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# Photo- and bio-reactivity patterns of dissolved organic matter from biomass and soil leachates and surface waters in a subtropical wetland

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ABSTRACT

Dissolved organic carbon (DOC) measurements and optical properties were applied to assess the photo- and bio-reactivity of dissolved organic matter (DOM) from different sources, including biomass leaching, soil leaching and surface waters in a subtropical wetland ecosystem. Samples were exposed to light and/or dark incubated through controlled laboratory experiments. Changes in DOC, ultraviolet (UV-Vis) visible absorbance, and excitation-emission matrix (EEM) fluorescence combined with parallel factor analysis (PARAFAC) were performed to assess sample degradation. Degradation experiments showed that while significant amounts of DOC were consumed during bio-incubation for biomass leachates, a higher degree of bio-recalcitrance for soil leachate and particularly surface waters was displayed. Photo- and bio-humification transformations were suggested for sawgrass, mangrove, and seagrass leachates, as compared to substantial photo-degradation and very little to almost no change after bio-incubation for the other samples. During photo-degradation in most cases the EEM-PARAFAC components displayed photo-decay as compared to a few cases which featured photo-production. In contrast during bio-incubation most EEM-PARAFAC components proved to be mostly bio-refractory although some increases and decreases in abundance were also observed. Furthermore, the sequential photo- followed by bio-degradation showed, with some exceptions, a "priming effect" of light exposure on the bio-degradation of DOM, and the combination of these two processes resulted in a DOM composition more similar to that of the natural surface water for the different sub-environments. In addition, for leachate samples there was a general enrichment of one of the EEM-PARAFAC humic-like component (Ex/Em: <260(305)/416 nm) during photo-degradation and an enrichment of a microbial humc-like component (Ex/Em: <260(325)/406 nm and of a tryptophan-like component (Ex/Em: 300/342 nm) during the bio-degradation process. This study exemplifies the effectiveness of optical property and EEM-PARAFAC in the assessment of DOM reactivity and highlights the importance of the coupling of photo- and bio-degradation processes in DOM degradation.



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## 1. Introduction

DOM plays diverse important ecological and environmental roles both on local ecosystem scales and globally. Locally, it serves as energy source for heterotrophic bacteria and thus fuels the microbial loop, and acts as a natural sunlight attenuator and pH buffer for aquatic ecosystems. Furthermore, as a carrier for organic and inorganic xenobiotics, DOM can impact the transport and fate of environmentally significant pollutants. Globally, as one of the largest and mobile carbon pools on Earth, the biogeochemical cycling of DOM is intricately associated with nutrient and element cycling and as well climate change.

DOM is ultimately produced from biomass like higher plants and phytoplankton or leached from soils and sediments. Dominant biomass and soils are believed to be main sources of DOM in the Florida coastal Everglades FCE (Maie et al., 2006; Yamashita et al., 2010). Previous studies reported that biomass leaching was fast for senescent leaves (Maie et al., 2006; Scully et al., 2004) and the incorporation of biomass leachates along the Everglades water flow path has clearly been demonstrated (Yamashita et al., 2010).

Better understanding the degradation and transformation processes of DOM has been a topic of particular interest to both ecologists and biogeochemists for decades. So far, photo- and bio-degradation are regarded as two major processes to transform and mineralize DOM (Obernosterer and Benner, 2004; Benner and Kaiser 2011), and heterotrophic bacteria have a proven ability to readily uptake labile DOM molecules such as free amino acids and carbohydrates. While the role of microorganisms in DOM degradation has long been recognized, the importance of solar irradiation has also been indicated in the literature through a wealth of reports (Moran and Zepp, 2000; Scully et al., 2004; Ortega-Retuerta et al., 2010; Shank et al., 2010; Benner and Kaiser 2011; Helms et al., 2013; Lu et al., 2013; Rossel et al., 2013; Lønborg et al., 2013). As such, solar radiation has been reported to result in photo-mineralization, photo-ammonification, photo-bleaching of chromophoric DOM (CDOM), or in photo-humification, photo-production of new DOM, and photo-formation of reactive oxygen species (Moran and Zepp, 2000; Shank et al., 2010). The photo-reactivity of DOM seems highly related to the degree of aromaticity (Helms et al., 2013) and long-term photo bleaching was reported to mineralize DOM nearly to completion (Vähätalo and Wetzel, 2008). It is not surprising then, that in clear and shallow wetland waters, photochemical transformations of DOM can be significant (Cawley et al., 2012). In addition, while DOM leached from wetlands vegetation was found to be photo-reactive (Scully et al., 2004), only limited bioavailability of DOM has been reported in wetlands such as the Everglades (Qualls and Richardson, 2003) and attributed in part to nutrient limitations. DOM bioavailability was also observed to be controlled by source, where protein-like materials were degraded much more efficiently compared to polyphenols (Scully et al., 2004). It is likely however, that photo- and bio-degradation processes of DOM act in tandem, and indeed photo-exposure can increase, decrease, or have no net effect on biodegradability of DOM depending on DOM source (Moran and Zepp, 2000). There is however, a general consensus that sunlight has a "priming effect" for bacterial uptake on old, aromatic, terrestrial-derived DOM, while the opposite effect has been observed on fresh, non-aromatic, algae-derived DOM (Moran and Covert, 2003).

Fluorescence spectroscopy has been successfully used to characterize DOM sources and opens new windows to study DOM dynamics in aquatic ecosystems (Jaffé et al., 2008; Helms et al., 2013). By decomposing the EEM data statistically into different fluorescent components, EEM-PARAFAC has been successfully applied in DOM studies (Stedmon al., 2003; Cory and McKnight, 2005; Miller et al., 2009; Jaffé et al., 2012), including photo-degradation and bio-degradation studies (Cawley et al., 2012; Lu et al., 2013; Fellman et al., 2009; Cory and Kaplan, 2012).

The Florida coastal Everglades (FCE) is one of the largest wetlands in the world and is undergoing a historic restoration which aims to restore the quality, quantity, timing, and distribution of water flow (http://www.evergladesplan.org/). DOM in this phosphorus-limited oligotrophic subtropical wetland primarily originates from local vegetation and soil OM oxidation. The majority of nitrogen (N) and phosphorous (P) in the Everglades are in organic forms and therefore associated with the DOM (Boyer et al., 1997). Therefore, the processes controlling DOM transformation and turnover in the FCE are critical in driving local nutrient cycling. Considering the complexity of DOM sources in wetland ecosystems and its ecological importance, a better understanding of the degradation mechanisms controlling its transformation and ultimate fate are needed. The objectives of this study were to characterize DOM leached from biomass and soils, and to assess photo- and bio-degradation processes comparatively to surface water DOM from across the Everglades using optical properties.

## 2. Sampling and experimental methods

### 2.1. *Sampling*

Biomass, soils and surface waters from this study were collected at stations used in the on-going, long-tern ecological research program of the Florida coastal Everglades (FCE-LTER; http://fcelter.fiu.edu/). Fig. 1 displays the locations of the sampling sites, which represent diverse sub-environments of this ecosystem (freshwater marsh-peat – SRS3; freshwater marsh-marl – TS/Ph2; fringe mangrove – SRS5; seagrass-dominated coastal bay – TS/Ph11). Senescent plant materials from *Cladium jamaicense* (sawgrass), *Elocharis cellulosa* (spikerush), *Rhizophora mangle* (red mangrove), fresh shoots of *Thalassia testudinidum* (seagrass), floating periphyton, top soils (including SRS peat soil, TS/Ph marl soil, mangrove mud, and Florida Bay calcitic marl sediment), and surface water samples from different sub-environments were collected in the FCE. Sawgrass (from TS/Ph2) and spikerush (from SRS3) samples were above-water senescent leaves. Floating periphyton at site TS/Ph2 was sampled, which was entangled with *Utricularia*. Mangrove samples consisted of yellow leaves hand-picked from trees at site SRS5. Seagrass samples consisted of whole shoots from site TS/Ph11. The five biomass materials