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Photochemical alteration of the molecular weight of dissolved organic matter

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Abstract

Molecular weight (MW) is a key control on the physical, chemical, and biological characteristics of dissolved organic mater (DOM). This study investigated the effect of photooxidation on the average MW of DOM by exposing DOM of diverse origins to simulated solar radiation at varying levels of dissolved oxygen and under different incident light wavelength regimes. During irradiation, high-molecular-weight fractions were destroyed and low-molecular-weight constituents were formed. The average MW decreased with irradiation time in all treatments in a manner that can be described by a quasi-exponential function, which suggests that solar radiation is incapable of completely mineralizing DOM even after prolonged exposure. Increasing the oxygen concentration accelerated the MW reduction while the removal of oxygen strongly suppressed this process. The fractional contributions from UV-B, UV-A, and visible radiations to full-spectrum photoinduced MW reduction varied considerably among the DOM samples examined, ranging from 19% to 60%, 17% to 36%, and 15% to 46%, respectively. The MW changes in time-series irradiations were inversely correlated with the ratio of the absorbance at 250 nm to that at 365 nm (i.e., the E_2/E_3 quotient). Photoinduced MW reduction was accompanied by a decrease of polydispersity, which is indicative of a reduced DOM heterogeneity.

Keywords: Photooxidation; DOM; Humic substances; Size-exclusion chromatography; Molecular weight; Polydispersity

1. Introduction

The size of dissolved organic matter (DOM), conveniently represented by its molecular weight (MW), greatly influences the biogeochemical cycling of DOM in aquatic ecosystems. The photoreactivity, optical properties, and bioavailability of DOM vary widely among different MW fractions (Amon and Benner, 1994; Amon and Benner, 1996a; Gao and Zepp, 1998; Opsahl and Benner, 1998; Kaiser and Sulzberger, 2004). MW is also one of the principal factors controlling the metal and hydrophobic binding affinities of DOM, and thus the transport, fate, and toxicity of inorganic and organic contaminants (Bartschat et al., 1992; Kukkonen, 1995; Chin et al., 1997). Moreover, the MW of DOM has important implications in water treatment in relation to by-product formation during disinfection, coagulation efficiency, and adsorption of organic materials onto activated carbon (Cabaniss et al., 2000, and references therein). Therefore, naturally occurring processes that significantly modify the MW of DOM can have profound environmental and ecological ramifications. During the past two decades, numerous studies have been conducted to quantify the molecular sizes of various humic isolates and natural samples (e.g., Thurman et al., 1982; Perminova et al., 2003; Perdue and Ritchie, 2004, and references therein), whereas much less attention has been focused on the factors altering this property.

Photooxidation of DOM is a key process occurring in natural waters that generates environmentally and biologically important products and modifies the physicochemical

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properties of DOM. Numerous efforts and much progress have been made in identifying and quantifying the photoproducts of DOM (Zafiriou et al., 1984; Blough and Zepp, 1995; Moran and Zepp, 1997), in evaluating the effects of DOM photoprocessing on its optical property (Osburn and Morris, 2003; Zepp, 2003) and bioavailability (Kieber et al., 1989; Hernes and Benner, 2003), and in elucidating the interactions among DOM photooxidation, metal ion (e.g., Fe and Cu) redox chemistry, and photochemical oxygen consumption (Miles and Brezonik, 1981; Amon and Benner, 1996b; Voelker et al., 1997; Gao and Zepp, 1998). In marked contrast, little effort or progress has been made in understanding the impacts of aquatic photochemistry on the major aspects of the physicochemical properties of DOM, including its molecular size, elemental and isotopic compositions, aromaticity, and hydrophobic, metal and proton binding affinities (Xie et al., 2004; Lou et al., 2006). Photoalteration of the MW of aquatic DOM has not been adequately studied, and many previous studies on this subject were conducted under experimental conditions that were quite different from those in natural aquatic environments, e.g., use of only soil humic substances or only ultraviolet (UV) wavelengths (Allard et al., 1994; Schmitt-Kopplin et al., 1998; Fukushima et al., 2001; Lepane et al., 2003).

In the present study, we conducted detailed time-series irradiations on both soil and aquatic DOM under simulated solar radiation and established quantitative relationships between the MW of DOM and irradiation time. We discuss the implication of these relationships for DOM photooxidation. As O_2 and the spectral composition of incident light strongly affect DOM photooxidation (Gao and Zepp, 1998; Xie et al., 2004), we also examined the impacts of oxygen and the spectral composition of incident light on the photoalteration of the MW.

2. Materials and methods

2.1. DOM samples

DOM solutions were prepared from Suwannee River humic (SRHA) and fulvic (SRFA) acids and a German forest soil humic acid (FSHA). SRHA and SRFH were purchased from the International Humic Substances Society (IHSS), and FSHA was provided by Dr. R. Ji. The isolation procedures and characterization of these materials can be found at the IHSS website (www.ihss.gatec.edu) and in Vinken et al. (2005). Before use, the humic substances were dissolved in Nanopure water and filtered with 0.2-μm polycarbonate membrane filters (Whatman). The initial concentrations of dissolved organic carbon ([DOC], in mg l^{-1}) were 23.6 for SRHA, 23.8 for SRFA, and 17.6 for FSHA. In addition to humic extracts, a natural DOM sample was collected from the Saguenay Fjord, Quebec, in July 2004. The Saguenay Fjord is a highly stratified water body with a thin freshwater surface layer (<10 m) underlain by a thick (250–350 m) saltwater layer inflowing from the Gulf of St. Lawrence. Surface water in this fjord is rich in highly colored DOM derived from land plants. Saguenay Fjord water (SFW) was taken with Niskin bottles at 2 m of depth and immediately filtered through a Pall AcroPak 1000 Capsule sequentially containing 0.8-μm and 0.2-μm polyethersulfone membrane filters. The filtered water was transferred into acid-cleaned, 20-l collapsible polyethylene bags (Cole-Parmer), stored in darkness at 4 °C, and brought back to the land-based laboratory at Rimouski for experiments. The initial [DOC] in the filtered SFW was determined to be 6.24 mg l^{-1}.

2.2. Irradiation

Time series of irradiations (up to 72 h) were conducted using a Suntest CPS solar simulator equipped with a 1000 W xenon lamp and a Suprax long-band cutoff filter to remove shortwave radiations (<290 nm). The irradiance and spectral composition of the incident light were monitored with an OL-754 spectroradiometer (Optronic Laboratories) and found to remain stable over the study period. The output at the irradiation surface was 583.0 W m^{-2} in the 280–800 nm wavelength range. Compared to the noontime cloudless natural sunlight recorded at Rimouski, Quebec (48.453 °N, 68.511 °W), on 24 May 2005, the light intensities within the solar simulator were 1.80 times higher in the UV-B (280–320 nm), 1.43 times higher in the UV-A (320–400 nm), and 1.05 times higher in the visible (400–800 nm). According to Miller and Zepp (1995), the daily light dose received by surface water approximates 7.6 h of noon-sun radiation. Hence, a 72-h exposure in the solar simulator is equivalent to 17.0 d of UV-B, 13.5 d of UV-A, and 9.9 d of visible radiation at Rimouski.

Quartz ampoules (12.5 cm in length, 3.5 cm in I.D.), fully filled with DOM samples and sealed with an aluminum-covered 1/4″ Teflon Swagelok cap, were horizontally immersed in a temperature-controlled water bath (20 ± 1 °C) located immediately beneath the exposure chamber of the solar simulator. Mylar-D films (50% transmittance cutoff at 324 nm) and UF-4 Plexiglas filters (50% transmittance cutoff at 408 nm) were used to evaluate the relative importance of UV-B, UV-A, and visible radiation in the photoprocesses examined. Note that the UF-4 filter was not 100% effective in screening out the UV radiation. However, the amount of UV radiation passing through the UF-4 filter (in the 385–400 nm range only) was only 2% of the amount of UV-A radiation that had passed through the Mylar-D film. The 50% transmittance wavelength of the Mylar-D films shifted from 324 to 326 nm after 12 h of exposure. To minimize this problem, Mylar-D films under irradiation were replaced every 12 h.

Prior to irradiation, samples were bubbled with air (medical grade), pure O_2, or pure N_2 to obtain varying initial levels of O_2, i.e., air-, O_2- and N_2-saturation, respectively. Full-spectrum irradiations were performed on all three O_2 treatments while wavelength-dependent irradia-