WATER RESEARCH 47 (2013) 5189–5199

Available online at www.sciencedirect.com

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Photochemistry of excited-state species in natural waters: A role for particulate organic matter

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ARTICLE INFO

Article history:
Received 19 March 2013
Received in revised form
28 May 2013
Accepted 31 May 2013
Available online 13 June 2013

Keywords:
Triplet excited state
Particulate organic matter
Laser flash photolysis
Black River
Photochemistry
Dissolved organic matter

ABSTRACT

Laser flash photolysis (LFP) was used to characterize a triplet excited state species isolated from Black River and San Joaquin wetlands particulate organic matter (POM). The solubilized organic matter, isolated from POM by pH-independent diffusion in distilled water, was named PdOM. UV–visible absorption spectroscopy, excitation–emission matrix spectroscopy (EEMs), and ^{1}H NMR were used to characterize the PdOM. While LFP of dissolved organic matter (DOM) is known to generate the solvated electron, LFP of the PdOM transient in argon-, air-, and nitrous oxide-saturated solutions indicated that this was a triplet excited state species (^{3}PdOM*). The lifetime and the reactivity of ^{3}PdOM* with sorbic acid, a triplet state quencher, were compared with that of the triplet excited state of benzophenone, a DOM proxy. A second excited state species (designated DOM*), with a longer lifetime, was reported in a number of previous studies but not characterized. The lifetime of DOM*, measured for seventeen organic matter isolates, lignin, tannic acid, and three wetlands plant extracts, was shown to differentiate allochthonous from autochthonous DOM. ^{3}POM* and DOM* were also observed in lake water and a constructed wetlands' water. Aqueous extracts of fresh and aged plant material from the same wetland were shown to be one source of these excited state species. This study provides evidence of a role for POM in the photochemistry of natural and constructed wetland waters.

1. Introduction

Dissolved organic matter (DOM) plays a critical role in the photochemistry of sunlit natural waters (Cooper et al., 1988; Zafiriou et al., 1984; Zepp et al., 1985). DOM is a highly complex mixture of organic compounds produced by the decomposition of plant (allochthonous), and microbially-processed (autochthonous) material (Stevenson, 1982). The absorption of actinic radiation by DOM results in the production of superoxide/hydroperoxyl radicals (O_2^{-}•/HO_2•) (Cooper and Zika, 1983; Garg et al., 2011; Zafiriou et al., 1984; Zhang et al., 2012), singlet oxygen ($^1O_2$) (Haag and Hoigné, 1986;

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http://dx.doi.org/10.1016/j.watres.2013.05.059

Haag et al., 1984; Latch and McNeill, 2006; Peterson et al., 2012; Shao et al., 1994), and the hydroxyl radical (•OH) (Haag and Hoigné, 1985; Santoke et al., 2012; Vaughan and Blough, 1998; Vione et al., 2006). An additional reactive species, the triplet excited state of natural organic matter (^{3}DOM*), is formed by the de-activation of the singlet excited state of DOM through intersystem crossing (Zepp et al., 1985). The ^{3}DOM* plays an important role in the photochemistry of natural waters (al Housari et al., 2010; Boreen et al., 2005; Canonica et al., 1995; Gerecke et al., 2001; Xu et al., 2011; Zeng and Arnold, 2012) but it appears that there are no direct measurements of its reactivity.

The reactions ^{3}DOM* cannot be studied directly by LFP because aqueous solutions of DOM produce solvated electrons (Fischer et al., 1987, 1985; Frimmel et al., 1987; Power et al., 1987; Zepp et al., 1987). Instead, studies of ^{3}DOM* reactivity involve the use of a DOM proxy such as benzophenone (Canonica et al., 2006, 2000; Encinas et al., 1985; Grebel et al., 2011; Jammoul et al., 2009). Early LFP studies (Fischer et al., 1985, Power et al., 1987) of DOM utilized high concentrations of humic acids (g/L) or concentrated, filtered natural water to characterize DOM transients with observed lifetimes of 3 ns (fluorescence), 2 μs (air-saturation), 5 μs and >100 μs (argon-saturation) (Power et al., 1987). Similar species were also reported under environmentally relevant conditions using 0.45 μm filtered natural water (Zepp et al., 1987).

The annual transport of riverine POM to the oceans is comparable with that of DOM (10^{15} g/yr.) (Hedges et al., 1997), making POM an important source of organic matter in natural waters. POM, composed of both non-living and living particulate matter (Minor and Nallathamby, 2004), is compositionally different from DOM (Azam, 1983; Jaffè et al., 2006; Paerl, 1974) and in many cases is primarily autochthonous in nature (Mao et al., 2007). POM is formed by a number of mechanisms including the aggregation of plant leachates (Lush and Hynes, 1973), the microbial reprocessing of DOM (Azam, 1983), and by a dynamic exchange between the water column and the sediments (Hedges and Keil, 1999). Solar radiation can induce POM by flocculation of allochthonous dissolved organic carbon (DOM) (von Wachenfeldt et al., 2008). This flocculation can be the result of the adsorption of DOM to iron oxides (Gao and Zepp, 1998), however this adsorption is a pH-dependent process with adsorption decreasing with at higher pH >7 (Tipping, 1981).

Particulate organic matter (POM) can also play a role in some photochemical reactions in natural waters. Light-scattering (Miller and Zepp, 1979a) and the partitioning of contaminants to the POM (Miller and Zepp, 1979b) influences photochemical degradation of contaminants and of POM itself (Shank et al., 2011) and of POM from sediments to produce a more labile form of DOM (Kieber et al., 2006). However, these processes have not been characterized.

The triplet excited-state of DOM (^{3}DOM*) believed to account for up to 75% of aquatic photochemistry of natural waters (Xu et al., 2011) has not been directly detected. The objective of this study was to identify and characterize a form of natural organic matter that would generate a triplet excited state species free of interference from solvated electron. In this study the POM isolated from Black River (Cape Fear, NC) water, an organic matter rich water (90 mg/L) fresh water (Ayatollahi et al., 2012), was shown to be a source of organic matter that generated the triplet excited state by laser flash photolysis. The solubilized organic matter (termed PdOM), was desorbed from the POM by pH-independent diffusion in distilled water. PdOM was significantly different from the bulk Black River DOM as demonstrated by ^{1}H NMR and excitation–emission fluorescence spectroscopy (EMMs). The ^{3}PdOM* transient was not quenched by N_2O and its lifetime was attenuated in air saturated solutions by sorbic acid (a known triplet state quencher). The absolute bimolecular reaction rate constant with sorbic acid was similar to that of benzophenone, a DOM proxy. Seventeen DOM isolates were screened for the potential to generate the ^{3}DOM* by LFP. Only Aldrich humic acid, DOM from effluent organic matter (EfOM), a constructed wetland, and Mono Lake generated ^{3}DOM*. LFP also generated a second excited state species previously reported as having a lifetime >40 μs (Power et al., 1987; Sharpless, 2012; Sultimova et al., 2008; Zepp et al., 1987). This transient was observed in all DOM samples and in aqueous extracts of plant material with lifetimes that ranged from 3.6 ± 0.1 ms to 16.1 ± 0.1 ms. To our knowledge, this is the first demonstration of a role for POM in the generation of a triplet excited state species from freshwater by LFP and without the co-generation of the solvated electron.

2. Methods

2.1. Reagents and DOM sources

Chemicals were obtained from (Sigma–Aldrich ≥99%). Benzophenone, (100 μM) was dissolved in MilliQ® water (Millipore, Billerica, MA) without buffering. Sorbic acid (100 mM) was prepared in MilliQ® water and adjusted to neutral pH to solubilize. Lignosulfonic acid, sodium salt (M.Wt. 8 kD, 18 kD, and 52 kD) and tannic acid (Sigma) were dissolved (16 mg/L) in 0.1 mM sodium phosphate (pH = 7). DOM reference material were obtained from the International Humic Substances Society (IHSS) (Supplemental information) or solid phase extracted from natural water.

2.2. Sample collection, preparation of particulate-desorbed organic matter (PdOM) and fresh plant extracts

Black River (BR) water (NC, USA), lake water (Canyon Lake, CA), and water from a constructed wetland were collected in acid-washed glass bottles and stored at 4 °C before processing (within 48 h of collection). Canyon Lake water was collected at the surface (0.5 m) and as a pooled fraction (0.5 m–13 m). Glass storage vials and glass fiber filters were pre-combusted for 2 h at 550 °C to remove organic contaminants. Water was either filtered or centrifuged at 6000 RPM for 5 min (Fisher model) to remove particulate matter. The supernatant (6000S) was saved for analysis. Filters: (5 μm, Isopore TMTP and Durapore® 0.22 μm GV, Millipore, Billerica, MA) were pre-washed with 4 L of MilliQ® to remove binding agents. Whatman GF/F glass fibers filters (0.7 μm, Whatman, GE Healthcare, Piscataway, NJ) and (1.2 μm, GF/F, Advantec GC50, Japan) were used after combustion. POM from 1 L water of BR water was isolated by centrifugation with a solids recovery of 300 mg/L (wet weight).