

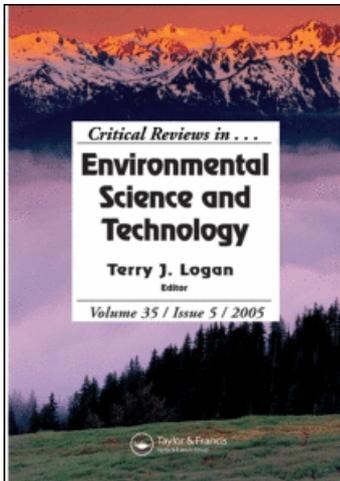
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George R. Aiken^a; Cynthia C. Gilmour^b; David P. Krabbenhoft^c; William Orem^d

^a U. S. Geological Survey, Boulder, CO, USA ^b Smithsonian Environmental Research Center,

Edgewater, MD, USA ^c U. S. Geological Survey, Wisconsin Water Science Center, Middleton, WI, USA

^d U. S. Geological Survey, Reston, VA, USA

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Dissolved Organic Matter in the Florida Everglades: Implications for Ecosystem Restoration

GEORGE R. AIKEN,¹ CYNTHIA C. GILMOUR,²
DAVID P. KRABBENHOFT,³ and WILLIAM OREM⁴

¹U. S. Geological Survey, Boulder, CO, USA

²Smithsonian Environmental Research Center, Edgewater, MD, USA

³U. S. Geological Survey, Wisconsin Water Science Center, Middleton, WI, USA

⁴U. S. Geological Survey, Reston, VA, USA

Dissolved organic matter (DOM) in the Florida Everglades controls a number of environmental processes important for ecosystem function including the absorption of light, mineral dissolution/precipitation, transport of hydrophobic compounds (e.g., pesticides), and the transport and reactivity of metals, such as mercury. Proposed attempts to return the Everglades to more natural flow conditions will result in changes to the present transport of DOM from the Everglades Agricultural Area and the northern conservation areas to Florida Bay. In part, the restoration plan calls for increasing water flow throughout the Everglades by removing some of the manmade barriers to flow in place today. The land-and water-use practices associated with the plan will likely result in changes in the quality, quantity, and reactivity of DOM throughout the greater Everglades ecosystem. The authors discuss the factors controlling DOM concentrations and chemistry, present distribution of DOM throughout the Everglades, the potential effects of DOM on key water-quality issues, and the potential utility of dissolved organic matter as an indicator of success of restoration efforts.

KEYWORDS: Dissolved organic matter, hydrology, leaching, mercury, nutrients, photochemistry, restoration

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Address correspondence to George Aiken, U.S. Geological Survey, 3215 Marine St., Boulder, CO 80303, USA. E-mail: graiken@usgs.gov

INTRODUCTION

Water quality remains one of the biggest issues facing restoration of the Everglades and is a significant challenge to both scientists and resource managers. A more complete understanding of all the factors that regulate water quality in the Everglades is required to anticipate future water-quality conditions that occur in response to the restoration effort. Dissolved organic matter (DOM) is an important, albeit often overlooked, chemical constituent in the waters of the Florida Everglades that plays important roles in many ecological and geochemical processes. The compounds that comprise DOM in aqueous systems often control ecological processes by influencing pH, serving as substrates for microbially mediated reactions (Findlay, 2003; Tranvik, 1998), controlling the depth of the photic zone (Lean, 1998; Wetzel, 2001), and influencing the availability of nutrients (Qualls and Richardson, 2003). DOM also exerts strong chemical controls on geochemical (Hoch et al., 2000; Waples et al., 2005) and photochemical (W. L. Miller, 1998; M. A. Moran and Covert, 2003; Stubbins et al., 2008) reactions, and interacts strongly with trace metals (Haitzer et al., 2002; Perdue, 1998) and organic pollutants (Chin, 2003), enhancing their apparent solubilities and transport. In addition, DOM plays a key role in the formation of disinfection by-products during the treatment of drinking-water supplies with disinfectants (Kraus et al., 2008; Singer, 1994), a problem of particular significance in Florida with its large and growing population.

In the Florida Everglades, issues of carbon reactivity and transport are especially relevant due to the high natural production of organic carbon in the peat soils and wetlands, and the relatively high carbon content of shallow groundwater systems in the region. In turn, this organic matter influences the transport and behavior of other chemicals and controls many ecosystem processes of interest for the restoration of the Everglades. Understanding the factors controlling DOM reactivity is especially important because land-use and water-management practices can result in significant changes in the nature and reactivity of the DOM from those present under more pristine conditions.

Prior to development, the Florida Everglades spanned an area of over 4000 square miles, stretching from the southern rim of Lake Okeechobee to the southwestern tip of Florida (Figure 1). Beginning in the early 20th century and peaking in the 1950s, massive drainage, reclamation efforts, and agricultural development dramatically changed the dynamics and ecological functioning of the landscape (S. M. Davis and Ogden, 1994). In particular, the export of agricultural drainage water from the Everglades Agricultural Area (EAA) resulted in nutrient enrichment of historically oligotrophic wetlands in the Water Conservation Areas (WCAs), changes in vegetation and ecosystem status (DeBusk and Reddy, 1998), and alterations in water redox status and chemistry. Each of these ecosystem changes has exerted a strong influence on both the concentration and reactivity of DOM present in the Everglades.

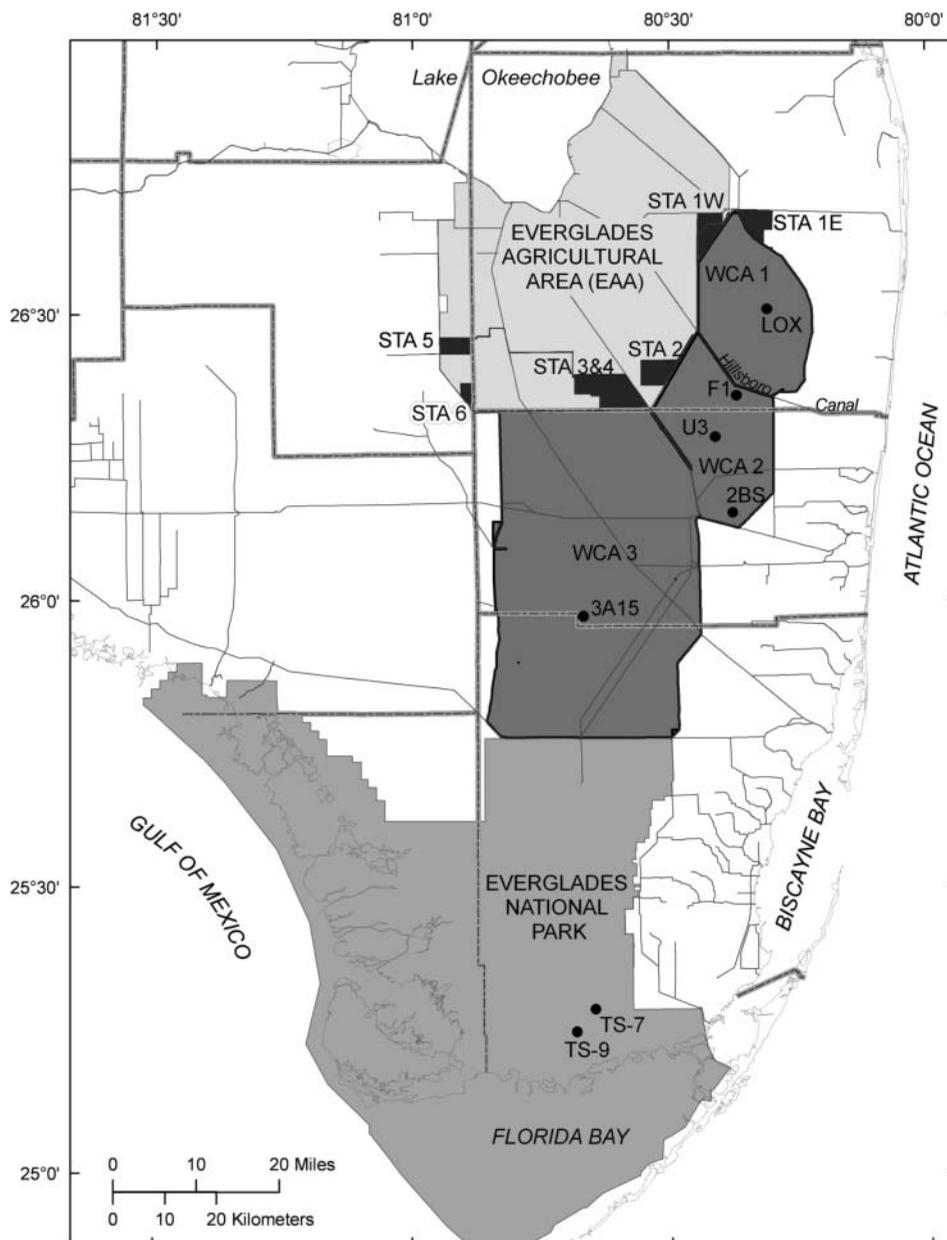


FIGURE 1. Map showing the Florida Everglades with selected sampling sites.

Execution of the Comprehensive Everglades Restoration Plan (CERP; Schrope 2001) will be one of the largest ecosystem restoration efforts attempted to date. Proposed attempts to return the Everglades to more natural flow conditions will result in changes in the quality, quantity, and reactivity of organic matter transported from the EAA and the northern WCAs to Florida

Bay. A concern related to CERP is that chemicals and nutrients associated with agricultural soils and land used for agricultural purposes will be remobilized when these lands are converted to storm water treatment areas (STAs), water storage reservoirs, and wetlands (Perry, 2008; U.S. Department of the Interior, 2005), which may impair water quality and adversely affect receiving waters. DOM is a key chemical driver of these processes and an important water-quality constituent; however, its significance has been largely underappreciated as evidenced by its absence in documents related to water-quality issues in the Everglades (see for instance U.S. Department of the Interior, 2005; Perry, 2008). In this paper, we review the factors controlling DOM concentrations and chemistry, present distribution of DOM throughout the Everglades, and potential effects of DOM on key water-quality issues related to ecosystem restoration.

ANALYTICAL CONSIDERATIONS

To appreciate the significance and potential influence of DOM on processes of interest, it is important to understand what the term *DOM* describes. Dissolved organic matter is a complex, heterogeneous continuum of high to low molecular weight organic compounds exhibiting different solubilities and reactivities. Once in an ecosystem, organic compounds can be truly dissolved, associated with colloids or bound to particles. Historically, organic matter in natural waters has been arbitrarily divided into dissolved and particulate organic carbon based on filtration, generally through 0.45 μm filters (Figure 2). No natural cutoff exists between these two fractions and the distinction is operational. Overlapping the dissolved and particulate fractions is the colloidal fraction, which consists of suspended solids operationally considered as solutes (Morel and Gschwend, 1987). Colloidal organic matter in natural waters is composed of living and senescent organisms, cellular exudates, and partially to extensively degraded detrital material, all of which may be associated with mineral phases (Lead and Wilkinson, 2007).

The study of the nature and environmental significance of organic matter in natural waters is hampered by its inherent chemical complexity, which poses a number of analytical problems that hamper our ability to define both its composition and reactivity (Aiken and Leenheer, 1993). A variety of approaches have been employed in the study of DOM in the Everglades. The simplest of these is the determination of dissolved organic carbon (DOC), dissolved organic nitrogen (DON), and dissolved organic phosphorous (DOP) concentrations (Qualls and Richardson, 2003). DOC concentration alone, however, doesn't provide enough information to assess DOM reactivity. A variety of methods have been employed to learn more about DOM composition. These include measurement of optical properties such as UV/Vis absorbance (Weishaar et al., 2003) and fluorescence (Lu et al., 2003; Maie

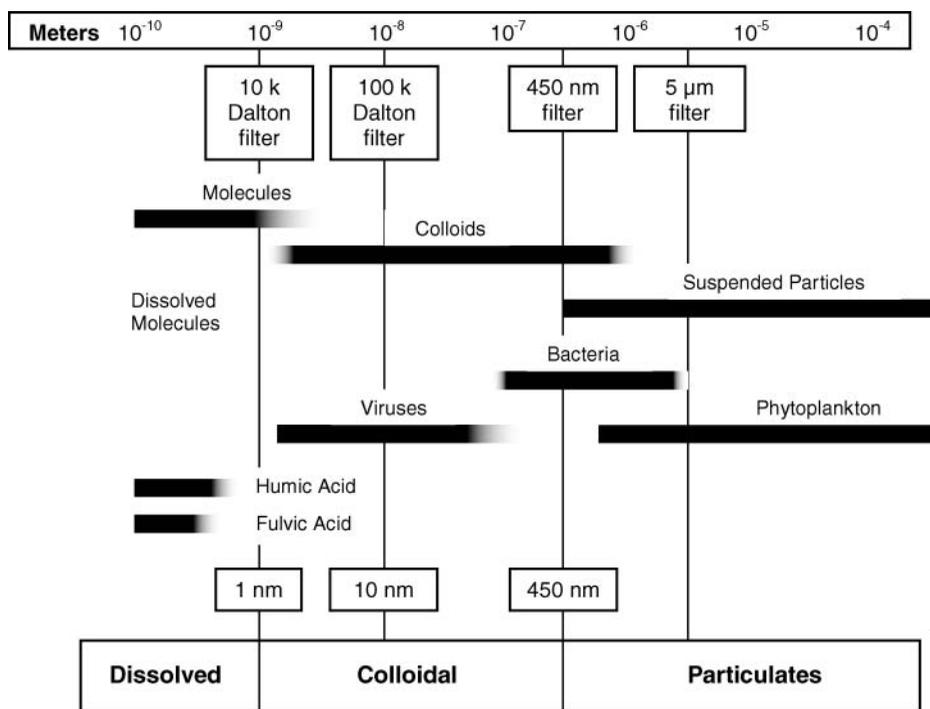


FIGURE 2. Conceptual diagram showing the size distribution of organic matter between particulate and dissolved organic carbon in natural waters.

et al., 2005; Maie et al., 2006a), and isotopic composition (Wang et al., 2002). DOM has been fractionated according to molecular size by ultrafiltration (Wang et al., 2002) and chromatographically according to polarity (Lu et al., 2003; Orem and Hatcher, 1987; Qualls and Richardson, 2003; Ravichandran et al., 1998). Detailed structural information has been obtained on fractionated samples by elemental analyses (Ravichandran et al., 1999), ¹³C-NMR (Lu et al., 2003; Maie et al., 2006b; Ravichandran et al., 1999), pyrolysis-GC-mass spectrometry (Lu et al., 2003), and tetramethylammonium hydroxide (TMAH) thermochemolysis analyses for lignin components, sugar, and phenol assays (Maie et al., 2006b). Trihalomethane formation potentials (THMFP), an indicator of the reactivity of DOM with drinking water disinfectants, were reported by Weishaar et al. (2003).

FACTORS CONTROLLING DOM

Wetlands are complex systems that result in both the production and consumption of biomass. C-fixation as plant biomass through photosynthesis is the first step in the C-cycle that ultimately is completed by oxidation of fixed

C back to CO₂ primarily through microbial oxidation. As part of this cycle, organic matter is stored as plant and microbial biomass, detritus, peat, or soil organic matter and as DOM. Net C-accumulation as peat is the result of greater rates of productivity relative to rates of oxidation and export of plant-derived organic matter. At the most basic level, the C-cycle is tightly related to the cycles controlling phosphorous, nitrogen (Craft and Richardson, 1993; Qualls and Richardson, 2008a), and sulfur.

The chemical characteristics of the DOM are influenced by the source materials (Maie et al., 2006b; Qualls and Richardson, 1995), which in the Everglades include predominantly plants, peat, periphyton, and detritus, and by biogeochemical processes, such as microbial metabolism and photochemical oxidation that are involved in carbon cycling within terrestrial and aquatic systems (Figure 3). These processes, which are most often considered in the context of the generation of greenhouse gases, carbon dioxide (CO₂), and methane (CH₄), influence the concentration and reactivity of DOM, an intermediate byproduct of metabolic activity. The factors that control these processes are nutrient availability (Rubio and Childers, 2006), plant communities (S. M. Davis, 1991; Osborne et al., 2007; Qualls and Richardson, 2003), the nature of organic substrates (Qualls and Richardson, 1995; Rubio and Childers, 2006), soil texture (Amador and Jones, 1997), electron acceptor availability, and hydrology (Figure 3). The interplay of these factors is complicated and can have profound influences on the rates of plant growth, microbial utilization of organic matter, and the establishment of anaerobic

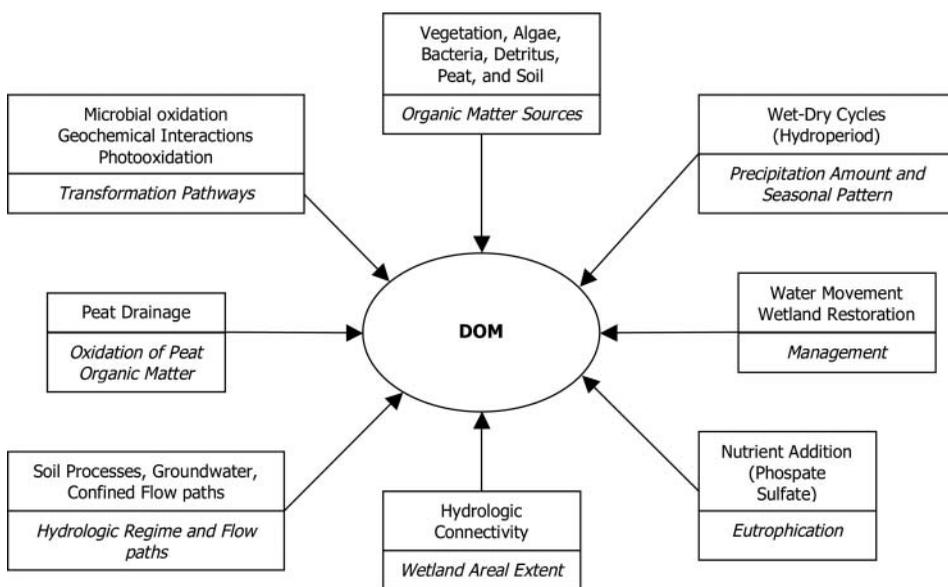


FIGURE 3. Conceptual diagram illustrating the important factors controlling the concentration and chemistry of DOM in the Florida Everglades.

conditions. The generation of DOM in wetlands, such as the Everglades, represents the balance between production, adsorption, desorption, photo-oxidation, and microbial utilization (Moore and Dalva, 2001; Qualls and Richardson, 2008a). Factors controlling DOM are discussed next in relation to four primary categories: leaching of organic matter sources, nutrient addition, hydrologic controls (e.g., hydrologic regime, hydrologic connectivity, and hydroperiod), and photochemistry.

Leaching

Most of the DOM in the Everglades originates from the degradation and leaching of organic detritus from algae, bacteria, and macrophytes living within the wetland environment. Leaching of hydrophilic materials from leaves and detritus is an important first step in the generation of DOM within the Everglades and a major process leading to early loss of biomass. For instance, S. E. Davis et al. (2003) reported that about 33% of the mass of *R. mangle* (Mangrove) leaves was lost after 3 weeks by leaching. Leached organic compounds, which include both N- and P-containing compounds, are likely important sources of energy and nutrition for heterotrophic communities in the Everglades and, as such, drive subsequent microbial oxidation of more recalcitrant organic materials (S. E. Davis et al., 2006; S. E. Davis et al., 2006). While not as well studied as N and P in the Everglades, DOM is a critical substrate for microbial activity (Findlay and Sinsabaugh, 2003). In a number of studies involving the leaching of organic compounds from plant materials, significant amounts of leached DOM have been found to be labile and rapidly utilized by microorganisms (Benner et al., 1986; S. E. Davis et al., 2006; Hur et al., 2009; Maie et al., 2006; Wickland et al., 2007). Benner et al. (1986) reported that much (64–94%) of the labile DOM in leachates from *R. Mangle* was incorporated into microbial biomass. The microbial utilization of the labile compounds leached from plant materials results in changes in the chemical composition, optical properties, and reactivity of the remaining compounds composing the DOM (Hur et al., 2009; Maie et al., 2006; Wickland et al., 2007).

Nutrient Addition

Microbial degradation of organic matter results in the formation of many of the compounds that compose DOM, especially nonvolatile organic acids that dominate the DOM in most aquatic environments. Nutrient addition can play a large role in controlling the rates of microbial metabolism and decomposition of organic matter in wetland systems (S. M. Davis, 1991). Qualls and Richardson (2000) showed quantitative relationships between litter decomposition and nutrient additions in mesocosm experiments in the northern Everglades. Amador and Jones (1995) showed that phosphorous

addition increased the metabolic mineralization of organic matter and exerted a strong influence on redox status (aerobic vs. anaerobic) in pristine, low-P peat soils from Everglades National Park. In a subsequent paper, Amador and Jones (1997) demonstrated the importance of nutrient availability relative to water depth in supporting microbial activity and resulting redox status of saturated Everglades soils. In this work, rates of metabolism in saturated soils determined in a laboratory setting were shown to increase as C:P ratios decreased. More recently, Penton and Newman (2007) showed that nutrient enrichment in the Everglades influences microbial enzyme activity necessary for organic matter decomposition.

Many of the effects of phosphorous enrichment on the Everglades, an historically oligotrophic, phosphorous-limited freshwater marsh, have been well documented (Noe et al., 2001). Of particular interest with regard to DOM, the addition of phosphorous in the northern portions of the Everglades strongly influences the nature of organic matter substrate. Increased concentrations of phosphorous have resulted in greater plant production (Davis, 1991), increased accretion of peat (Craft and Richardson, 1993), the generation of anaerobic conditions in the pore waters in the nutrient-rich areas in northern WCA-2A (see Figure 1), and the subsequent generation of greater concentrations of DOC (Table 1). Qualls and Richardson (1995) showed that there was an inverse correlation between the P stored in peats and the distance from areas with the highest phosphorous inputs. In addition, the majority (75–80%) of the stored phosphorous was in the form of organic phosphorous (Qualls and Richardson, 1995; Reddy et al., 1998).

TABLE 1. Average dissolved organic carbon concentrations and specific UV absorbance data for surface water samples collected in the northern Everglades from 1995 to 2007

Area	Site	n	Average DOC (mgC L ⁻¹)	Average SUVA (L (mgC m) ⁻¹)
Lake Okeechobee	Various	5	14.0 (±1.2)	2.2 (±0.17)
Loxahatchee	WCA-1	8	26.8 (±7.1)	2.6 (±0.3)
Hillsboro Canal (composite)	S10E	12	37.3 (±9.2)	3.4 (±0.2)
	S10D			
	S10C			
WCA2A	F1	28	41.8 (±13.3)	3.6 (±0.3)
	U3	27	40.6 (±13.4)	3.2 (±0.3)
WCA2B	2BS	20	28.9 (±7.8)	2.8 (±0.4)
WCA3	3A15	21	18.8 (±4.9)	2.7 (±0.4)
Everglades National Park	TS-7	8	14.6 (±8)	2.2 (±0.4)
	TS-9	7	14.6 (±8)	2.4 (±0.5)
Constructed wetlands (outflows)	STA1W(ENRP)	10	29.8 (±9.8)	3.4 (±0.2)
	STA-2	1	42.7	3.2
	STA-3/4 Cell 1A	1	40.4	3.5
	STA-3/4 Cell 2A	1	65	3.0
	STA-3/4 Cell 3	1	48.6	3.2

Hydrologic Controls

The hydrology of the Everglades exerts strong controls on both the generation and transport of DOM. Of fundamental significance for the generation of DOM, water depth resulting from drainage or natural changes in hydroperiod is a critical factor controlling redox conditions and carbon metabolism in organic soils (Stephens et al., 1984). Saturation of soils with water favors the establishment of anaerobic conditions due to the slow replenishment of oxygen consumed by microbial oxidation of organic matter in pore waters. Oxygen availability is a critical factor controlling microbial respiration and organic matter turnover in soils and wetlands (Benner et al., 1986; DeBusk and Reddy, 1998; Freeman et al., 2001; Moore and Dalva, 2001). DeBusk and Reddy (1998) showed that aerobic organic matter mineralization rates are approximately 3 times faster than rates under anaerobic conditions. Under anaerobic conditions, therefore, peat formation is favored. Water depth exerts a dual control on redox status and microbial metabolism by acting as a barrier to the reoxygenation of pore waters and controlling the diffusion of nutrients and labile organic matter within the pore waters (Amador and Jones, 1997).

In addition, flow throughout the Everglades controls the transport of nutrients and the export of both DOM and POM from one area to another (Larsen et al., 2010a) and between surface water and groundwater (Harvey et al., 2004). Present day surface water flows are controlled by delivery of water by canals, precipitation, and groundwater discharge (Harvey et al., 2006). In the northern Everglades, approximately 60% of the water delivered to WCA-2A is derived from the EAA (Hurley et al., 1998). These inflows deliver increased concentrations of nutrients and DOM (Qualls and Richardson, 2003; Wang et al., 2002), both of which can influence the consumption and generation of DOM in the wetland system. Once in the Everglades wetland environment, the composition of DOM delivered by canals changes along surface water flow paths reflecting the combined effects of DOM decomposition and the generation of autochthonous DOM. Lu et al. (2003) reported decreases in DOM aromaticity and humic substance content of DOM with distance from canal sites in the southern Everglades. These decreases were accompanied by increases in concentrations of protein-like compounds and carbohydrates reflecting the in situ production of DOM within the wetlands.

Surface water flows deliver dissolved and particulate constituents from the northern more altered Everglades to more pristine wetlands further south and, ultimately, to coastal waters, such as Florida Bay and Biscayne Bay. While the contributions of nutrients from Everglades waters delivered to Florida Bay have been deemed relatively low compared to other sources, these waters are responsible for an estimated 85% of the refractory DOM in Florida Bay (Sutula et al., 2003). Implementation of flow regimes outlined by CERP may increase the export of both nutrients and DOM to coastal waters.

Photochemistry

Interactions of DOM with sunlight are important drivers of a number of reactions in surface waters in the Everglades. From an ecological perspective, absorption of light by DOM influences the depth of the photic zone, which is that part of the water column that has sufficient light to promote photosynthesis (Wetzel, 2001). DOM in most aquatic systems exhibits an exponential decrease in absorbance from the ultraviolet into the visible portion of the spectrum (Miller, 1998). Chimney et al. (2006) reported rapid attenuation of light at wavelengths shorter than 450 nm with less attenuation of longer wavelengths for waters associated with the Everglades Nutrient Removal Project. While the effect of light attenuation on photosynthesis wasn't determined in this study, it was concluded that high DOC concentrations could limit photosynthesis. Absorption of light is a function of both concentration and chemistry of the DOM, with aromaticity being a key factor controlling the absorptivity of DOM (Stubbins et al., 2008). An important, easily determined optical proxy for DOM aromatic carbon content is specific ultraviolet absorbance determined at a wavelength of 254 nm ($SUVA_{254}$), defined as UV absorbance at that wavelength (expressed per meter) divided by DOC concentration (Weishaar et al., 2003). Samples with greater $SUVA_{254}$ values are more efficient absorbers of light than samples with lower $SUVA_{254}$. The most aromatic samples in surface waters in the Everglades are found in areas influenced by canal water from the EAA, such as northern WCA-2A (Table 1). Export of DOM with high $SUVA_{254}$ to more pristine locations could influence photosynthesis, especially for benthic primary producers.

Photochemical degradation of DOM also plays important roles in C-cycling, either directly by the photochemical production of volatile C species (Keiber et al., 1990; Mopper and Keiber, 2002; Stubbins et al., 2008) or indirectly through the production of CO_2 by sequential photochemical/biological oxidation (Miller and Moran, 1997; Mopper and Keiber, 2002). In the latter reaction, relatively refractory DOM is altered by either direct or indirect photo-oxidation to yield more biologically labile compounds that, in turn, can stimulate microbial activity (Pullin et al., 2004; Scully et al., 2003). As such, these reactions are an important part of the ecology of the Everglades. Finally, DOM photochemical interactions influence the geochemistry of redox sensitive inorganic species such as iron (McKnight et al., 1998) and mercury (Hg; Amyot et al., 1997).

Concentration and composition of DOM are both influenced by photochemical oxidation (Schmitt-Kopplin et al., 1998). Generally, aromatic DOM is the most reactive with light, and the presence of aromatic-rich, aquatic humic substances can increase DOM reactivity (Anesio et al., 2005; Stubbins et al., 2008). For DOM from the Everglades, exposure to sunlight results in decreased DOC concentration, decreased DOM aromaticity ($SUVA_{254}$), and an increased proportion of hydrophilic organic molecules. For instance, Qualls

and Richardson (2003) reported decreased DOC and DON concentrations for Everglades (WCA-2A) pore water exposed to light for 21 days. In these experiments, pore water DOM was studied because it was not exposed to sunlight in the field and, therefore, was thought to be more reactive than surface water DOM. Significantly, these authors also observed that nitrogen associated with DON was converted to ammonium, demonstrating that photochemical oxidation of DOM is an important mechanism for release of nutrients associated with DOM in surface water (Qualls and Richardson, 2008a).

SPATIAL AND TEMPORAL DISTRIBUTION

Surface Water DOM

DOM in the Everglades varies in concentration and chemistry both spatially (Qualls and Richardson, 2003; Scheidt and Kalla, 2007; Wang et al., 2002) and with hydroperiod (Lu et al., 2003; Scheidt and Kalla, 2007). In general, DOC concentrations are greatest in areas influenced by agricultural practices, are lower in more pristine locations, and decrease with distance from northern, eutrophic sites in WCA-2A into WCA-2B, WCA-3A, and farther south into Everglades National Park. This trend is illustrated by average DOC concentration data for select sites obtained over a 12 year time period (Table 1; site locations on Figure 1). DOC concentrations are greatest in the Stormwater Treatment Areas (STAs) associated with the EAA, canals draining the EAA (e.g., Hillsboro Canal) and in areas of northern WCA-2A (e.g., Site F1) influenced by agricultural waters, which contain higher concentrations of nutrients than the waters naturally present in the Everglades. The wetland at site F1, which is near the Hillsboro Canal and dominated by *T. domingensis* (cattail; Qualls and Richardson, 2003; Wang et al., 2002), contains greater concentrations of DOM and greater DON/DOC ratios than more pristine sites farther south (Qualls and Richardson, 2003). In contrast to F1, concentrations of DOM in samples from Lake Okeechobee (which is upstream from EAA), and from the Loxahatchee Wildlife Refuge (WCA-1; an area in the northern Everglades that is less influenced by agricultural practices), are lower than those observed in the neighboring regions of the EAA and the eutrophic areas of WCA-2A.

DOC concentrations vary substantially through time, depending on season and antecedent water conditions. Figure 4a presents DOC concentration versus time for sites in WCA-2A (F1), WCA-2B (2BS), WCA-3A (3A15) and Everglades National Park (TS-7). The graph also illustrates the spatial differences in DOC concentration, which are consistently greater at F1 and decrease moving south toward TS-7. Each site exhibits seasonal variations with greatest DOC concentrations observed during dry periods (generally in the spring) when water levels are low throughout the Everglades. During

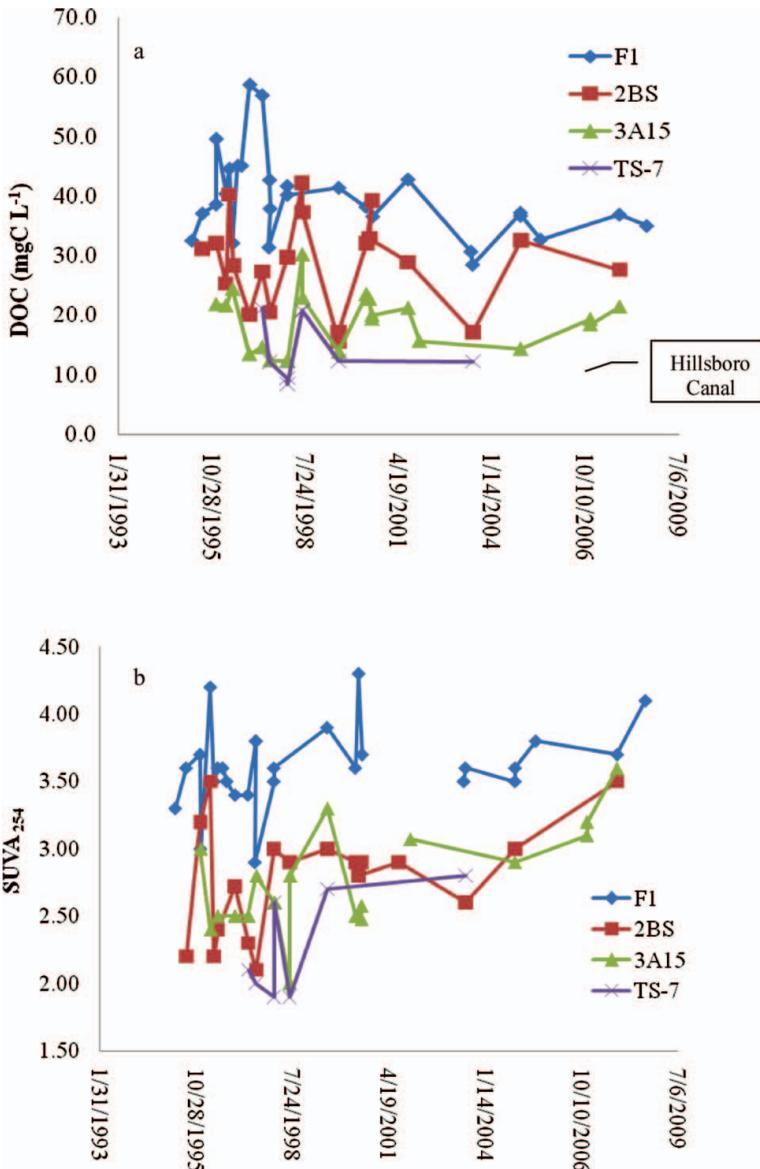


FIGURE 4. Graphs showing the seasonal and spatial variability in (a) dissolved organic carbon (DOC) concentration and (b) specific ultraviolet absorbance (SUVA₂₅₄) for select sites in the Everglades. (This figure is available in color online).

these periods, DOC concentrations increase dramatically due to evaporation of the surface water. Sites located near the canals, such as F1, are less affected by evaporative losses. The lowest DOC concentrations are associated with high water periods (generally from May to October) and are likely due to dilution by rainwater (Lu et al., 2003).

In terms of the nature of DOM, optical properties of DOM, such as $SUVA_{254}$ or fluorescence properties, indicate compositional differences between impacted and pristine locations (Lu et al., 2003; Qualls and Richardson, 2003). For instance, $SUVA_{254}$ is an excellent indicator of the presence of aromatic compounds and is often related to DOM reactivity (Weishaar et al., 2003). Data presented in Figure 4b show that $SUVA_{254}$ decreases from north to south, with impacted sites in the northern Everglades consistently having the greatest values. At sites such as F1, $SUVA_{254}$ data are more consistent over time than the DOC concentration data, indicating that even though the concentration of DOM at these locations is temporally variable, the nature, or quality, of the organic matter is relatively invariant (Figure 4b). Greater variability with time was observed for samples from more pristine locations. SUVA values are higher at these locations during dry periods than for wet periods because of the greater influence of the peat organic matter during the dry periods compared to sawgrass and periphyton during wetter periods.

Pore Water DOM

Pore waters in the eutrophic areas (F1) have substantially greater DOC concentrations (Figure 5a) than in more pristine areas, which is likely the result of increased microbial activity resulting from greater nutrient concentrations

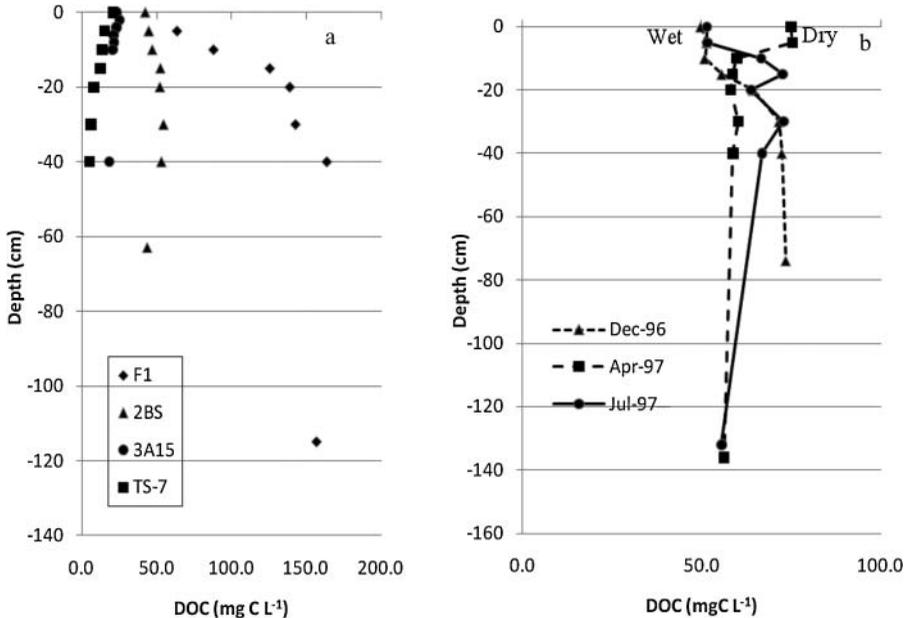


FIGURE 5. Graph showing dissolved organic carbon concentration (DOC) versus depth for (a) four locations (F1, 2BS, 3A15, and TS-7) in the Everglades for June 1998, and (b) the effect of hydroperiod on pore water DOC concentrations at site U3.

and the availability of electron acceptors, such as sulfate. In most cases pore waters have greater DOC concentrations than the overlying surface waters, except during very dry periods (Figure 5b). During the wet periods of the year, DOC concentrations in the surface water are greatly diluted resulting in lower DOC concentrations at shallow depths in the peat compared to deeper samples. However, as the surface water evaporates during dry periods, DOM becomes more concentrated and eventually exceeds the concentrations in the pore water. The SUVA₂₅₄ profiles for pore waters are relatively consistent from site to site compared to surface waters and show little variation with hydroperiod indicating that the nature, or quality, of the dissolved organic matter dissolved from the peat is relatively constant from site to site.

DOM REACTIVITY ISSUES RELEVANT FOR RESTORATION EFFORTS

With regard to the water quality and ecosystem effects in the Everglades, the reactivity of DOM is of critical importance. Effective implementation of the restoration plan hinges on improving or maintaining water quality with regard to a number of important chemical constituents.

DOM-Mercury Interactions

Interactions of mercury (Hg) with dissolved organic matter (DOM) play important roles in controlling the chemical speciation and geochemistry of Hg in surface waters, wetland soils, and pore waters, the partitioning of Hg and methylmercury (MeHg) between dissolved and particulate phases and biota in the water column, and the photoreactivity of Hg and MeHg. In numerous studies of northern temperate environments, strong correlations have been noted between the concentrations of total dissolved Hg and DOM (Brigham *et al.*, 2009; Dittman *et al.*, 2010). In the Everglades, however, correlations between these species are much weaker (Hurley *et al.*, 1998). This difference is likely due to differences in the sources, cycling, and transport of these species in the Everglades compared to other systems. The spatial distribution of total mercury throughout the Everglades is complicated, varying spatially and seasonally (Liu *et al.*, 2009), with concentrations of dissolved Hg generally being less than 5 ng/L (Hurley *et al.*, 1998; Liu *et al.*, 2009), whereas DOM concentrations are generally greater than those found in most aquatic environments and can be generated in situ or transported from other areas in the Everglades.

DOM can influence the chemistry of Hg by acting as a ligand and directly binding Hg and by interacting with HgS such that greater concentrations of HgS are maintained in solution than would be predicted by speciation models (Figure 6). Determination of binding constants (Figure 6a) is hampered

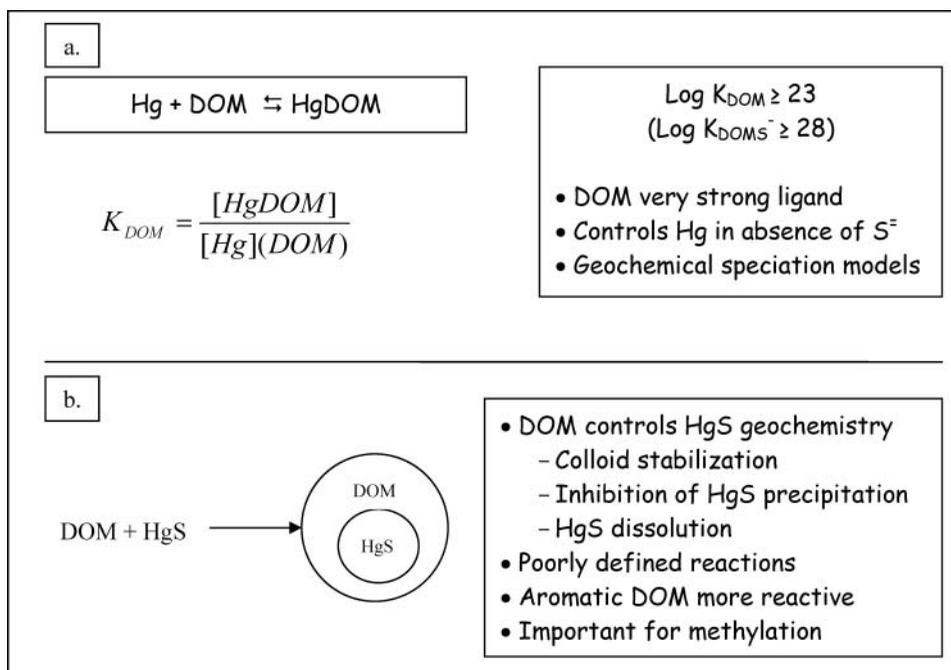


FIGURE 6. Schematic diagram illustrating dissolved organic matter (DOM) interactions with (a) mercury (Hg) and (b) mercuric sulfide (HgS). $\text{Log } K_{\text{DOMS}^-}$ is the binding constant between DOM and Hg expressed as a function of the reduced organic sulfur content of the DOM.

by the intrinsic complexity of the DOM, by the lack of stoichiometric information, and by analytical limitations (Gasper et al., 2007). In recent years, improvements in analytical approaches have permitted the determination of the strength of strong binding interactions between Hg and DOM from a range of environments (e.g., Han and Gill, 2005; Hsu and Sedlak, 2003). Laboratory experiments using a variety of organic matter isolates from surface waters in the Florida Everglades indicate that a small fraction of DOM molecules containing reactive thiol functional groups bind Hg very strongly ($K_{\text{DOM}}' = 10^{23.2 \pm 0.5} \text{ L kg}^{-1}$; Haitzer et al., 2002).

In fully oxygenated Everglades water (sulfide free), the binding of Hg^{+2} by DOM dominates dissolved inorganic mercury speciation (Benoit et al., 2001; Reddy and Aiken, 2001). However, under the anaerobic, sulfidic conditions found in sulfur-impacted Everglades soils in northern WCA-2A and WCA-3A, Hg-sulfide complexes become important in the complexation of Hg (Benoit et al., 1999; Miller et al., 2007) because the affinity of sulfide for mercury greatly exceeds the affinity of DOM for mercury. Under these conditions, Everglades DOM has been shown to interact strongly with HgS, a relatively insoluble compound, to inhibit HgS aggregation (Figure 6b; Ravichandran et al., 1999) and to promote dissolution of solid HgS (Ravichandran

et al., 1998; Waples et al., 2005) under conditions found in Everglades pore waters. In these studies the chemical composition of the DOM, especially aromatic carbon content, was demonstrated to be important in controlling DOM interactions with HgS. In solution, interactions of HgS with DOM have been hypothesized to reduce the concentration of small neutrally charged, bioavailable forms of Hg. Neutral forms of HgS (HgS^0) are thought to be more likely to partition across cell membranes and more available for methylation by sulfate reducing bacteria (Benoit et al., 1999) than charged species. Therefore, reactions that influence the chemistry of HgS are critical for understanding Hg methylation. The influence of DOM on bioavailability of HgS through control of HgS surface properties is a topic of ongoing research.

A consequence of strong interactions between DOM with both Hg^{+2} and HgS is that DOM influences the partitioning of Hg to particles and soil organic matter such that concentrations of dissolved Hg increase in the presence of high concentrations of DOM (Drexel et al., 2002). This is significant because many of the processes (both abiotic and biotic) involved in Hg cycling in the Everglades are hypothesized to be strongly dependent on the concentration of total dissolved Hg. In addition, Hg-DOM interactions are thought to be important for the transport of Hg in aquatic systems (Brigham et al., 2009). Field- and lab-based partitioning coefficients indicate that Hg strongly interacts with Everglades POM, but that DOM influences the strength of these interactions (Drexel et al., 2002). In a field- and lab-based study, aquatic humic substances from F1, the northern, eutrophic site, were found to be more effective at competing with the peat for Hg(II) than similar samples from a more pristine site (2BS), reflecting different degrees of Hg reactivity from different areas of the Everglades. Recently, Liu et al. (2009) demonstrated that, at the landscape scale, DOM was an important factor controlling the distribution of both Hg and MeHg between surface water and soil, floc, and periphyton.

Finally, DOM plays a key role in the photochemistry and redox transformations of both Hg and MeHg in natural waters (Garcia et al., 2005). Photoreduction of Hg(II) and MeHg results in the formation of dissolved gaseous Hg^0 , a form of Hg that has a high vapor pressure and, subsequently, is subject to volatilization from surface waters to the atmosphere (Amyot et al., 1997). The presence of greater amounts of DOM (DOC concentrations up to approximately 20 mg C/L) has been shown to attenuate the production of Hg^0 in lake studies (Garcia et al., 2005). In most studies, the primary effect of the DOM on Hg reduction has been ascribed to attenuation of light penetration into the water column. However, mechanistic understanding of the role of DOM in controlling either the photoreduction itself, or subsequent photooxidation is lacking. Photoreduction is a key process controlling Hg cycling in surface waters and has received some attention in studies in the Everglades (Lindberg et al., 2002; Lindberg and Zhang, 2000), although the role of DOM in mediating the formation and stability of Hg^0 has not been

addressed in these studies. Based on observations in other systems, DOM throughout the Everglades should exert a strong influence on photoreduction that will vary spatially and temporally depending on both the concentration and aromaticity ($SUVA_{254}$) of the DOM.

DOM-Copper Interactions

Trace metals such as copper, manganese, and zinc have long been added to Everglades Sawgrass Muck soils in the EAA to improve soil fertility and, in the case of Cu, as fungicides for a large number of crops (Allison, 1930; Kretschmer and Forsee, 1954). A concern related to the Everglades Restoration Plan is that metals associated with agricultural soils and land used for agricultural purposes will be remobilized when these lands are converted to storm water treatment areas (STAs), water storage reservoirs, and wetlands (U.S. Department of the Interior, 2005). Of the different trace-metal soil amendments, copper, in particular, is harmful to algae (McKnight, 1981) and a variety of aquatic organisms, including fish (Moran et al., 1987; Richards et al., 2001). Concerns for possible deleterious effects of Cu in the Everglades have focused largely on periphyton, an important component of the Everglades ecosystem (U.S. Department of the Interior, 2005). However, other aquatic organisms could also suffer from its presence. For instance, Hoang et al. (2008) demonstrated that Cu released from soils formally used as citrus farms was harmful to Florida apple snails and accumulated in and posed a potential threat to predators of the snail, which include the Florida snail kite.

Studies of the fate of Cu in agricultural soils have shown residual Cu to be bound to soil organic matter (Strawn and Baker, 2008). In the Everglades, Cu has been shown to accumulate in decomposing litter (Qualls and Richardson, 2008b). In addition, P-enriched areas in the northern Everglades also contain elevated concentrations of Cu, and there is a gradient in Cu concentration that mirrors the P-gradient in these soils (Qualls and Richardson, 2008b). Hoang et al. (2008) demonstrated that Cu associated with Everglades soils could be readily desorbed, resulting in dissolved concentrations substantially greater than U.S. EPA water-quality criteria for freshwater organisms and far in excess of concentrations required for acute effects to plants and algae and chronic effects for aquatic organisms (Schuler et al., 2008). The effects of DOM on Cu release were not investigated in this study.

DOM-Cu interactions have been extensively studied in a number of environmental settings and are significant for Everglades restoration in that they can control the solubilization of Cu bound to soils, influence the toxicity of Cu to aquatic organisms (McKnight, 1981), and drive the transport of Cu in rivers (Breault et al., 1996) to estuaries and marine systems (Tang et al., 2001). Binding of Cu by DOM is an important control on the toxicity of Cu in aquatic systems. It is generally recognized that Cu toxicity is determined by cupric (Cu^{+2}) ion activity, not total Cu concentration (De Schampelaere et al.,

2004; McKnight, 1981; Richards et al., 2001). For instance, McKnight (1981) demonstrated that the concentration of free copper determined the response of phytoplankton to Cu added to a reservoir to control algal blooms, and the free copper concentration was controlled by complexation with aquatic humic substances. The role of DOM in controlling the toxic effects of Cu has been incorporated into the Biotic Ligand Model (BLM), a computer model that estimates the effects of water chemistry on the speciation of metals and their acute toxicity to aquatic biota (Di Toro et al., 2001; Smith et al., 2006). Recent studies have shown that both the chemistry and concentration of DOM influence the toxicity of Cu. In studies on the toxicity of Cu to fish (Richards et al., 2001) and *Daphnia magna* (De Schamphelaere et al., 2004), DOM rich in aromatic moieties (high SUVA₂₅₄) was found to inhibit the effects of Cu to a greater degree than less aromatic DOM. In the context of the Everglades, these results are significant because DOM originating in areas influenced by EAA waters is more aromatic than DOM from non-impacted areas of the Everglades. Effects of this DOM on Cu mobilization, transport, and bioactivity warrant further investigation.

DOM-Ca Interactions

The biogeochemistry of Ca⁺² and calcium carbonate (CaCO₃) are important for a number of processes in south Florida including the formation of calcareous periphyton (McCormick et al., 2000), the associated generation of marl soils in the southern Everglades (S. M. Davis et al., 2005), and the ecology of coral in coastal waters (Ramseyer et al., 1997). DOM is known to strongly interact with Ca⁺² and CaCO₃, resulting in the inhibition CaCO₃ crystal growth (Hoch et al., 2000; Inskeep and Bloom, 1986; Lin et al., 2005). Consequently, calcite geochemistry in many waters is controlled by DOM (Chave and Seuss, 1970; Reynolds, 1978). In a study of the influence of DOM on the rates of precipitation and subsequent morphology of CaCO₃ in the Everglades, Hoch et al. (2000) demonstrated that DOM from the northern Everglades (F1) was more reactive than DOM from a site less impacted by agricultural influences (2BS) and noted that reactivity was related to the aromaticity of the organic matter. Organic matter from the northern Everglades, therefore, would be expected to exert stronger controls on calcite biogeochemistry.

The predrainage Everglades likely contained DOM similar to that found today in the more pristine portions of the Everglades. Studies in different ecosystems related to DOM influences on calcite geochemistry have primarily focused on the nature of the chemical interactions (Hoch et al., 2000; Lin et al., 2005; Reynolds, 1978) and have not addressed the potential ecological impacts of these interactions. In the Everglades, export of aromatic DOM from northern locations could substantially influence elements of the system related to CaCO₃ biogeochemistry. Of these, potential impacts on periphyton growth are important because periphyton fill a critical ecological niche at the

base of Everglades food webs (Browder et al., 1994; Gaiser, 2009). In addition, DOM influence coral formation, both directly (Ramseyer et al., 1997) and indirectly by adversely influencing microbial communities important for coral development (Shank et al., 2008). Given the importance of periphyton and coral to a healthy greater Everglades system, the significance of DOM influences on their development need to be considered. Finally, DOM might affect the reactivity of calcium silicate slag with P. The addition of calcium silicate slag to organic soils after flooding is a potential approach to reducing the mobilization of P (Chimney et al., 2007).

IMPLICATIONS FOR ECOSYSTEM RESTORATION PROJECTS

Constructed Wetlands and Stormwater Treatment Areas

One of the primary goals of CERP is the improvement of water quality by the removal of nutrients, especially phosphorous, that are key drivers of eutrophication in the northern Everglades. To assist in accomplishing this goal, constructed wetlands, known as STAs, have been designed to use biological processes to reduce concentrations of P in waters entering the Everglades from the EAA (Perry, 2008). Despite the potential advantages of these and other constructed wetlands in removing nutrients, several undesirable consequences, such as the generation of DOM or increased methylation of Hg, can result. Wetlands are complex systems with competing biogeochemical processes that, in addition to producing and consuming biomass, also result in the generation of DOM. These processes are interdependent and proper management designed to accomplish the goal of nutrient removal while minimizing unintended consequences requires an understanding of underlying biogeochemical processes and the influences of factors such as hydrologic (water depth) and vegetation types on processes of interest.

Within the STAs, processes regulating C cycling can act to remove DOM from inflow waters or can increase DOM export from the wetland. Gu et al. (2006) reported that during wet periods, DOM exported from the Everglades Nutrient Removal Project (presently STA-1W) was often less than inflow waters; however, during drier periods, more DOM was exported than delivered to the wetland. Significantly, waters leaving the STAs have relatively high DOC concentrations and high SUVA₂₅₄ values similar to those measured in eutrophic sites in northern WCA-2A (Table 1). In contrast, DOC concentrations and SUVA₂₅₄ were lower for samples from Lake Okeechobee, which is a water body that is also influenced by additions of nutrients from EAA. The STAs and Lake Okeechobee differ in terms of water depth and plant communities, important factors that can control DOM concentrations and chemistry. In general, the chemistry and reactivity of DOM resulting from microbial sources, such as algae and periphyton, differs from DOM evolved from higher plant sources, such as *T. domingensis*, with higher plants generating

DOM enriched in aromatic C (McKnight and Aiken, 1998). Periphyton (McCormick et al., 2006) and emergent vegetation are two management options for P removal that can yield different DOC concentrations and chemistry.

Aquifer Storage and Recovery

Aquifer storage and recovery (ASR) is one of the approaches proposed by CERP to help manage water supplies in south Florida (Perry, 2008). A large number of wells will be used to deliver and store water in receiving aquifers during periods when water is plentiful. Subsequently, during drier periods or when water is needed, the stored water would be available for distribution at the surface. While ASR technology has been tested at some locations in south Florida (Reese, 2002), it has not been used at the scale proposed by CERP (Perry, 2008) and much needs to be learned about optimizing the benefits while minimizing unintended consequences resulting from geochemical and microbial reactions. Processes that could adversely affect recovered waters are leaching of materials, such as As, U, and trace metals from geologic formations (Arthur et al., 2005; Arthur et al., 2007), reactions between compounds in injected waters with those in the aquifer, and inclusion of aquifer solutes in recovered waters. In addition, receiving waters can be contaminated by organic compounds, such as pesticides, and DOM can stimulate microbial activity within the aquifer.

The introduction of potentially reactive organic matter into an aquifer can be a significant factor in controlling a number of geochemical, microbial, and environmental processes. For instance, in addition to directly binding metals and controlling their transport, DOM has also been implicated in the geochemistry of arsenic (As) through the formation of DOM-Fe-As complexes (Ritter et al., 2006). The ability of DOM to influence geochemical reactions is a function of both concentration and DOM composition. The overall influence of DOM in the geochemistry of groundwater and aquifer solids associated with ASR requires more study.

Of particular significance is the potential for DOM to stimulate microbial activity in the aquifer. Enhanced microbial activity could result in oxygen consumption resulting in anoxic conditions with attendant solubilization of metals, such as Fe and Mn, under reducing conditions. In addition, these reactions contribute to microbial transformation of the organic matter and potentially fuel undesirable side reactions, such as sulfate reduction. In laboratory incubation experiments designed to address the implications of ASR for Hg biogeochemistry in the Everglades, sulfate reduction was observed to be an important process leading to the consumption of both DOM and sulfate (Krabbenhoft et al., 2007). In these experiments, the remaining DOM was more aromatic and potentially more reactive with regard to geochemical processes than the original DOM.

Finally, in addition to harmful organic compounds already present in potential ASR injection waters, efforts to disinfect these waters can result in the formation of new organic compounds of interest. It is anticipated that waters from sources such as Lake Okeechobee will be chlorinated to eliminate harmful pathogens (Perry, 2008). A consequence of reactions between chlorine and DOM is the formation of chlorinated organic molecules commonly referred to as disinfectant byproducts (DBPs), a class of compounds whose presence in drinking water is regulated by the USEPA (U.S. Environmental Protection Agency, 1998). One concern for the implementation of ASR, therefore, would be the fate of injected DBPs resulting from source water chlorination. In an ASR study in California, Fram et al. (2003) reported that trihalomethanes (THMs), a class of compounds comprising DBPs, behaved conservatively under aerobic conditions and were present in recovered waters. In addition, residual chlorine present in the injected waters continued to react with DOM to form new DBPs.

FUTURE DIRECTIONS AND MEASURES OF SUCCESS

Efforts to return the Everglades to more natural flow conditions will result in changes to the present production and transport of organic matter in the system. Under the present flow regime (Figure 7a), more pristine areas of the Everglades (e.g., the southern portion of WCA-3, Everglades National Park, and central area of Loxahatchee Wildlife Preserve [WCA-1]) have been mostly spared exposure to waters from the northern Everglades. A challenge of the plan outlined by CERP (Figure 7b) is to address the needs of these areas for greater water flow without adversely impacting these ecosystems with water of lesser quality. Constituents that may be transported to more pristine areas are nutrients, DOM, and those metals (e.g., Hg, Cu) and organic molecules (e.g., herbicides, pesticides) that interact strongly with DOM. Imported DOM can influence the ecology of these areas by serving as a substrate and source of nutrients for the microbial community and by the absorption of light. In addition, processes regulating in situ production of DOM may be altered by changing water quality.

Three general areas are important to focus future efforts in the study of Everglades DOM. First, given DOM reactivity, influence on ecosystem dynamics and significance to the success of water management (e.g., ASR), further research is warranted to more clearly understand its effects on overall water quality and ecosystem health. Second, to effectively utilize DOM to monitor the outcomes of water management decisions, it is important to establish present trends in seasonal variability in DOM concentration and composition at appropriate monitoring sites throughout the Everglades. Historical data, such as those reported by the U.S. EPA (e.g., Liu et al., 2009; Scheidt and Kalla, 2007) can be useful in this effort; however, it is important

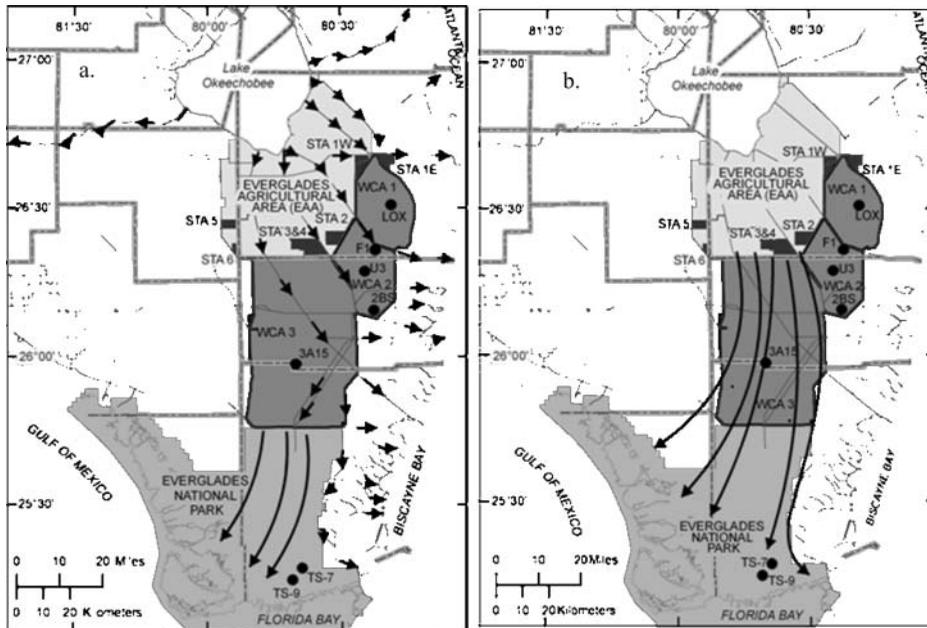


FIGURE 7. Maps of the Florida Everglades showing (a) present flow conditions and (b) anticipated flows based on the Comprehensive Everglades Restoration Plan (CERP).

to establish sufficiently complete databases to define the effects of hydroperiod and season on the DOM observed at these stations. Finally, consideration of management options could be important to mitigate negative impacts of DOM in downstream receiving waters. This is particularly important with regard to constructed wetlands and the return of lands formerly devoted to agriculture to water storage and nutrient removal purposes. For instance, factors such as vegetation, water depth, and hydrologic treatments are all likely to influence both DOC concentration and reactivity.

To assist with the measurement and interpretation of DOM data, the link between the nature and reactivity of DOM and its optical properties can be exploited to provide powerful monitoring tools to assess the impacts of management practices on overall water quality, on DOM transport and transformation (e.g., Lu et al., 2003), and on the transport of other chemical constituents of interest (Dittman et al., 2009). Utilizing optical data is an attractive approach for studying DOM because data collection is easy and straightforward, the data provide information about both the concentration and composition of DOM (Spencer et al., 2009; Weishaar et al., 2003), and detector systems can be employed for a variety of process-based studies and separation techniques to study DOM composition. DOM optical properties, such as UV/Vis spectroscopy, spectral slope, $SUVA_{254}$, and fluorescence spectroscopy, have been shown to be useful in a number of disciplines in the water sciences for studying and monitoring both the concentration and

nature of DOM in aquatic systems (Helms et al., 2008; Spencer et al., 2009). In addition, optical data can be obtained in situ, allowing for the collection of high-frequency environmental data in real time that can be used to better understand the influences of sources and processes occurring within the system on the chemistry and export of DOM (Saraceno et al., 2009; Spencer et al., 2007).

Finally, because DOM composition and optical properties are sensitive to sources, photoreactions, redox status, microbial oxidation, and other reactions, analyses of DOM can provide important information on the effects of disturbance (e.g., hurricanes, fire) and hydrology on DOM composition. For example, in a recent study of the factors controlling the formation of ridge and slough topography in the Everglades, Larsen et al. (2010b) utilized DOM concentration and optical data obtained along a ridge and slough transect to gain insight into the relative rates of organic matter decomposition, the degree of hydrologic mixing, the effects of a hurricane, and POM redistribution within the study area to an extent not possible without these data. Assessment of DOM composition and transport is important for both short- and long-term evaluation of the effects of ecosystem management approaches and can provide a basis for understanding the accompanying concomitant changes in biogeochemical processes resulting from these actions. In the Everglades and ecosystems throughout the world, the sensitivity, ease of analysis, and cost effectiveness of DOM analyses combine to make DOM an important tracer of disturbance effects on carbon cycling and the effectiveness of restoration and management strategies.

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