sandoval et al. 2016). The seven sampling sites selected for the study are long-term monitoring locations established by the Florida Coastal Everglades Long Term Ecological Research project (FCE-LTER). We sampled three sites in SRS: SRS2, SRS4 and SRS6, and four sites in TS: TS2, TS3, TS7, and TS10 (Figure 5.1) monthly from late 2004 to early 2014. SRS2 is located in freshwater peat marsh, SRS4 receives muted tidal influence (average salinity: 5.1) and SRS6, located near the mouth of the Shark River, receives strong tidal influence (average salinity: 23.2). TS2 and TS3 are located in freshwater marsh dominated by marl soils. TS7 is situated in the coastal mangrove fringe (average salinity: 16.6), and TS10 is located in Florida Bay, a shallow bay characterized

by high salinity (average salinity: 36.9), considerable seagrass coverage (Zieman et al. 1989) and seasonal hydrologic connectivity with the TS estuary (Sutula et al. 2001).

5.3.2 Sampling, DOC analysis and PARAFAC modeling:

Surface water samples were collected every month just below the surface and filtered through 0.7 μm combusted GF/F filters (Whatman) into pre-rinsed, acid-washed opaque HDPE bottles (Nalgene) then transported to lab on ice and stored in a refrigerator prior to analysis.

Figure 5.1 Map of Everglades National Park. The map indicates spatial extents of Shark River and Taylor Sloughs, and the sampling sites used in this study. S12 indicates the location of water management inputs to Shark River Slough.

DOC concentration ($[\text{DOC}]$) was measured via high-temperature combustion on a

Shimadzu TOC analyzer after acidification to purge inorganic carbon. EEMs were measured using a Horiba Jovin Yvon SPEX Fluoromax-3 spectrofluorometer equipped with a 150 W xenon arc lamp, and fluorescence intensity was converted to quinine sulfate units following Coble et al. (1993). PARAFAC modeling was applied to decompose EEMs into fluorescence components using an alternating least squares algorithm (Bro 1997). 1394 samples were used to construct an eight-component model (“FCE” dataset on www.openfluor.org), which was validated according to methods described in Stedmon and Bro (2008). Details of the spectral characteristics of the eight model components (C1-C8) established for the FCE model are presented in Chen et al., (2010) and Yamashita et al., (2010), but are briefly described here for general reference. C1 through C6 are humic-like while C7 and C8 are protein-like. Within the humic-like group, C4 is consistent with microbial fluorescence characteristics while both C2 and C6 appear to be most prevalent in upstream agricultural regions (Yamashita et al. 2010), with C6 enriched in groundwater relative to surface waters and vice versa for C2 (Chen et al. 2010). For additional details regarding sampling, DOC analysis and EEM-PARAFAC modelling, readers are referred to Chen et al., (2013) and references therein.

5.3.3 Ancillary data collection:

Water level (WL), rainfall (RF) and evapotranspiration (ET) data were retrieved from the Everglades Depth Estimation Network (EDEN; sofia.usgs.gov/eden/). The three parameters are monthly averages of daily values based on the sites used for hydrologic budget calculations presented in Saha et al., (2012) and Sandoval et al., (2016) (SRS and TS, respectively). Here, WL is presented in feet (1 foot = 0.3048 m) relative to the NAVD 88 geodetic vertical datum (ft NAVD 88). Nutrients, dissolved organic carbon

(DOC), and salinity values were collected from several long-term FCE-LTER datasets (fcelter.fiu.edu/data/) to cover all the sites used in the study (Briceño, 2016; Gaiser & Childers, 2016, Troxler & Childers, 2013; Troxler, 2017). Inflow rates were calculated for SRS as monthly average discharge for the sum of the four S12 water control structures. TS inflows were calculated as monthly average discharge for the sum of 23 culverts running underneath the ENP park road, following Sandoval et al., (2016). Figure 5.5 uses WL values collected from EDEN gages adjacent to individual sites (SRS2: P36; TS2: TSB) rather than transect-wide spatial averages.

5.3.4 Statistics:

All statistical tests were performed using the JMP® Version 12 statistical package (SAS Institute Inc., Cary, NC, 1989-2007). First, PARAFAC components were converted into percentages to remove the seasonal influence of DOC concentration on compositional dynamics (Chen et al. 2013). Behavior of individual components has been discussed (e.g., Yamashita et al., 2010, Chen et al., 2013; Chen & Jaffé, 2014), and we sought to reduce dataset complexity by grouping PARAFAC components via hierarchical clustering. Data from all sites were clustered using Ward's minimum variance method (Ward, 1963) after data standardization (Figure 5.2). Four groups were selected from clustering: C1+C3+C5 (terrestrial components), C2 (potentially derived from agriculture), C4+C6 (microbial components) and C7+C8 (protein-like components), and are referred to by these designations throughout the remainder of the manuscript.

Figure 5.2 Hierarchical clustering of the eight PARAFAC components. A cutoff distance of 0.20 established four clusters.

Normal distributions were tested using the Shapiro-Wilk test with p-values < 0.05 indicating non-normal distributions. Because the majority of sample populations used for this study were non-normal, the Kruskal-Wallis non-parametric test was used to determine statistical likelihood of different samples originating from the same distribution (Kruskal & Wallis, 1952). Mann-Kendall tests for monotonic trends (Hirsch et al. 1982) were performed using the “Kendall” package in R (McLeod, 2011). In addition, we applied cumulative sums methods to interpret change in trends by constructing standardized cumulative sums (“Cusums”) charts (Manly & McKenzie, 2000), following methods described in Briceño et al., (2014). Cusum plots are valuable for deriving patterns, trends, and driver-response relationships for complex or highly variable time-series (e.g., Briceño et al. 2014). The features present in a Cusum plot are indicative of variations around the dataset mean, where an increasing Cusum trend

represents a period of values consistently above average and, conversely, negative slopes indicate values consistently below the average. Monotonic increasing and decreasing trends display as bowl-shaped and dome-shaped curves, respectively (Briceño, unpublished). In addition, Cusum plots are robust to gaps (Briceño, unpublished), which are prevalent in the current dataset.

5.4 Results and Discussion

5.4.1 Relating hydrology to DOM dynamics by transect

Table 5.1 presents the average values of relevant hydrologic parameters for 2002-2008, based on hydrologic budgets constructed for SRS and TS by Saha et al. (2012) and Sandoval et al. (2016), respectively. The two primary freshwater inputs to ENP are RF (natural freshwater delivery) and inflows through water control structures along the borders of ENP (managed freshwater delivery). Of these two sources, RF inputs are considerably larger than inflow for both transects. SRS hydrology is seasonally controlled by inflows through the S12 structures located directly upstream of SRS2 (Figure 5.1), which exert considerable influence on DOC transport to the estuary (Cawley et al., 2014; Regier et al., 2016; Regier & Jaffe, 2016). In contrast, TS freshwater hydrology is less influenced by management inputs than precipitation regimes, as evidenced by much lower inflow rates (Table 5.1). TS also has a lower ratio of rainfall (the largest input) to ET (the largest output), leading to longer periods of dry-down, particularly as TS is characterized by a shallower water depths relative to average ground elevation (<https://sofia.usgs.gov/eden/>). Finally, although the magnitude of groundwater inputs is similar between SRS and TS (Table 5.1), the ratio of groundwater to surface

water (rainfall + inflows) is higher for TS (groundwater is equivalent to 37% of surface water inputs) than for SRS (groundwater is equivalent to 28% of surface water inputs).

To test for significant relationships between DOC concentrations, DOM composition and surface water hydrology, we conducted Kruskal-Wallis (KW) non-parametric tests using WL, RF and inflows. The three hydrologic parameters were divided into above-average and below-average groups for each transect. Next, DOM parameters for SRS and TS were tested for significant differences with results presented in Table 5.2 (TS10 was excluded from KW tests in Table 5.2 as Florida Bay is less directly influenced by freshwater inputs).

SRS marshes experience shorter periods of dry-down than TS marshes, and are characterized by deep deposits of organic-rich peats, compared to relatively organic-poor marl soils at TS2 and TS3. Higher DOC inputs from SRS soils are therefore expected, which would be further concentrated by low WLs during the dry season. Consistent with this expectation, [DOC] values are lower during the wet season than the dry season (Table 5.2). In contrast, higher [DOC] at TS sites during the wet season (Table 5.2) can be attributed to rewetting of marl soils by rainfall (Chen et al., 2013). Table 5.2 also indicates differences in the hydrologic drivers of [DOC] changes between the two transects. SRS [DOC] is significantly related to WL and inflows, both of which peak in the late wet season. TS [DOC] is only significantly related to rainfall, consistent with seasonal rewetting and leaching of dried marl soils, especially as rainfall is not a major source of DOC. The difference in relationships between [DOC] and hydrologic factors predicts SRS is more likely to be influenced by changes in water management while TS is linked primarily to seasonal rainfall patterning.

Table 5.1: 2002-2008 average values for hydrologic parameters †

Parameter *	SRS	TS
Rainfall	1295	1113
ET	1367	1468
Inflows	410	148
Groundwater	481	470

* all data presented in mm / yr

† SRS data from Saha et al. 2012, TS data from Sandoval et al. 2016

Table 5.2: p-values for Kruskal-Wallis tests of significance between hydrology and DOM characteristics

DOM	SRS			TS		
	Water level	Rainfall	Inflows*	Water level	Rainfall	Inflows**
DOC (ppm)	0.0131 (-)	0.1913 (-)	0.0145 (-)	0.6066 (+)	0.0070 (+)	0.6653 (+)
% Terrestrial	<0.0001 (+)	<0.0001 (+)	<0.0001 (+)	<0.0001 (+)	<0.0001 (+)	<0.0001 (+)
% C2	0.0010 (-)	0.0065 (-)	0.0235 (-)	<0.0001 (-)	0.1168 (-)	0.0996 (-)
% Microbial	<0.0001 (-)	<0.0001 (-)	<0.0001 (-)	<0.0001 (-)	<0.0001 (-)	<0.0001 (-)
% Protein	0.1775 (-)	0.8419 (+)	0.0351 (+)	0.0006 (-)	0.0604 (-)	0.0001 (-)

* discharge measured at S12 structures

** discharge measured at TS2 following methods in Sandoval et al. 2016

+ increases with increasing water level / rainfall / inflow

- decreases with increasing water level / rainfall / inflow

Unlike [DOC], % terrestrial and % microbial (the two PARAFAC groups with the largest average percentages) show consistently significant relationships to all hydrologic parameters (Table 5.2), with a higher terrestrial signature in the wet season and a higher microbial signature in the dry season (Chen et al., 2013). The relative increase of % terrestrial during the wet season can be explained as the result of flushing of humic-like DOM from marshes and mangroves along both transects (Jaffe et al. 2004; Chen et al., 2013; Cawley et al. 2014). The consistent relationships between % microbial and hydrologic variables in Table 5.2, where % microbial increases during the dry season, are likely linked to increased aerobic activity concurrent with lower WLs. Previously, it was shown that total organic carbon (TOC) concentrations from Everglades vegetation leachates were higher for poisoned samples compared to non-poisoned samples, indicating biological consumption of TOC (Davis et al. 2006). Likewise, bio-degradation experiments using DOC collected in the Everglades presents evidence of susceptibility to microbial processing of plant leachates and to a lesser extend soil leachates (Chen and Jaffe, 2014; Chen & Jaffe, 2016), and our data suggest this may be more pronounced during the dry season. In addition to microbial production, the C6 component, which represents a portion of the microbial-like PARAFAC grouping is enriched in Everglades groundwater (Chen et al. 2010). Thus, seasonal C6 patterns likely represent a combination of microbial activity and groundwater inputs when low WL and high groundwater inputs coincide, notably observed in TS (Sandoval et al., 2016).

The percentage of C2 was significantly related to WL, RF and inflows in SRS but only to WL in TS (Table 5.2). C2 is thought to be primarily sourced from upstream agricultural areas, and transported to ENP through canals (Yamashita et al., 2010), where

it is consistently most abundant in the freshwater marsh sites of SRS (Chen et al. 2013). In contrast to expectations of water management as the primary hydrologic driver, Table 5.2 indicates %C2 is more significantly related to RF ($p=0.0065$) than inflows ($p=0.0235$) in SRS (Table 5.2). Values in Table 5.2 represent transect-wide test results (SRS2, SRS4 and SRS6), and we suggest the significant relationship between %C2 and RF in Table 5.2 represents increased hydrologic connectivity along the SRS flowpath during onset of the wet season and subsequent increased mobilization of C2-enriched DOM at SRS2 downstream (Chen et al. 2013). Site-specific KW tests support this mechanism, where, at SRS2, %C2 has a more significant connection to inflows ($p = 0.0074$) than RF ($p = 0.0156$).

As with [DOC], % C2 is inversely related to wet season hydrology. We attribute this in part to C2's photochemical properties. The apparent persistence of C2 during the dry season may be due to its photorefractory properties (Chen et al. 2013; Chen & Jaffe, 2014), suggesting it will persist more than other fluorophores during dry season conditions conducive to photochemical (increased sunlight penetration of a shallower water column) degradation processes. Therefore, while C2 experiences minimal reduction via photo or biodegradation processes, the remaining PARAFAC components are likely degraded, enriching the C2 signal of the DOM pool. Additionally, C2 may be partially sourced from photo-production (Chen et al. 2013), as reported in other wetlands (Cawley et al. 2012).

Change in the percentage of the protein-like group was significantly explained by inflows for SRS and by WL and inflows for TS (Table 5.2), although relationships between % protein-like and each of three hydrologic parameters in Table 5.2 were

weaker for SRS. C7 and C8 protein-like fluorescence components are generally more abundant in the southern portion of ENP and Florida Bay (Yamashita et al., 2010) and account for only a small percentage of the PARAFAC pool, particularly for SRS. Higher protein content in DOM in the TS region has been attributed to in-marsh sources where canal water inputs into marsh environments become enriched in protein-like DOM as waters slowly move through the wetland (Lu et al., 2003). In the estuarine areas of TS, the higher abundance of protein-like components may be driven in part inputs of DOM enriched in protein-like fluorophores originating in Florida Bay, a region with considerably higher concentrations of protein-like fluorescence than other TS sites (Maie et al. 2012; Chen et al. 2013; Ya et al., 2015). Florida Bay inputs do not influence TS2 or TS3, sites where C7 is higher during the wet season and C8 is higher during the dry season (Chen et al. 2013). Potential drivers of protein-like patterns at TS2 and TS3 are discussed in the next section.

5.4.2 Linking DOM composition and water level

Relationships between DOM and hydrology were also explored quantitatively using linear regression. WL was used in preference to rainfall and inflows as it represents a cumulative average of all freshwater and groundwater inputs. DOC concentration and the relative abundances of the four PARAFAC groups were plotted against WL for upstream (SRS2 and TS2) and downstream (SRS6 and TS7) sites in each transect, with results presented visually in Figure 5.3 and regression statistics in Table 5.3. For TS2, three outliers were identified based on visual inspection of regression fits for microbial and protein-like plots. Regressions for all parameters at TS2 were run with and without the outliers, and regression values improved for two factors (% microbial and

% protein-like). R^2 values without the outliers are presented in parentheses in Table 5.3 and discussed in this section. No outliers were removed for other sites.

As previously shown in Table 5.2, DOC concentrations at freshwater sites have opposite relationships to seasonal hydrology, where DOC is higher at SRS2 during the dry season and higher at TS2 during the wet season. SRS6 [DOC] shows a considerably weaker relationship to WL compared to SRS2, which is surprising as a clear negative relationship between DOC and salinity exists at SRS6 ($R^2 = 0.37$, $p < 0.0001$). As lower DOC levels in the estuary are attributed to dilution of freshwater DOC inputs, driven by both rainfall and management inflows (Regier & Jaffe, 2016), and mangrove DOM inputs are higher during the wet season (Cawley et al. 2014), weaker seasonal trends at SRS6 can be explained as destructive interference of seasonal signals, where DOC is diluted during the wet season during a simultaneous increase of DOC inputs from mangroves. Both TS sites show similar increasing DOC patterns consistent with explanations for Table 5.2, although the relationship between DOC and WL at TS2 is considerably less significant than SRS2. We attribute this to rainfall driving DOC seasonal patterns at TS2, while WL tracks inflow and therefore peaks later in the wet season (Sandoval et al. 2016).

Figure 5.3 Linear regressions of DOC concentration and the four PARAFAC groupings against water level. The left two columns are SRS sites (circles), and the right two columns are TS sites (triangles), where freshwater sites are in red and saltwater sites are marked in blue. Dry season samples are lighter shading, and darker shaded shapes are wet season samples. Gray triangles for TS2 show outliers removed for regression statistics in Table 5.3.

Table 5.3 R^2 values for linear regressions in Figure 3

	<i>SRS2</i>	<i>SRS6</i>	<i>TS2</i> *	<i>TS7</i>
DOC	0.41	0.10	0.09	0.35
% Terrestrial	0.31	0.26	0.21	0.49
% C2	0.13	0.06	0.22	0.40
% Microbial	0.41	0.32	0.07 (0.61)	0.38
% Protein-like	0.06	0.00	0.02 (0.34)	0.40

* values in parentheses indicate R^2 values after removal of three outliers

For the % terrestrial, all four sites in Figure 5.3 exhibit increasing trends with higher WL (see also Table 5.2). Of the four sites, TS2 has the weakest correlation, which may be associated with lower water management related inputs of terrestrial DOM to TS during the wet season in comparison to SRS (Table 5.1). Conversely, higher inflows to SRS increase hydrologic connectivity to DOC-rich peat marshes enriched in terrestrial components north of ENP to the SRS flowpath, enhancing the seasonal differences observed in % terrestrial at SRS2 compared to TS2. Bio and photo-degradation experiments on soil leachates and surface waters collected at SRS3 (8.05 km downstream of SRS2) and TS2 indicate much lower starting and ending concentrations for terrestrial components at TS2 (Chen & Jaffe, 2014), matching the relatively shallow slope of % terrestrial vs. WL in Figure 5.3. In contrast, % microbial exhibits a larger range at TS2 in comparison to SRS2 (Figure 5.3), and the same is true comparing SRS6 and TS7. Enhanced seasonality of the percentage of microbial components in TS may be attributed to enrichment in DOM associated with microbial activity during the dry season, as previously suggested based on fluorescence index (FI) patterns (Chen et al. 2013).

In SRS, DOC inputs to the estuary link to upstream hydrologic conditions at short-term (hourly to daily) and long-term (monthly to yearly) time-scales (Regier et al. 2016; Regier & Jaffe, 2016), and strong conservative mixing of % C2 along the Shark River salinity gradient indicates negligible C2 inputs from the mangrove forest (Cawley et al. 2014). %C2 correlates to [DOC] throughout the GEE (Yamashita et al. 2010), and this pattern is consistent at SRS2, where %C2 correlates with [DOC] ($R^2 = 0.30$). However, the relationship between %C2 and WL for SRS2 is considerably weaker than the relationship between [DOC] and WL (Table 5.3), which can be attributed in part to

the photochemical properties of C2, as discussed previously, but also may be related to the time-lag between onset of the wet season and delivery to ENP of C2 originating upstream in the EAA. For reference, the geodesic distance from outflow structures of EAA to SRS2 is approximately 90 km, and average flow velocities are generally lower than 2 cm s^{-1} (Leonard et al., 2006; Harvey et al., 2009). Even using the unrealistic assumption of a direct flowpath and a constant velocity of 2 cm s^{-1} , transit time from the EAA outflow to SRS2 is approximately 52 days, and substantially lower velocities observed in interior marshes (Harvey et al. 2009) and non-linear flowpaths are likely to considerably increase this conservative estimate. This very rough estimate suggests the potential for a lag time equal to, or greater than, two months between onset of the rainy season and delivery of C2 from the EAA to SRS2. Therefore, while our data fits with the explanation that a considerable portion of C2 in SRS is sourced from north of ENP, it is also clear that a combination of photochemical properties and transit time complicate seasonal relationships to WL.

In contrast to SRS2, TS2 shows a positive correlation between % C2 and WL, which could be interpreted as increased DOC delivered via water management inputs. However, Table 5.1 indicates that water management likely plays less of a role in TS compared with SRS. While it is likely that canal inputs of C2 contribute in some capacity to the seasonal pattern at TS2, we suggest an additional mechanism proposed by Chen et al. (2010) may be responsible for C2 inputs: photo-production of the photo-refractory C2 component from more photo-labile components, particularly C6. Since C6 is enriched in groundwater relative to C2, and vice versa for surface waters (Chen et al.

Figure 5.4 Ratios of C2 to C6 by month for four upstream sites to assess influence of groundwater as a potential C2 source. Wet season points are in black in gray shaded areas, dry season points are in gray. Average C2:C6 values for each site are represented as horizontal black lines.

2010), we expect C6 to be higher during periods of groundwater discharge. As groundwater inputs decrease during the wet season in SRS and TS (Saha et al. 2012; Sandoval et al. 2016), C6 inputs from GW decrease, and remaining C6 is photo-degraded, the relative content of C2 would increase compared with C6. To test this theory, C2:C6 ratios for the four upstream sites (SRS2, SRS4, TS2, and TS3) were plotted by month (Figure 5.4). During the dry season, all sites had significantly lower C2:C6 ratios ($p < 0.05$), indicating either reduced C2 inputs or enhanced C6 inputs, consistent with increased groundwater discharge. Both of these options are anticipated as

the wet season experiences higher water management inputs (increased C2) and reduced groundwater inputs (lower C6). While all sites showed significant seasonal changes in % C6, the TS sites did not show significant seasonal differences for % C2 (TS2: $p = 0.9648$; TS3: $p = 0.1334$). Therefore, at TS2 and TS3, patterns in the C2:C6 ratio are driven by changes in C6 rather than C2. The consistently low C2:C6 values during the mid and late dry season (January-April) for TS sites match reported timing for groundwater discharge (January-June) for TS (Sandoval et al. 2016). The lack of significance in % C6 patterns for SRS sites, combined with less clear C2:C6 seasonal patterns in Figure 5.4, likely correspond to a difference in timing of groundwater discharge between SRS and TS, where groundwater discharge for SRS spans May-November (Saha et al. 2012). Results from Figure 5.4 indicate that, while groundwater likely plays a role in DOM composition in both transects, there appears to be clearer evidence of a seasonal source of C6 via groundwater discharge to TS, which might then, at least in part be photo-converted into C2.

Previous studies of photo-degradation rates of Everglades water, soil and biomass samples suggest that DOM in surface waters is generally less reactive than either soil or plant leachates (Chen & Jaffe, 2016). Thus, if reactivity time-scales are longer than average residence times, a photo-conversion mechanism is unlikely. Recently published water residence times for TS report average residence times greater than 30 days for the time-period of the study, with an average of approximately 27 days during the wet season and around 42 days during the dry season (Sandoval et al. 2016). Half-life values for C6 photodegradation in surface waters at TS2 predict that both labile and refractory C6 pools will experience >95% loss during the wet season and >99% loss during the dry season

(Chen & Jaffe, 2016), based on residence times in Sandoval et al. (2016). Although data were not available to estimate similar C2 photo-generation rates, relatively rapid photo-production of C2 in TS11 sediment leachates (located near TS10) was observed at weekly time-scales (Chen & Jaffe, 2016). Laboratory studies of photochemical properties like Chen & Jaffe (2016) do not account for environmental factors like shading from vegetation, optically active constituents of the water column (both dissolved and particulate materials), and attenuation through the water column. However, the time-scales presented here for water residence time and photo-degradation/photo-production rates provide support for the C6 to C2 conversion as a temporally feasible mechanism.

The relationships between % protein-like fluorescence and WL for SRS sites are very weak, with no linear relationship observed for SRS6, while stronger correlations are present for both TS sites. The plot for TS7 in Figure 5.3 agrees with previous discussion of Table 5.2 results regarding seasonal inputs of protein-like components from Florida Bay to the estuary. A positive relationship between WL and % protein-like fluorophores at TS2 is not explained by Florida Bay inputs, but rather may be linked to hydrologic conditions in TS marshes during the wet season which attenuate rates of photodegradation. Photochemistry experiments using Everglades DOM indicate the C7 and C8 fluorophores are concentrated in biomass leachates for Everglades plants and are simultaneously highly susceptible to photo-degradation (Chen & Jaffe, 2014). Since DOC in the water column can act as a natural sunscreen (e.g., Bracchini et al., 2004) for photo-active compounds like our C7 and C8 PARAFAC components, sites may exhibit a stronger protein-like signature during peak WL (peak attenuation of sunlight) or peak

DOC concentrations (attenuation via absorbance). At TS2, where peak [DOC] occurs during peak wet season (peak WL), ideal conditions exist for shielding photo-sensitive protein-like fluorophores from degradation. This is corroborated by significant KW test results at TS2 for WL and inflows ($p = 0.0027$ and $p = 0.0019$, respectively). In contrast, peak WL is seasonally opposite to peak [DOC] at SRS2, where protein-like fluorophore percentages are consistently low, and site-specific KW test results show no significant relationships between the three hydrologic parameters in Table 5.2 and the percentage of SRS protein-like DOM. Thus, while hydrologic control of protein-like fluorescence in SRS aren't evident based on Table 5.2 or Figure 5.3, separate drivers appear to influence the seasonal patterns of protein-like components at the TS2 and TS7.

5.4.3 Long-term trends of PARAFAC groupings

Long-term datasets are essential to assess changes in ecosystem function controlled by drivers operating at annual to decadal time-scales (e.g., climate change and adaptive management). We examined our DOM fluorescence data for monotonic trends using Mann-Kendall (MK) tests with results presented as tau values along with significance of trends in Table 5.4. Of the parameters tested, only % C2 showed consistent, highly significant trends ($p < 0.01$) for both the SRS and TS transects. Although [DOC] trends were not significant (Table 5.4), strong spatial correlations observed between [DOC] and C2 have been reported (Yamashita et al. 2010). Previously reported long-term decreasing trends in DOC concentration and fluxes for the Shark River (Regier et al., 2016), along with decreasing TOC concentrations in the Florida Keys based on a data record spanning more than two decades (Boyer and Briceño, 2014), also agree with decreasing %C2 trends presented in Table 5.4. Thus, our data suggests

that the source of consistently observed decreasing trends in organic carbon throughout the Everglades may be related to changes in carbon exported from the northern GEE (due to the change in percentage of C2), potentially including DOM exported from the EAA through canals and the water conservation areas.

The steeper slope (larger negative tau value) of the % C2 trend for SRS compared to TS suggests a more rapid decline of C2 in the former drainage system. Since we expect C2 to be sourced primarily from upstream, particularly for SRS, individual MK tests were performed for SRS2 and TS2. While no significant trend was detected at TS2 (tau = 0.085, p = 0.9207), a highly significant decreasing trend was present for SRS2 data (tau = -0.260, p = 0.0003), which supports the hypothesis of a reduction in canal C2 inputs via water management structures to SRS (Yamashita et al. 2010; Regier et al.,

Table 5.4: Mann-Kendall trend test results

	SRS	TS
[DOC]	-0.116	-0.252
% terrestrial	0.193 **	0.025
% C2	-0.346 ***	-0.255 ***
% microbial	0.134	0.087
% protein-like	-0.165 *	0.018

* p < 0.05

** p < 0.01

*** p < 0.001

2016). In order to determine if the MK trend for C2 was related to the quantity of water or the composition of the DOM in that water, a MK test was conducted for average discharge from the S12 structures. A non-significant trend in discharge (tau = 0.064, p > 0.05) indicated that water management inflows are not declining during the time-period of the study, and may in fact be increasing. Therefore, the decrease in C2 in SRS cannot be explained simply as a reduction in managed inflows, but rather indicates a reduction in

the amount of C2 in DOM entering ENP. Moreover, consistent and significant declining C2 trends for all SRS sites (Appendix 5.1) affirm the assumption that C2 is conservatively transported along the SRS flowpath (Cawley et al. 2014).

Additional evidence that upstream DOM inputs to ENP are decreasing during the study-period was gained using chloride (Cl^-) concentration data collected independent of our dataset. Synoptic spatial sampling indicated clear correlations between C2 and DOC, and of both variables to Cl^- throughout the GEE (Yamashita et al. 2010). Cl^- concentrations are also high in canals compared to surrounding marshes (Chen et al. 2006; Scheidt & Kalla, 2007). Moreover, long-term data show increased Cl^- from the 1960s through the 1990s concurrent with increased canal inflows (Miller et al. 2004). Based on these relationships, we used Cl^- as a spatiotemporal proxy for canal inputs of DOM to Everglades' freshwater marshes. Long-term data (late 1970s to present) was collected from three South Florida Water Management District control structures located along canals connecting ENP to the EAA to test if Cl^- trends in canal waters corroborated decreasing C2 trends on decadal time-scales across the GEE (data obtained from DBHYDRO: http://xportal.sfwmd.gov/dbhydroplsql/show_dbkey_info.main_menu). We selected the S8 structure located along the boundary of the EAA and Water Conservation Area 3A (WCA-3A), the S151 structure (situated southeast of S8 at the nexus of two canals) and the S333 structure, located along the L-29 canal which runs along the northern border of ENP and flows through the S12 structures into SRS (Appendix 5.2). All three sites showed significant decreasing trends from the late 1970s to 2016 (S8: $\tau = -0.152$, $p < 0.0001$; S151: $\tau = -0.255$, $p < 0.0001$; S333: $\tau = -0.193$, $p < 0.0001$). The strong spatial correlations between DOC, C2 and Cl^- (Yamashita et al. 2010) along

with consistent decreasing trends in C2 (Table 5.4, Appendix 5.2), and longer-term decreases in Cl^- concentrations (Appendix 5.2) all substantiate the hypothesis that canal inputs to ENP from upstream have been steadily decreasing during the time-period of the present study. Specifically, the trends in C2 suggest reduced influence of inputs from the northern GEE, potentially the EAA.

5.4.4 Predicting DOM response to climate change

Recent climate change scenarios based on downscaling of global climate models predict a temperature increase of ca. 1.5 °C (and a consequential increase in ET) and a change in RF of $\pm 10\%$ for the GEE (Obeysekera et al., 2014). Model outputs indicate a 10% increase in RF yields a modest increase in WL in ENP (approximately 5 cm, or 0.16 ft) while decreased RF produces a more dramatic decrease of 20 cm (0.66 ft) accompanied by an estimated 20% decrease in surface water duration (Nungesser et al. 2015).

Increased and decreased rainfall scenarios are labeled herein as +ET+RF and +ET-RF, respectively to keep nomenclature consistent with previous studies (e.g., Obeysekera et al., 2014; Regier et al., 2016). We applied these predictions to the relationships between WL and DOM quantity and quality established in this study in order to predict potential biogeochemical responses to climate-mediated changes in hydrology. Although Figure 5.3 established quantitative relationships between WL, DOC concentration and DOM composition, many regressions were quite weak or even non-significant (Table 5.3). To better visualize changes in DOC and DOM as a function of WL, the cumulative sums (Cusums) statistical method was used, where Cusums of [DOC] and the PARAFAC groups were plotted against a gradient of WL. SRS2 and TS2 sites were selected for Cusums as the sites most likely to be impacted by changes in freshwater delivery under

the rainfall scenarios and Cusums are presented in Figure 5.5. It is important to note that water depth was used in Figure 5.5 instead of WL (see Methods). Using water depth makes discussion of findings for this section considerably simpler as the majority of literature discussing the climate scenarios we apply (Obeysekera et al. 2014) use water depths relative to surface elevation.

Figure 5.5 Cumulative sums (Cusums) of DOC and PARAFAC groups plotted against an increasing gradient of water table depth. Gray points show each data-point overlain with smoothing lines. The vertical black line is average water depth for the dataset while the shaded area spans average water depth for dry (lower depth) and wet (higher depth) seasons. Dashed black and gray lines are predicted average depths based on +ET+RF and +ET-RF scenarios, respectively.

Unlike Figure 5.3, where some PARAFAC groupings showed little or no correlation to WL, all Cusum curves for SRS2 and TS2 consistently exhibit either bowl or dome shaped curves, indicating relatively monotonic relationships to increasing water depth (bowls are increasing trends, domes are decreasing trends). The inflection points either at the highest point of the dome or the lowest point of the bowl correspond to a shift between above average and below average values, meaning water depth values associated with

inflection points represent a threshold for each DOM parameter. For instance, water depths greater than one ft at SRS2 correspond to below average % microbial, and vice versa for depths less than one ft. In the case of % microbial, the average wet and dry seasonal water depths straddle the inflection point, indicating that, for this set of data, the changes in microbial components at SRS2 are strongly related to the average difference in water depth between wet and dry seasons. One other parameter has an inflection point located within the average seasonal range of water depth: % terrestrial at TS2. However, all other metrics in Figure 5.5 have inflection points located outside the average seasonal range for water depth. As such, average depth conditions either correspond to consistently above or below average values of DOM parameters. For SRS, where inflection points are located below the average dry season water depth, large shifts in DOM composition are not expected for water depths greater than 0.75 ft (except for microbial). Likewise, all components at TS2 except % terrestrial do not shift dramatically until water depth exceeds 1.25 – 1.5 ft (well above the average wet season level). The positioning of inflection points relative to average seasonal water depths provides initial predictions of how [DOC] and DOM compositional features at SRS2 and TS2 will respond to short-term changes in WL. For both SRS2 and TS2 sites, deeper water levels predict higher % terrestrial and lower % microbial. At SRS, higher WL appears to correspond to lower [DOC], %C2 and % protein-like. The opposite is true for TS2, where higher WL predicts increased [DOC] and higher percentages of both %C2 and % protein-like.

The +ET+RF scenario predicts a modest increase of 0.16 ft in average water depth for the GEE (Nungesser et al. 2015), leading to higher than average water depths at

SRS2 which imply an increase in overly wet conditions, although Cusum plots for SRS2 indicate no considerable change in DOM (Figure 5.5). Deeper average water depths are expected increase the extent of soil saturation both spatially (larger flooded areas) and temporally (longer hydroperiods), which has been predicted to lead to shifts in local vegetation communities (van der Valk, 2015). For example, at SRS2, where vegetation is dominated by emergence sawgrass communities, longer inundation intervals may shift environmental conditions to be more favorable towards plants adapted to longer hydroperiods, like spikerush (Armentano et al. 2006; Childers et al. 2006), a plant enriched in the C4 fluorophore in comparison to sawgrass (Chen & Jaffe, 2014). In this manner, the influence of shifting hydrologic conditions on vegetation communities could potentially alter DOM composition. A deeper surface water table is also be associated with changes in nutrients and redox conditions which may encourage peat accretion (Larsen et al. 2007), potentially reducing the amount of DOM exported downstream.

In stark contrast to the +ET+RF, the +ET-RF change in water depth of -0.66 ft applied to Cusums in Figure 5.5 predicts dramatic shifts in DOM composition, dropping water levels below average dry season values at both sites. For SRS2, the decrease in water depth transitions Cusum values across all inflection points, indicating a strong shift to above average values for DOC concentration, % C2, % microbial and % protein-like and below average values for % terrestrial. While DOM has been reported to be relatively stable in terms of photo- and bio-degradation (Chen and Jaffe, 2014) on times-scales of water residence times in ENP, reduced light attenuation at shallower depths might enhance the photo-degradation of the labile DOM pool under these conditions. In addition, the predicted increase of labile DOM under shallower water conditions may

create ideal conditions for biological or photochemical mineralization of DOC to CO₂ (Jimenez et al. 2012).

As for SRS2, the +ET-RF scenario predicts significant shifts in DOC concentration and DOM composition at TS2, although the change in water depth associated with this scenario does not indicate movement across any inflection points (as observed for SRS2), meaning a change from above to below-average values (or vice versa) as a result of shifting water levels is not predicted. Instead, the average water depth is predicted to decrease below the average surface elevation. Figure 5.5 indicates that TS2 DOM dynamics appear to be more resilient to overly dry conditions compared to SRS2 (shallower slopes to the left of the inflection point). However, as hydro-period has been linked to changes in DOC concentration (Mackay et al. 2011) and implicated as a potential driver of molecular diversity in wetlands (Hertkorn et al. 2016), the predicted persistence of dry-down conditions may alter both DOC concentration and DOM composition. While % microbial is predicted to increase at TS under this scenario, DOC concentrations and the other three PARAFAC groups are predicted to decrease. Because groundwater inputs coincide with dry season water depths at TS2 (Sandoval et al. 2016), the predicted increase in microbial signature may be associated with higher groundwater inputs of PARAFAC component C6 (Chen et al., 2010). The combination of lower water depth and decreased DOC concentrations will likely reduce sunlight attenuation, resulting in high levels of photo-degradation of C6 which may lead to higher mineralization rates to CO₂, as predicted for SRS2 along with potential for increased photo-production of C2. However, Jimenez et al. (2012) found decreased net ecosystem exchange at lower water table depths at the TS 1b site (4.62 km upstream of TS2), along with an attenuated

response to temperature, which is surprising as the marl soils of TS are expected to be less efficient as a carbon sink than the deep, organic-rich peat soils of SRS. This contrasts with SRS findings, and suggests that DOM at TS (reported to be a sink of CO₂ by Jimenez et al. (2012)), may not be as strongly impacted by consistently lower water depths as SRS2.

The predicted responses of DOC and DOM composition at SRS2 and TS2 match other reports that the +ET-RF scenario could lead to substantial environmental changes in the Everglades. These include degradation of geomorphology, altered ecological community structure and, as suggested here, potential for massive loss of organic carbon sequestered in peat and marl soils (Obeysekera et al. 2014; Nungesser et al. 2015; Orem et al. 2015). As biogeochemistry, geomorphology and hydrology interact within the Everglades ecosystem, it remains difficult to conclusively state how changes in water management or regional climate will ultimately affect the transport and fate of organic carbon throughout the system. To this point, our findings provide detailed insight into the strong yet complex linkages between DOM composition and hydrology and provide predictions on DOM response to shifting climatic conditions.

5.5 Conclusions

Analysis of ten years of DOM fluorescence data and interpretation of relationships to hydrology revealed that, while compositional features are clearly linked to seasonal hydrologic parameters, the temporal and spatial patterns and trends of DOM are complex, representing a spectrum of sources and reactivity. General spatial and temporal patterns track previous analysis of the first 4 years of this dataset (Chen et al. 2013) and, along

with long-term trend analysis, indicate that the abundance of most DOM fluorescent components were not observed to change dramatically during the course of this study, with the exception of C2. Our comparison of the longer-hydroperiod, organic rich SRS and shorter-hydroperiod marl-dominated TS transects shows different, and sometimes opposite hydrologic responses of DOM composition in adjacent but hydrologically disconnected regions of ENP. SRS is strongly influenced by upstream inputs and water management, which increases the relative abundance of terrestrial DOM while diluting the bulk DOC pool during the wet season. In contrast, DOM dynamics at TS respond more strongly to rainfall and are less influenced by water management. Components clustered into terrestrial and microbial groupings showed consistent seasonal correlations to hydrology, while relationships of C2 and protein-like components to hydrology were more variable between sites. Groundwater was observed to play an important role in delivery of photo-labile C6, primarily to TS freshwater sites, and our data strongly suggests that this is an important source for photo-production of C2 at the TS sites. Over the course of this study, the C2 component associated with inputs from canals draining the northern Everglades significantly declined. Equivalent decreases in C1- throughout the GEE but not in water management inflows to SRS present additional evidence that the influence of inputs from EAA and other upstream regions to the ENP DOM pool is decreasing steadily. Finally, application of climate change scenarios indicate minimal change in DOM composition over relatively short time-scales is expected if precipitation increases, but decreased rainfall may lead to more significant alterations in DOM composition, and potentially the balance of the carbon cycle, particularly for SRS. Continued investigation of DOM composition through collection and analysis of long-

term datasets is essential for interpreting response and resilience to climate change and shifts in management in complex hydrologically driven ecosystems.

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CHAPTER VI

CONCLUSIONS

6.1 Conclusions

Key findings of the research presented in each chapter are already summarized in the respective Conclusions sections. The following summarizes the two most important findings from each of the four chapters, and then explains the relevance of these conclusions as a whole, as it improves current Everglades restoration and resiliency science.

Chapter 2

- Stable organic biomarkers monitored in flocculent matter throughout the DPM experimental test plot suggests preferential mobilization of slough organic matter (relative to ridge organic matter) during increased flow conditions.
- The strong slough-like character of entrained sediments supports this finding.

Chapter 3

- Variables related to freshwater discharge accurately modeled long-term DOC export patterns from the Shark River, with clear links to the salinity gradient, patterns in precipitation, water management and long-term climate.
- Climate change scenarios involving increased rainfall suggest minimal changes in DOC fluxes while decreased rainfall is predicted to dramatically reduce DOC export from the estuary.

Chapter 4

- High-frequency proxy measurements of DOC indicate large changes in concentration at hourly, daily and multi-day scales, controlled by the balance between freshwater inflows (rainfall and management inputs) and tidal action.

- Rapid signatures of ebb-tide DOC inputs, attributed to flushing of mangrove porewaters, were observed for the first time in this system.

Chapter 5

- Hydrologic drivers, including rainfall, managed inflows and groundwater, showed strong connections to DOM compositional features, though the relationships differed between Shark River Slough and Taylor Slough.
- Application of climate change scenarios (as in Chapter 3) indicated that the quality and quantity of DOM in Shark River Slough will be strongly impacted by decreasing water levels associated with reduced rainfall, compared to less severe changes predicted for Taylor Slough.

The Florida Everglades, is a vast and complex mosaic of ecosystems, and, even in its historic state, a comprehensive understanding of interconnected hydrologic and biogeochemical cycles would have been a daunting task for environmental scientists. In its current state, additional layers of complexity, including anthropogenic disruption of natural processes, complex socio-economic demands and a shifting global climate convolute the story further. Efforts to “get the water right” (Sklar et al. 2005) are essential steps towards restoration of freshwater connectivity along the GEE flowpath, and are expected to restore ecosystem function, including biogeochemical cycling of carbon and nutrients (Orem et al. 2015). The results presented within the current body of work clearly indicate the power of water management to restore landscape topography, regulate carbon transport, and maintain the environmental *status quo* in the face of rising seas and uncertainty of future freshwater availability. However, the variability in organic

carbon across temporal and spatial scales is clearly evident in each chapter, indicating the necessity of continued research. The future of the Everglades and, because of reliance on its ecosystem services (Richardson et al. 2014), the population of South Florida, depends on careful adaptive management of the natural resources contained within Florida Everglades. In particular, the application of comparable measures across the broad spectrum of ecologically relevant time-scales (i.e. Chapters 3 and 4) are required to provide a more complete understanding of function and response to the diverse set of environmental drivers influencing the Everglades ecosystem. Additionally, the wide array of drivers identified throughout the projects of this dissertation highlight the necessity of a more integrated, transdisciplinary approach to environmental science, both in the Everglades as well as globally. Careful adaptive management and strong science driving restoration activities in the GEE can serve as a global example for other wetland reclamation or resiliency projects.

APPENDICES

Appendix 2.1 Paq values for roots and leaves collected for dominant vegetation species present in the DPM test-plot. All samples were collected prior to the first flow event, and serve as site-specific validation of the Paq.

Appendix 2.2 Principal component analysis of samples collected throughout the study (n=393). All four biomarkers were reduced to two principal components (PC1 and PC2). PC loadings for ridge, slough and marsh sites are shown as average values for each site (ridge sites are green triangles, slough sites are blue dots and marsh trap sites are brown open diamonds). The average of ridge, slough and marsh trap sites are shown for reference.

Appendix 3.1: Data collection for multi-variate analyses

Samples for TN and TP were collected at SRS-5 with an ISCO auto-sampler as 3-day composite samples (Gaiser & Childers, 2016a), averaged to monthly intervals. DOC grab samples were collected monthly at SRS-5 concurrent with retrieval of TN and TP samples (Gaiser & Childers, 2016b). DOC samples were filtered through Whatman GF/F filters and quantified on a Shimadzu TOC analyzer after acidification and purging to remove inorganic C. The El Niño Southern Oscillation (ENSO) was quantified using the Multivariate ENSO Index, which factors in sea-level pressure, surface wind vectors, water and air temperatures and cloudiness (<http://www.esrl.noaa.gov/psd/enso/mei/index.html>). The Atlantic Multi-decadal Oscillation (AMO) was calculated from Kaplan sea surface temperatures (<http://www.esrl.noaa.gov/psd/data/timeseries/AMO/>) with no smoothing applied. Salinity and discharge were both measured at USGS Gage #252230081021300 (<http://waterdata.usgs.gov/>). Salinity was averaged from daily maximum and minimum values. Discharge was tidally filtered using the PL33 low-pass filter for removal of tidal fluctuations (Flagg et al. 1976). Daily water level, rainfall and evapotranspiration were collected from 17 Everglades Depth Estimation Network (EDEN, <http://sofia.usgs.gov/eden/> (Telis 2006)) sites spatially distributed along the SRS flow-path, with water level reported as monthly averages while both rainfall and evapotranspiration are monthly sums (rainfall and evapotranspiration calculations mirror coincident values reported by Saha et al. 2012). Canal inflows through water management infrastructure controlled by the South Florida Water Management District were reported as monthly sums of daily inflows through the S-12 structures located along

Tamiami Trail, measured as discharge by USGS gages (waterdata.usgs.gov). Sea-level was reported as monthly aggregations of daily values measured in Key West (fcelter.fiu.edu/). Drought data was acquired for the four counties comprising ENP: Miami-Dade, Collier, Broward and Monroe. Monthly percent drought was calculated by averaging weekly D0-D4 coverage values for the four counties (droughtmonitor.unl.edu).

Appendix 3.2: Validation of DOC flux model

All model components were validated as being significant predictors via t-ratios with all p-values < 0.0001 (Supplementary Table 5). The very large ANOVA-derived F-ratio (136.58, $p < 0.0001$) for the model as a whole indicates a strongly significant relationship is present between the independent (predictor) variables and predicted DOC flux. The model was tested for sensitivity to season by plotting separately for wet season and dry season points with no major differences detected ($R^2 = 0.83$ for both dry and wet). Model sensitivity testing was conducted by manipulating individual model components while leaving all other parameters static and predicting DOC fluxes. The results for changing each parameter by 1 standard deviation are presented in Supplementary Table 7 and indicate that model is most sensitive to shifts in salinity. No issues arising from Durbin-Watson tests for multi-collinearity (Makridakis et al. 1978) or variable inflation factor tests for auto-correlation following guidelines from O'Brien (2007) were detected for any parameters. Heteroscedasticity was visually observed in model residuals with higher DOC flux values equating higher variance (Figure 4), which may be indicative of lower power at higher DOC fluxes. However, the observed heteroscedasticity is not statistically supported by the Brown-Forsythe test ($p = 0.18$) which was used in preference to Levene's test (also not significant, $p = 0.12$) due to non-normality of the data (Brown &

Forsythe 1974; Levene 1960). The average error for the model (root-mean-square error/mean of predicted flux) is 37.1% (Supplementary Table 6), although large uncertainty in this model is not unexpected as it is based on diverse array of predictor variables measured at relatively low temporal resolution.

Appendix 3.3: Comparing Shark River DOC fluxes to global estimates

Global riverine export of DOC has been estimated at 170 Tg C yr⁻¹ by NEWS-DOC, a model calibrated and validated with 68 different large river systems (Harrison et al. 2005). For comparison, flux values from this study were transformed using an areal extent of 1700 km² for the Shark River catchment (Saha et al. 2012) and expanded to include discharge from the other four rivers draining the SW mangrove fringe of ENP (Levesque 2004) for an average DOC export rate of 8429 kg C km⁻² yr⁻¹ for the region. This value is higher than any rivers reported in Harrison et al. 2005 (maximum of 6986 kg C km⁻² yr⁻¹, average of 2355 kg C km⁻² yr⁻¹). The difference in flux rates between large global rivers and the Shark River catchment is not unexpected as high-order rivers are generally characterized by median DOC levels (Creed et al. 2015) due to homogenization of headwaters with highly variable DOC concentrations (Freeman et al. 2007). Also, catchments with high percentage of wetland coverage (like SRS) generally have higher levels of DOC (Harrison et al. 2005).

Appendix 3.4 Conceptual ecological model for the South Florida water column used to select potential model predictor variables. Modified from Wingard & Lorenz (2014). Bold arrows track inputs to “Hydrology and water quality”, originating from “Climate Change” and “Water Management & Land Use”.

Appendix 3.5 - principal component loadings for Figure 3

	Intra-annual		Inter-annual	
	PC1	PC2	PC1	PC2
DOC	0.06	-0.39	0.14	-0.45
Disc	0.91	-0.09	0.78	0.19
Flux	0.88	-0.16	0.80	0.18
TN	-0.17	-0.16	-0.52	0.18
TP	-0.16	0.39	-0.68	-0.15
Sal	-0.84	0.39	-0.87	-0.25
Temp	0.43	0.82	0.19	0.93
Inflow	0.85	-0.06	0.81	-0.20
ENSO	0.19	0.13	0.70	0.26
SL	0.62	0.24	-0.29	0.30
ET	-0.06	0.90	-0.73	0.41
RF	0.40	0.72	0.00	-0.91
WL	0.91	-0.25	0.82	0.16
Drght	-0.59	0.08	-0.87	0.20
AMO	0.48	0.36	0.39	-0.56

PC1 - principal component 1; PC2 - principal component 2

Appendix 3.6 monthly coefficients of determination

	DOC	Disc	Flux	TN	TP	Sal	Temp	Inflow	ENSO	SL	ET	RF	WL	Drght	AMO
DOC		0.00	0.03 *	0.01	0.03 *	0.03 *	0.05 **	0.00	0.00	0.01	0.04 *	0.01	0.01	0.00	0.01
Disc	0.00		0.96 ***	0.00	0.03	0.61 ***	0.10 ***	0.55 ***	0.01	0.19 ***	0.01	0.13 ***	0.61 ***	0.16 ***	0.08 ***
Flux	0.03 *	0.96 ***		0.00	0.05 **	0.63 ***	0.08 ***	0.48 ***	0.01	0.15 ***	0.02	0.11 ***	0.58 ***	0.16 ***	0.06 **
TN	0.01	0.00	0.00		0.00	0.00	0.01	0.03 *	0.02	0.01	0.00	0.02	0.02	0.02	0.03 *
TP	0.03 *	0.03	0.05 **	0.00		0.06 **	0.02	0.01	0.00	0.01	0.05 **	0.02	0.03 *	0.02	0.00
Sal	0.03 *	0.61 ***	0.63 ***	0.00	0.06 **		0.00	0.40 ***	0.02	0.11 ***	0.17 ***	0.01	0.78 ***	0.23 ***	0.08 ***
Temp	0.05 **	0.10 ***	0.08 ***	0.01	0.02	0.00		0.09 ***	0.02	0.24 ***	0.57 ***	0.53 ***	0.04 *	0.02	0.17 ***
Inflow	0.00	0.55 ***	0.48 ***	0.03 *	0.01	0.40 ***	0.09 ***		0.00	0.37 ***	0.01	0.02	0.64 ***	0.24 ***	0.13 ***
ENSO	0.00	0.01	0.01	0.02	0.00	0.02	0.02	0.00		0.00	0.01	0.02	0.00	0.17 ***	0.01
SL	0.01	0.19 ***	0.15 ***	0.01	0.01	0.11 ***	0.24 ***	0.37 ***	0.00		0.01	0.09 ***	0.35 ***	0.03 *	0.06 **
ET	0.04 *	0.01	0.02	0.00	0.05 **	0.17 ***	0.57 ***	0.01	0.01	0.01		0.33 ***	0.09 ***	0.00	0.05 **
RF	0.01	0.13 ***	0.11 ***	0.02	0.02	0.01	0.53 ***	0.02	0.02	0.09 ***	0.33 ***		0.02	0.02	0.14 ***
WL	0.01	0.61 ***	0.58 ***	0.02	0.03 *	0.78 ***	0.04 *	0.64 ***	0.00	0.35 ***	0.09 ***	0.02		0.26 ***	0.14 ***
Drght	0.00	0.16 ***	0.16 ***	0.02	0.02	0.23 ***	0.02	0.24 ***	0.17 ***	0.03 *	0.00	0.02	0.26 ***		0.08 ***
AMO	0.01	0.08 ***	0.06 **	0.03 *	0.00	0.08 ***	0.17 ***	0.13 ***	0.01	0.06 **	0.05 **	0.14 ***	0.14 ***	0.08 ***	

*** p<0.001; ** p<0.01; * p<0.05

Appendix 3.7 annual coefficients of determination

	DOC	Disc	Flux	TN	TP	Sal	Temp	Inflow	ENSO	SL	ET	RF	WL	Drght	AMO
DOC		0.03	0.09	0.16	0.09	0.00	0.15	0.03	0.14	0.08	0.00	0.21	0.02	0.01	0.00
Disc	0.03		0.96 ***	0.07	0.08	0.32	0.10	0.73 ***	0.22	0.03	0.13	0.00	0.55 **	0.28	0.00
Flux	0.09	0.96 ***		0.08	0.11	0.36 *	0.09	0.66 **	0.33 *	0.00	0.14	0.00	0.45 *	0.32	0.00
TN	0.16	0.07	0.08		0.08	0.22	0.01	0.12	0.15	0.17	0.04	0.04	0.19	0.10	0.07
TP	0.09	0.08	0.11	0.08		0.43 *	0.07	0.12	0.20	0.31	0.49 *	0.09	0.23	0.39 *	0.06
Sal	0.00	0.32	0.36 *	0.22	0.43 *		0.15	0.21	0.63 **	0.08	0.32	0.11	0.57 **	0.51 **	0.11
Temp	0.15	0.10	0.09	0.01	0.07	0.15		0.00	0.12	0.02	0.10	0.61 **	0.12	0.00	0.19
Inflow	0.03	0.73 ***	0.66 **	0.12	0.12	0.21	0.00		0.12	0.00	0.40 *	0.12	0.48 *	0.57 **	0.08
ENSO	0.14	0.22	0.33 *	0.15	0.20	0.63 **	0.12	0.12		0.14	0.10	0.14	0.17	0.37 *	0.00
SL	0.08	0.03	0.00	0.17	0.31	0.08	0.02	0.00	0.14		0.18	0.01	0.02	0.13	0.02
ET	0.00	0.13	0.14	0.04	0.49 *	0.32	0.10	0.40 *	0.10	0.18		0.07	0.22	0.72 ***	0.33
RF	0.21	0.00	0.00	0.04	0.09	0.11	0.61 **	0.12	0.14	0.01	0.07		0.00	0.02	0.18
WL	0.02	0.55 **	0.45 *	0.19	0.23	0.57 **	0.12	0.48 *	0.17	0.02	0.22	0.00		0.34 *	0.27
Drght	0.01	0.28	0.32	0.10	0.39 *	0.51 **	0.00	0.57 **	0.37 *	0.13	0.72 ***	0.02	0.34 *		0.14
AMO	0.00	0.00	0.00	0.07	0.06	0.11	0.19	0.08	0.00	0.02	0.33	0.18	0.27	0.14	

*** p<0.001; ** p<0.01; * p<0.05

Appendix 3.8 Model error and significance

Initial Model

Term	Estimate	Std Error	% Error	t-ratio	Prob> t
Intercept	1.76E+10	1.39E+09	8%	12.68	<.0001
Sal org	-8.57E+08	6.80E+07	8%	-12.61	<.0001
Inflow	9.99E+04	1.49E+04	15%	6.72	<.0001
RF	2.85E+07	4.27E+06	15%	6.69	<.0001
AMO	-1.47E+09	4.02E+08	27%	-3.65	0.0004

Final Model

Term	Estimate	Std Error	% Error	t-ratio	Prob> t
Intercept	4.41E+10	2.63E+09	6%	16.79	<.0001
logSal	-1.48E+10	9.04E+08	6%	-16.36	<.0001
Inflow	7.06E+04	1.34E+04	19%	5.27	<.0001
RF	2.84E+07	3.67E+06	13%	7.74	<.0001
AMO	-1.46E+09	3.45E+08	24%	-4.24	<.0001

Appendix 3.9 Mann-Kendall results

<i>Parameter</i>	<i>tau</i>	<i>p-value</i>
DOC	-0.11	<0.05
Disc	-0.02	0.74
Flux	0.06	0.30
TN	0.21	<0.05
TP	0.29	<0.05
Sal	0.14	<0.05
Temp	-0.01	0.90
Inflow	-0.02	0.67
ENSO	-0.15	<0.05
SL	0.19	<0.05
ET	0.01	0.79
RF	0.00	0.97
WL	0.01	0.84
Drght	0.10	0.06
AMO	-0.05	0.31
50-year RF*	-0.02	0.50
50-year Temp*	0.07	<0.05

*All tests for 2001-2014 data unless marked

Appendix 4.1 CDOM absorbance values for three Shark River sites (SRS-5 values estimated as average of SRS-4 and SRS-6 measurements) during a portion of the study time-period (11/2014 to 05/2015). SRS-4: open diamond; SRS-5: closed circle; SRS-6: open triangle. A₂₅₄ is absorbance at 254 nm, a₂₅₄ is the absorption coefficient reported in m⁻¹.

Appendix 4.2 fDOM measurements during sequential removal of turbidity. The regression line is fitted to all points <100 FNU ($r^2=0.98$, $n=216$) indicating consistent linear attenuation of the fDOM signal under low (<100 FNU) turbidity conditions.

Appendix 4.3 Patterns in fDOM and salinity during periods of high turbidity. Figure S3a presents three consecutive tidal cycles with high (>100 FNU) turbidity with the fDOM:salinity ratio for these data in Figure S3b.

Appendix 4.4 Temporal (gray diamonds) and spatial (open circles) correlations between FDOM fluorescence and DOC measured in the laboratory ($r = 0.96$, $RMSE = 9.8$ QSU, $n = 53$, $p < 0.0001$). This relationship was used to calculate DOC estimates based on *in situ* fDOM measurements.

Appendix 4.5 Graphical representation of the steps taken to integrate and quantify FDOM spikes. First, FDOM values for the original tidal cycle (A) were set so the lowest FDOM values at the beginning and end of the cycle were at 0 (B). Next, the FDOM spike was removed (C) and the area for each cycle (with and without the spike) was integrated. By subtracting the area of the full cycle (B) from the area of the cycle with the spike removed (C) the area of the spike (D) was obtained.

Appendix 5.1 Temporal trends and Mann-Kendall statistics for sites in Shark River Slough.

Appendix 5.2 Figure S2a presents a map of the three South Florida Water Management District structures where long-term chloride data was collected. S151 is located at the nexus of canals on which S8 and S333 structures are located. S2b shows consistent decreasing trends for long-term data collected at the three structures.

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PUBLICATIONS AND PRESENTATIONS

Regier, P., He, D., Jara, B., Saunders, C., Hansen, C., Coronado-Molina, C., Jaffé, R. (in prep) Sheetflow effects on sediment transport in a degraded ridge-and-slough wetland: insights using molecular markers. *Organic Geochemistry*.

Regier, P. and R. Jaffé (February 2017) Presented a poster entitled “Short-term Dissolved Organic Carbon Dynamics Reflect Tidal, Water Management and Precipitation Patterns in a Subtropical Estuary” at the ASLO Ocean Sciences Meeting in Honolulu, HI

Regier, P. and R. Jaffé (2016) Short-Term Dissolved Organic Carbon Dynamics Reflect Tidal, Water Management, and Precipitation Patterns in a Subtropical Estuary. *Frontiers in Marine Science*

Regier, P., H. Briceño and R. Jaffé (2016) Long-term environmental drivers of DOC fluxes: Linkages between management, hydrology and climate in a subtropical coastal estuary. *Estuarine, Coastal and Shelf Science*

Regier, P., H. Briceño and R. Jaffé (August 2016) Presented a talk entitled “Assessing environmental drivers of DOC fluxes in the Shark River estuary: modeling the effects of climate, water management and salinity” at the ESA Fall Meeting in Fort Lauderdale, FL

Regier, P., H. Briceño and R. Jaffé (February 2016) Presented a poster entitled “Assessing environmental drivers of DOC fluxes in the Shark River estuary: modeling the effects of climate, water management and salinity” at the ASLO Aquatic Sciences Meeting in New Orleans, LA

Regier, P., He, D., Saunders, C., Coronado-Molina, Jara, B., C., Jaffé, R. (April 2015) Presented a talk entitled “Use of Biomarkers in Everglades Restoration” at the Greater Everglades Ecosystem Restoration conference in Coral Springs, FL

Regier, P., He, D., Saunders, C., Coronado-Molina, Jara, B., C., Jaffé, R. (December 2014) Presented a poster entitled “Sheetflow Effects and Canal Backfilling on Sediment Source and Transport in Everglades Freshwater Wetlands: Analysis of Molecular Organic Biomarkers” at the AGU Fall Meeting in San Francisco, CA