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Photochemical flocculation of terrestrial dissolved organic matter and iron

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Abstract

Dissolved organic matter (DOM) rich water samples (Great Dismal Swamp, Virginia) were 0.1-μm filtered and UV-irradiated in a solar simulator for 30 days. During the irradiation, pH increased, particulate organic matter (POM) and particulate iron formed. After 30 days, 7% of the dissolved organic carbon (DOC) was converted to POC while 75% was remineralized. Approximately 87% of the iron was removed from the dissolved phase after 30 days, but iron did not flocculate until a major fraction of DOM was removed by photochemical degradation and flocculation (>10 days); thus, during the initial 10 days, there were sufficient organic ligands present or the pH was low enough to keep iron in solution. Nuclear magnetic resonance and Fourier transform infrared spectroscopies indicated that photochemically flocculated POM was more aliphatic than the residual non-flocculated DOM. Photochemically flocculated POM was also enriched in amide functionality, while carbohydrate-like material was resistant to both photochemical degradation and flocculation. Abiotic photochemical flocculation likely removes a significant fraction of terrestrial DOM from the upper water column between headwaters and the ocean, but has previously been ignored. Preliminary evidence suggests that this process may significantly impact the transport of DOM and POM in ocean margin environments including estuaries.

Abbreviations: A, absorbance, optical density; a, absorption coefficient; a300, absorption coefficient at 300 nm; Ads, adsorbed material; Arom., aromatic; CDOM, chromophoric (or colored) dissolved organic matter; cm, centimeters, 10^{-2} meters; CP, cross polarization; CSA, chemical shift anisotropy; DIC, dissolved inorganic carbon; Diss, dissolved (supernatant fraction of centrifuged samples or the fraction <0.1 μm); DOC, dissolved organic matter; DOM, dissolved organic matter; DON, dissolved organic nitrogen; FTIR, Fourier transform infrared; hv, light or photon (shorthand i.e., Planks constant x frequency); l, path length; λ, wavelength; ln, natural logarithm; Me, metal; MilliQ, ultrapure deionized water from MilliQ-UV dispenser (Millipore); N/D, not determined; NMR, nuclear magnetic resonance; PM, particulate material; POM, particulate organic matter; ppm, chemical shift frequency in parts per million (relative to tetramethyl silane standard in delta notation); r^2, square of the correlation coefficient; S, spectral slope (subscript denotes wavelength interval); S_R, spectral slope ratio; $SUVA_{254}$, specific UV absorption at 254 nm; tDOM, terrestrial dissolved organic matter; TN, total nitrogen; TOC, total organic carbon; TOSS, total suppression of spining sidebands; TPPM, two-pulse phase modulation

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1. INTRODUCTION

Terrestrial dissolved organic matter (tDOM) appears to be efficiently removed in ocean margin environments including coastal zones, estuaries, and buoyant river plumes; yet the physical, chemical, and biological processes that lead to this removal remain poorly understood (Hedges et al., 1997; Del Vecchio and Subramaniam, 2004; Spencer et al., 2009). It has been proposed that significant amounts of riverine DOM are delivered to estuarine, continental shelf, and continental slope sediments by various processes, including: precipitation, co-precipitation, aggregation, coagulation, micelle formation, hydrophobic interactions, adsorption to or encapsulation into pre-existing particles (Stumm and Morgan, 1981; Guo et al., 2007). Here, all physico-chemical processes that convert dissolved (<0.1 μm) material to particulate material are referred to as flocculation. Prior studies investigating the role of abiotic flocculation in estuarine biogeochemistry have focused on the influences of salt, mixing, particle interactions, and pH on the solubility, stability, or removal of dissolved and colloidal riverine organic matter (Sholkovitz, 1976; Turner and Rawling, 2001), humic substances (Eckert and Sholkovitz, 1976; Fox, 1983), carbohydrates (Wang et al., 2010), metals (O'melia and Stumm, 1967; Boyle et al., 1977), phosphorus (Forsgren et al., 1996), clay minerals (Black et al., 1965; O'melia and Stumm, 1967), and algal biomass (Sukenik et al., 1988). In spite of the large number of previous studies, the factors resulting in flocculation remain poorly understood.

Sondergaard et al. (2003) showed that mixing-induced flocculation caused only a 2–5% decrease in DOC along a salinity gradient of 0–25. In another study based on end-member mixing experiments and estuarine transects, mixing-induced flocculation was insufficient to account for the apparent removal (and non-conservative behavior) of humic acids (Fox, 1983). Guo et al. (2007) showed that salt effects alone were not sufficient to account for changes in the chromophoric DOM (CDOM) composition of a river water sample. Flocculation therefore must be accompanied by additional factors, such as adsorption to mineral surfaces, interactions with pre-existing particles, or other uncharacterized processes.

In addition to salt effects and mixing-induced flocculation, surface-active materials that collect on air bubbles may form particles from DOM upon bubble dissolution (Johnson, 1976) or bursting (Baylor and Sutcliffe, 1963). Surface-active compounds, including polysaccharides, mucopolysaccharides and glycoproteins, may also play a significant role in the formation of organic-enriched surface micro-layers (Henrichs and Williams, 1985; Compiano et al., 1993), marine snow (Alldredge and Silver, 1988; Mopper et al., 1995), or mineral/organic aggregates (Kranck and Milligan, 1980).

Photochemical mineralization of DOM (conversion to inorganic forms) and the decrease in ultraviolet and visible absorption, i.e., photobleaching, have been widely studied (Zepp and Schlotzhauer, 1981; Del Vecchio and Blough, 2002). Photochemical mineralization is a possible removal mechanism for humic acids and colored DOM in estuaries (Stedmon and Markager, 2005; White et al., 2010). However, reports of a link between photochemical alteration of DOM and the flocculation of DOM have received relatively little attention. Thus, little is known about the relationship between these two processes and how photo-induced flocculation may impact processes such as transport and removal of dissolved and particulate materials and pollutants, biological utilization of organic matter and the organic content of coastal sediments.

Gao and Zepp (1998) observed that after three days of simulated sunlight exposure, dark-colored particles formed in a 0.22 μm filtered and oxygen saturated Satilla river water sample. They reported that particulate matter accounted for 45% of the iron and about 13% of the organic carbon and speculated that the causes of photochemically induced aggregation are changes to double layer repulsion and van der Waals interactions from decarboxylation, and/or the loss of DOM's ability to complex iron leading to formation of polymeric iron oxides. Maurice et al. (2002) and Porcal et al. (2013) observed similar phase changes for organic carbon and iron in wetland influenced streams. Von Wachenfeldt et al. (2008) found that light exposure correlated with increases in particulate organic carbon (POC) at the expense of DOC for 5 μm filtered humic lake and mire water samples. Thorn et al. (2010) found that humic and fulvic isolates became decarboxylated, more hydrophobic, much less aromatic, and less soluble after extensive photodegradation. Photochemical flocculation of iron and aluminum has also been observed in lakes (Kopáček et al., 2005, 2006). The mechanism proposed by Kopáček et al. (2005) proceeds by the iron-mediated degradation of organic iron-binding ligands causing release of inorganic iron, which is susceptible to oxidation and/or hydrolysis to form insoluble (hydr)oxides. Dissolved iron in terrestrially dominated waters (and in the open ocean) is dominantly organically complexed (Rue and Bruland, 1995; Powell and Wilson-Finelli, 2003; Laglara and van den Berg, 2009). Additionally, the concentration of carboxyl groups affects the solubility of DOM (VanLoon and Duffy, 2010) and DOM's ability to form stable complexes with iron (Barbeau, 2006). It is thus anticipated that photochemical decarboxylation of DOM affects solubility of both DOM and iron. Dissolved O_2 and photochemically produced reactive oxygen species oxidize free iron(II) to iron (III), leading to the formation of insoluble iron hydroxides (Faust and Zepp, 1993; Kuma et al., 1996) which may prove important when iron binding ligands are actively photodegraded. Iron also participates directly in the degradation of photo-active organic complexes via ligand–metal charge transfer reactions (Faust and Zepp, 1993).

The residence time of tDOM within the euphotic zone of the oceans is poorly constrained. Most of the world's major rivers form large buoyant plumes often becoming entrained in highly stratified surface waters between 30° S and 30° N latitudes (Moore et al., 1986; Dagg et al., 2004). This highlights the importance of photochemical processes because tDOM-containing water masses will receive considerable light exposure upon export to the ocean margins, thus