



# Photochemistry of marine and fresh waters: A role for copper–dissolved organic matter ligands



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## ABSTRACT

The photodegradation of marine dissolved organic matter (DOM) plays a critical role in the global carbon cycle. The photodegradation of both DOM and particulate organic matter (POM) leads to the formation of carbon monoxide and/or the production of labile organic matter that can be rapidly biodegraded. DOM also regulates metal speciation, particularly important for the bioavailability of nutrient metals required by phytoplankton. Copper is one of these essential nutrients but is also toxic in elevated concentrations. Its speciation is regulated by DOM photodegradation however, DOM–copper ligands are not well characterized because of their low concentrations in natural waters. Copper immobilized metal affinity chromatography (IMAC) was used to isolate high and low affinity DOM ligands from both Pacific near-shore seawater and freshwater from the Black River (NC). Laser flash photolysis (LFP) was used to characterize excited state species from these fractions and to identify excited state species in the open ocean through a depth profile from 5 to 4532 m (North Atlantic, Bermuda Atlantic Time Series Station (BATS)). LFP generated transients characteristic of the solvated electron ( $\tau = 3.5 \pm 0.1 \mu\text{s}$ ), a microbial-sourced triplet excited state ( $\tau = 1.1 \mu\text{s} \pm 0.1 \mu\text{s}$ ), and a long-lived transient, DOM<sup>\*</sup>, with a millisecond lifetime. Unlike the seawater triplet excited state, a copper ligand from Black River water generated a triplet excited state with a lifetime of  $3.4 \pm 0.1 \mu\text{s}$ . Fractions were also characterized by excitation–emission matrix fluorescence spectroscopy (EEMs), UV–visible, and <sup>1</sup>H NMR spectroscopy. EEMs spectra correlated the marine excited state species with the protein-like, microbial fraction while the freshwater transients were associated with chromophoric DOM (CDOM). <sup>1</sup>H NMR with spectral database matching identified ninety-seven compounds as potential sources of these excited state species in the Pacific seawater IMAC fractions. Aqueous extracts of marine macro-algae (*Sargassum natans* (Atlantic Ocean), *Macrocystis pyrifera*), and surf grass (*Phyllospadix torreyi*) were analyzed to investigate potential additional sources of these excited state transients. To our knowledge, this is the first study to characterize DOM–copper ligands in seawater using a combination of EEMs, NMR and laser flash photolysis.

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## 1. Introduction

Marine DOM is primarily autochthonous in nature and is both produced and metabolized by phytoplankton and microbes. Marine photochemistry plays an important role both in the photosynthetic production (Azam, 1983; Biddanda and Benner, 1997) and mineralization of this DOM (Cooper et al., 1988; Zafiriou et al., 1984; Zepp et al., 1985). The absorption of sunlight by DOM results in the generation of

reactive oxygen species (Blough, 1997; Blough and Zepp, 1995; Kieber et al., 1989; Latch and McNeill, 2006; Miller, 1983; Miller and Zepp, 1995; Zafiriou, 1977), the solvated electron (Thomas-Smith and Blough, 2001; Wang et al., 2007), and the triplet excited state (Sharpless, 2012; Zepp et al., 1985). Chromophoric dissolved organic matter (CDOM) is a source of these reactive species (Coble et al., 2004; Ortega-Retuerta et al., 2010; Vodacek et al., 1997) that is mediated by halide ions (Grebel et al., 2009) resulting in photo-bleaching of the CDOM.

In general, the photodegradation of DOM generates a low molecular weight, bioavailable form of DOM (Benner and Bopaiah, 1998; Kieber et al., 1989; Piccini et al., 2009), carbon monoxide, and carbon dioxide (Miller and Moran, 1997; Miller and Zepp, 1995; White et al., 2010). However, these photochemical reactions can depend on the source of

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DOM because algal-derived DOM can generate a recalcitrant form of DOM (Pérez and Sommaruga, 2007; Tranvik and Kokalj, 1998; Tranvik and Bertilsson, 2001).

Approximately 90% of marine DOM is derived from phytoplankton photosynthesis (Biddanda and Benner, 1997). While the composition of marine DOM is largely unknown, carbohydrates, amino acids, and proteins are known products of the bacterial degradation of the phytoplankton (Azam, 1983; Biddanda and Benner, 1997; Grossart and Simon, 2007). The lifetime of DOM is used as a measure of its recalcitrance (Hansell, 2013). DOM produced at the marine surface is labile, with a lifetime of days to weeks, and undergoes bacterial degradation to produce a semi-labile (lifetime of months) form of organic matter that is then transformed to refractory DOM (lifetime of years) in the deep ocean (Hansell, 2013). The seasonal variation in the concentration of labile/semi-labile DOM is approximately 60–70  $\mu\text{mol/kg}$  at the ocean surface and decreases to 40  $\mu\text{mol/kg}$  from 100 to 1000 m depending on the local primary productivity and location of the pycnocline (highest concentration of bacteria).

The trace metals iron (Fe), copper (Cu), nickel (Ni), zinc (Zn), and cadmium (Cd) are essential nutrients in marine surface waters (Vraspir and Butler, 2009). The speciation of these ions is mediated by metal-specific DOM ligands making DOM a key regulator of trace metal biogeochemistry (Bruland et al., 1991; Hoffmann et al., 2012; Morel and Price, 2003). The effects of DOM–metal ligand cycling in natural waters has been extensively studied (Bruland et al., 1991; Christl et al., 2005; Porcal et al., 2009; Riedel et al., 2012) but, with the exception of iron, these ligands are uncharacterized (Manceau and Matynia, 2010; Vraspir and Butler, 2009). In the case of copper ( $\text{Cu}^{2+}$ ), DOM regulates both its toxicity and bioavailability (Bundy et al., 2013; Lorenzo et al., 2007; Manceau and Matynia, 2010). Copper–DOM ligands also influence photochemical reactions of DOM in natural waters (Barbeau et al., 2001; Mopper and Zika, 1987; Rose and Waite, 2003). Photo-irradiation of both marine (Li et al., 2009; Moffett and Zika, 1987) and freshwater DOM (Brooks et al., 2007; Pisani et al., 2011; Porcal et al., 2009) releases  $\text{Cu}^{2+}$ , generating a form of DOM that is readily degraded by bacteria (Benner and Bopaiah, 1998; Cuss and Guéguen, 2012; Shank, 2006; Shiller et al., 2006).

Electrochemical studies determined that there are strong (L1) and weak (L2) classes of copper ligands (Gledhill and Van den Berg, 1994; Shank et al., 2004). The binding affinity is pH (Cabaniss and Shuman, 1988) and chloride ion dependent (Lores and Pennock, 1998), both important parameters in the transition of DOM from fresh to salt water in estuaries and the near shore ocean. The L1 sites (strong affinity) were associated with low molecular weight, soluble organic compounds and two weaker binding affinity binding sites (L2 and L3) were associated with colloidal material (Gordon, 1992; Wells et al., 1998). It has been suggested that the L1 and L2 designations are not indicative of a single species but are the average of a number of compounds in a given sample (Town and Filella, 2000). The copper-binding compounds from marine DOM may be source related because copper-binding labile compounds produced by phytoplankton have a protein-like fluorescence while the fraction from bacteria has a more marine-like fluorescence (Lorenzo et al., 2007).

Immobilized metal affinity chromatography (IMAC), developed for the isolation of proteins (Porath, 1992) has been used in a number of studies for the isolation and  $\text{Fe}^{3+}$  and  $\text{Cu}^{2+}$  binding ligands from DOM. These ligands were characterized by gel electrophoresis (Gordon, 1992), UV–visible spectroscopy (Burba et al., 2000; Wu et al., 2002), and excitation–emission matrix fluorescence spectroscopy (EEMs) (Paunovic et al., 2008). Phytoplankton and marine bacteria were implicated as sources of high and low affinity copper ligands (Gordon, 1992). A short-lived high affinity fraction, was associated with the chlorophyll *a* maximum, while the long-lived low affinity fraction was distributed throughout the water column (Gordon, 1992). Marine DOM–copper ligands in the surface ocean, isolated by ultrafiltration and IMAC, were shown to constitute 2–4% of the surface DOM (Midorikawa and Tanoue, 1998).

Laser flash photolysis (LFP) is used for the direct study of the triplet excited state of DOM while indirect studies use proxy compounds (Canonica et al., 2000; Jammoul et al., 2009) because LFP of most sources of DOM also generates the solvated electron and singlet oxygen (Boreen et al., 2004; Fischer et al., 1987; Power et al., 1987; Zepp et al., 1985). Solar simulator studies have shown that the quantum yield of the solvated electron (at 366 nm) from humic substances was at least two orders of magnitude lower than the results from laser flash photolysis (Thomas-Smith and Blough, 2001). However, LFP studies from this group (Cottrell et al., 2013) have shown that effluent organic matter, Aldrich humic acid, particulate organic matter from the Black River (Cape Fear, NC), and water from constructed wetlands can generate a triple excited state transient without the generation of the solvated electron, making LFP a useful tool for characterizing DOM transients.

The goals of this study were: (1) to use LFP to characterize the source of excited state species in marine water from both near-shore North Pacific Ocean sites (Crystal Cove, Newport Beach, and Dana Point, CA) adjacent to a large urban area and from a well-studied remote ocean site in the North Atlantic Ocean (Bermuda Atlantic Time Series Station); (2) to characterize IMAC-isolated copper ligands from the Pacific seawater by UV–visible spectroscopy, EEMs and  $^1\text{H}$  NMR (1-D and 2-D NMR) with spectral database matching; and (3) to probe these fractions for excited state transients by laser flash photolysis (LFP). Water soluble extracts of marine plants were also characterized as part of an effort to characterize sources of DOM that did not generate the solvated electron (Cottrell et al., 2013). To our knowledge, this is the first reported use of LFP,  $^1\text{H}$  NMR with spectral database matching, and EEMs to characterize both seawater and DOM–copper ligands.

## 2. Materials and methods

### 2.1. Sample collection and preparation

All water samples were collected in acid washed glass bottles and stored at 4 °C after collection and/or processing. Black River whole water (sample station B210, <http://www.uncw.edu/cms/aelab/LCFRP/lcfrp%20station%20map.htm>) and Pacific seawater were analyzed within one week of collection. Pacific seawater was collected on 05/27/10, 12/01/10, 12/08/10 (five sites), 01/02/11, 07/12/11, 07/31/11 and 02/21/13 and processed immediately or filtered before storage. North Atlantic, Bermuda Atlantic Time Series Station (BATS) seawater (N31° 48.607 W063° 40.915), obtained during the July 5, 2012 cruise (5, 110, 750, 1500, 3000, 4523 m), was collected in Niskin bottles, then transferred to acid washed glass bottles and stored at 4 °C. EEMs and laser flash photolysis (LFP) were performed within two weeks of collection. Seawater was filtered through Durapore GV filters (0.2  $\mu\text{m}$ , Millipore, Billerica, MA) that were prewashed with 4 L of MilliQ® water (Synergy system, Millipore) to remove binding agents. Particulate organic matter (POM) from the Pacific seawater was isolated as the retentate on a 0.2  $\mu\text{m}$  Durapore filter. The solids retained on the filter were collected in LC–MS water (Fisher Scientific), sonicated for 10 s. and then re-centrifuged (4800  $\times g$ ). The supernatant was used for analysis.

Leaf fronds from the brown macro-algae *Sargassum natans* (Sargasso Sea), and *Macrocystis pyrifera* (Pacific) as well as Pacific surf grass (*Phyllospadix torreyi*) were washed in MilliQ® water and then immersed in either seawater or MilliQ® water and placed at 4 °C in the dark for 48 h. The supernatant was removed, centrifuged (4800  $\times g$ , 10 min) then diluted with either seawater or MilliQ® water for spectroscopic analysis and for LFP.

### 2.2. Solid phase extraction of Pacific seawater for $^1\text{H}$ NMR

Solid phase extraction (SPE) using Bond Elut PPL cartridges (Agilent Technologies, Inc.) was used to isolate Pacific seawater DOM (Dittmar et al., 2008) for NMR studies. The seawater was acidified to 2% acetic acid (v/v, final concentration) and de-gassed. The

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