Marine Chemistry 155 (2013) 81–91

Contents lists available at ScienceDirect

Marine Chemistry

journal homepage: www.elsevier.com/locate/marchem

Photochemical bleaching of oceanic dissolved organic matter and its effect on absorption spectral slope and fluorescence

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ARTICLE INFO

Article history:
Received 21 September 2012
Received in revised form 23 May 2013
Accepted 30 May 2013
Available online 14 June 2013

Keywords:
Colored dissolved organic matter
Carbon
Light absorption
Fluorescence
Photochemistry
Excitation emission matrix
Spectral slope

ABSTRACT

Photobleaching of open-ocean dissolved organic matter (DOM) is typically treated as a removal mechanism; however, photobleaching also encompasses a poorly characterized suite of transformative processes. To examine the qualitative changes to DOM optical properties during photobleaching, 674 m N. Pacific DOM, concentrated and desalted by reverse osmosis with electrodialysis (RO/ED), was subjected to 68 days of continuous irradiation in a UV solar simulator. Approximately 84% of chromophoric and fluorescent DOM (CDOM and FDOM respectively) and 38% of dissolved organic carbon (DOC) were lost during the irradiation. Based on these results the concentration of photochemically refractory DOC in the surface pacific is estimated to be 27 μmol of carbon per liter. In addition, the spectra of the remaining CDOM and FDOM were shifted towards shorter wavelengths, a result which has important implications for the interpretation of fluorescence excitation emission matrix (EEM) spectra because the relative positions of fluorescence maxima are often attributed to differences in FDOM source. Qualitative indices derived from CDOM and FDOM spectra for the irradiated deep DOM sample resembled those for surface waters of the North Pacific Ocean indicating that photobleaching has a significant influence upon the optical properties of DOM in the open ocean.

1. Introduction

Chromophoric dissolved organic matter (CDOM) is the main UV light-absorbing substance in the open ocean (Zepp, 2002; Kitidis et al., 2006). In spite of the large source of allochthonous CDOM from rivers and coastal wetlands (Blough and Del Vecchio, 2002; Del Vecchio and Blough, 2004b; Spencer et al., 2009), the dominant source of CDOM in the open ocean is thought to be the heterotrophically altered autochthonous material that is produced in and immediately beneath the euphotic zone and also released at depth from sinking particles (Chen and Bada, 1992; Hayase and Shinozuka, 1995; Rochelle-Newall and Fisher, 2002; Nelson et al., 2004, 2007; Yamashita and Tanoue, 2004; Swan et al., 2009). CDOM plays an important role in protecting organisms in the upper water column from harmful UV radiation (Williamson et al., 2001; Zepp, 2002) and represents a significant interference for remote sensing of ocean chlorophyll (Carder et al., 1989). Further, the products of photochemical degradation of CDOM represent a source of nutrients for phytoplankton (Tarr et al., 2001; Stedmon et al., 2007; Vähätalo and Järvinen, 2007), metabolic substrates for heterotrophs (Kieber et al., 1989; Miller et al., 2002), and climatologically relevant gasses (Johannessen and Miller, 2001; Cutter et al., 2004; Stubbins et al., 2006; Toole et al., 2006). The loss of UV and visible light absorption and fluorescence that occurs during photochemical degradation of CDOM is referred to as photobleaching (Zika, 1980; Kieber et al., 1990Chen and Bada, 1992; Skoog et al., 1996). The basin-scale impact of CDOM photobleaching in surface waters of the remote Pacific Ocean has recently been highlighted by large-scale surveys (Swan et al., 2009; Yamashita and Tanoue, 2009), which show that CDOM absorbance and fluorescence are strongly depleted in the surface mixed layer.

Although there is substantial evidence for widespread CDOM photobleaching from its distribution in the ocean (Hayase et al., 1988; Chen and Bada, 1992; Nelson et al., 2007; Swan et al., 2009;

Abbreviations: *A*, absorbance; *a*, Napierian absorption coefficient; BIX, fluorescence biological index; CDOM, chromophoric dissolved organic matter; DOC, dissolved organic carbon; DOM, dissolved organic matter; EEM, fluorescence excitation emission matrix spectroscopy; FDOM, fluorescent dissolved organic matter; FI, fluorescence index, often McKnight's fluorescence index; HIX, fluorescence humification index; *L*, path length; M:C, ratio of EEM Peak M to Peak C; NELHA, Natural Energy Laboratory of Hawaii; NPOC, non-purgeable organic carbon; RO/ED, reverse osmosis coupled with electrodialysis; $S_{xxx-xxx}$, spectral slope, subscripts denote wavelength range; S_R, spectral slope ratio, $S_{275-295}$:$S_{350-400}$; SUVA, specific UV absorption, decadal absorption coefficient divided by [DOC]; UV, ultraviolet light, <400 nm; WRU, Water Raman Units.

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http://dx.doi.org/10.1016/j.marchem.2013.05.015

Jørgensen et al., 2011) and direct observations of photobleaching of CDOM in terrestrially-impacted waters (Skoog et al., 1996; Del Vecchio and Blough, 2002, 2004a; Twardowski and Donaghay, 2002; Helms et al., 2008), photobleaching of open-ocean CDOM has not been widely examined (Opsahl and Benner, 1998; Ortega-Retuerta et al., 2010; Stubbins et al., 2012), and little has been reported with respect to the changes in the spectral distribution of absorption and fluorescence during photodegradation of open-ocean CDOM (Hayase et al., 1988; Chen and Bada, 1992).

The aim of this study was to explore how deep ocean DOM changes qualitatively (i.e., relative wavelength dependence of absorption and fluorescence) during photodegradation as an indication of how the optical properties of this same DOM would be altered when transported from depth to the euphotic zone. Photobleaching was assessed for a deep ocean DOM sample concentrated and desalted using reverse osmosis coupled with electrodialysis (RO/ED). RO/ED has higher extraction efficiencies than commonly reported for solid phase extraction and ultrafiltration, and the optical and chemical properties of the RO/ED DOM closely resemble those of the unextracted DOM (Koprivnjak et al., 2006, 2009). The use of deep ocean DOM from the Pacific Ocean provided starting material with minimal direct contribution from terrestrial environments and broadly representative of the DOC pool of the deep ocean, which is one of the longest lived and most abundant carbon stores on Earth (Hansell, 2013). In previous studies irradiating natural deep ocean seawater it took less than 28 days before CDOM light absorption at wavelengths greater than 350 nm was reduced below the detection limits of a standard spectrophotometer with a 10 cm path length cuvette (Stubbins et al., 2012). In the current study, the seventeen-fold increase in CDOM light absorption in the RO/ED concentrate compared to seawater allowed photobleaching to be studied over a longer irradiation period without reducing CDOM optical properties below instrument detection limits, thus providing novel insight into the optical properties of extensively photodegraded CDOM.

2. Material and methods

2.1. Cleaning procedures

All glassware was cleaned with ~1 M HCl and rinsed with MilliQ UV ultrapure grade water (Millipore), designated below as "MilliQ water". Glassware was combusted at 450 °C for ≥4 h. Plasticware was cleaned with ~1 M HCl and rinsed with MilliQ water. Stainless steel equipment was cleaned with mild detergent and copiously rinsed with MilliQ water. All containers were rinsed several times with sample prior to filling. Filter capsules (0.1 μm pore size, Whatman PolyCap) were rinsed briefly with acetonitrile, flushed with >20 L of MilliQ water, and conditioned with approximately 1 L of sample prior to use.

2.2. Sample collection, handling, and irradiation

Four North Pacific Ocean water samples were collected at 23° N, 158° W (station ALOHA) aboard R/V Kilo Moana. Sampling depths were 5 m (surface subtropical gyre), 125 m (chlorophyll a maximum), 770 m (oxygen minimum layer), and 3500 m (lower circumpolar water). Samples were gravity-filtered through 0.1 μm capsule filters and stored frozen in pre-combusted glass containers. Two of the four ALOHA samples (5 m and 3500 m) were concentrated by reverse osmosis and desalted by electrodialysis aboard the ship. The isolation and characterization of these samples are described elsewhere (Helms, 2012). Nine large-volume water samples were also collected from the 674 m depth pumping system at the Natural Energy Laboratory of Hawaii, Authority (NELHA) in Kona, Hawaii. The water was pumped through 0.1 μm capsule filters into the 200 L polyethylene tank of the RO/ED system. The sample used for the irradiation study was reduced from 220 L to 8.3 L (concentration factor of 26.6) and had a final conductivity of 47.1 μS cm^{-1}. The isolated sample was frozen and shipped back to the laboratory in Norfolk, VA, where it was immediately re-frozen and stored at −20 °C until used in the experiments described below.

Aliquots of the RO/ED concentrate (NELHA 674 m) were transferred to ~550 mL quartz flasks and placed inside a solar UV simulator containing 12 Q-Panel UVA340 bulbs, which provided a spectral shape similar to that of natural sunlight from approximately 300–365 nm (Q-Panel), but under-represented solar irradiance at wavelengths greater than about 365 nm. The light output from the solar simulator was monitored during the course of the irradiation experiment using a Biospherical PUV 2510 radiometer. A description of the solar simulator can be found in Minor et al. (2007). The samples were irradiated constantly during the experiment. Sub-samples were collected and analyzed at exposure intervals ranging from 5 days to 68 days. Based on the measured intensity of the lamps and the fact that samples were irradiated continuously, each 24-hour day of light exposure is approximately equivalent to 4 days of natural sunlight at 35° latitude (Leifer, 1988; Kieber et al., 2006; Minor et al., 2007; Helms et al., 2008).

At the end of each irradiation period, an aliquot of sample was tested for microbial activity using ^{3}H labeled thymidine (TrD) incorporation (Fuhrman and Azam, 1982; Smith and Azam, 1992). A fresh 5 μm filtered water sample was collected from a pond adjacent to the laboratory at Old Dominion University and used as a "live-control" to test the effectiveness of the assay. All irradiated samples yielded radioactivity measurements less than 1% of killed controls; thus, all measured changes to DOM optical properties were principally due to photochemical reactions because microbial activity was negligible.

2.3. UV–visible absorption and fluorescence spectroscopy

UV–visible absorption spectra (190–900 nm) were measured using an Agilent 8453 diode array spectrophotometer with a 5 cm or 10 cm quartz cuvette. MilliQ water was used as the blank. Absorbance values were corrected for instrument baseline drift, refractive index, and temperature variations according to Green and Blough (1994) and converted to Napierian absorption coefficients using the formula:

$$a = 2.303A/L \quad (1)$$

where a = Napierian absorption coefficient (m^{-1}), A = absorbance, and L = path length (m) (Green and Blough, 1994). CDOM absorption spectra are modeled using an exponential function of decreasing absorption with increasing wavelength:

$$a_{\lambda} = a_{\lambda_{ref}} e^{-S(\lambda-\lambda_{ref})} \quad (2)$$

where a = Napierian absorption coefficient (m^{-1}), λ = wavelength (nm), λ_{ref} = reference wavelength (nm), and S = spectral slope (nm^{-1}) (Helms et al., 2008). Specific UV absorbance (SUVA) was determined by dividing the absorbance (at 254 nm and at 300 nm) by the DOC concentration.

The spectral slope over the wavelength range of 300–700 nm was calculated using non-linear regression of the absorption spectra (Twardowski et al., 2004). All other spectral slopes were calculated by linear regression of the natural log-transformed absorption spectra (Helms et al., 2008). Spectral slope ratio (S_R) was calculated by dividing $S_{275–295}$ by $S_{350–400}$ (Helms et al., 2008). Slope spectra (Loiselle et al., 2009) were generated using linear regression slopes of the natural log absorption spectrum over a sliding 21 nm interval (i.e., central value ± 10 nm) with 1 nm resolution. First and second derivative spectra were obtained for absorption and natural log absorption using linear regression over 21 nm intervals (i.e., central value ± 10 nm).