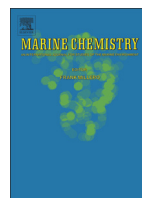




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Illuminating the deep: Molecular signatures of photochemical alteration of dissolved organic matter from North Atlantic Deep Water

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ABSTRACT

Duplicate, filtered samples of North Atlantic Deep Water (NADW) were irradiated for 28 days in a solar simulator. Duplicate dark controls were placed alongside the irradiated samples. After 28 days, samples were extensively photo-degraded based upon colored dissolved organic matter (CDOM) photo-bleaching (>95%). Samples were solid phase extracted using PPL resin to isolate, concentrate and desalt the dissolved organic matter (DOM) in the samples. Ultrahigh resolution electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry (FTICR-MS) enabled 3024 molecular formulas to be identified in the dark control. Photo-degradation decreased molecular diversity, with 2402 formulas assigned post-irradiation. Molecular formulas were classified based upon their photo-lability as 1) photo-resistant; 2) photo-labile; and, 3) photo-produced. Photo-resistant DOM made up 73% of all formulas and was dominated by highly unsaturated molecular signatures consistent with carboxylic-rich alicyclic molecules, suggesting that these apparently bio-refractory compounds may also survive multiple passages through sunlit surface waters and thus accumulate for timeframes exceeding ocean ventilation. Photo-labile DOM was enriched in low molecular weight formulas, aromatic molecular formulas, and sulfur and phosphorous containing formulas. Compounds containing both sulfur and nitrogen were particularly photo-labile and may represent an underappreciated component of the photo-reactive CDOM pool. Photo-produced DOM was enriched in higher molecular weight formulas, as well as aliphatic and peptide formulas. Molecular formulas are indexed by their photo-lability classification in the supplementary information.

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1. Introduction

Oceanic dissolved organic carbon (DOC) constitutes a major pool of global carbon, approximately equivalent in size to the atmospheric load of carbon dioxide (Dittmar and Stubbins, 2014). Thus, the long-term stability of oceanic DOC is of direct consequence for the radiative balance of the earth. The majority of the oceanic store of DOC is contained in the deep ocean (Hansell, 2013). Plots of DOC versus salinity in the deep ocean indicate that net removal of DOC is extremely slow, leading to the definition of the deep ocean DOC pool as refractory

Abbreviations: *a*, Napierian absorption coefficient; *Al_{mod}*, modified aromaticity index; BPCA, benzenepolycarboxylic acid; CDOM, chromophoric dissolved organic matter; CHO, molecular formula containing only carbon, hydrogen and oxygen; CHON, molecular formulas containing C, H, O and nitrogen; CHOS, molecular formulas containing C, H, O and sulfur; CHOP, molecular formulas containing C, H, O and phosphorous; CHONS, molecular formulas containing C, H, O, N and S; Da, daltons; DBC, dissolved black carbon; DOC, dissolved organic carbon; DOM, dissolved organic matter; ESI, electrospray ionization; FTICR-MS, Fourier transform ion cyclotron mass spectrometry; NADW, North Atlantic Deep Water; UV, ultraviolet.

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(Hansell, 2013). This view of extreme recalcitrance in the deep ocean is supported by bulk radiocarbon mixing models, which suggest that the refractory DOC in the deep ocean has a turnover time of around 6000 years (Bauer, 2002). More recent radiocarbon dating of operationally defined fractions of marine DOC has revealed that bulk (i.e., average) apparent DOC ages do not represent the average value for a normally distributed pool of molecules (Follett et al., 2014; Walker et al., 2011). Follett et al. (2014) radiocarbon dated DOC fractions produced during a time series of ultraviolet (UV) irradiance. Decay and mixing models fitted to the generated data indicate the presence of a highly radiocarbon depleted pool of DOC (−1000 to −600 δ¹⁴C) that occurs at elevated concentrations in the deep ocean and has an apparent turnover time of 30,000 years, assuming no external sources of radiocarbon depleted DOC exist (Follett et al., 2014).

In the darkness of the abyss, it appears that a fraction of ancient carbon persists. However, in surface waters this ancient carbon is actively cycled. For instance, the most radiocarbon depleted fraction identified by Follett et al. (2014) occurs at significantly lower concentrations in the surface (9 μM) than in the deep (24 μM), suggesting a surface removal process is at play. Other research has shown that radiocarbon depleted carbon is utilized by surface microbes (Cherrier et al., 1999).

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Both the quantitative loss (Follett et al., 2014) and the increased bioavailability (Cherrier et al., 1999) of deep ocean refractory DOM once it enters surface waters may be facilitated by photochemical processes.

In sunbathed surface waters, DOC is bombarded by photons. When light is absorbed by the colored fraction of dissolved organic matter (CDOM), a multitude of photoreactions ensue (Mopper et al., 2015). Some DOC is mineralized directly to inorganic forms such as carbon dioxide or carbon monoxide (Powers and Miller, 2015; Stubbins et al., 2006). The fraction of DOC that survives photo-degradation is altered (Mopper et al., 2015). Depending upon the nature of the original DOC and irradiation conditions, photo-alteration can increase the bioavailability of DOC (Mopper et al., 2015). The photo-generation of bioavailable DOC from refractory DOC has been invoked to explain the utilization of ancient carbon by surface microbes mentioned in the previous paragraph (Cherrier et al., 1999). Thus, photochemistry plays a direct (photo-mineralization to dissolved inorganic carbon) and biologically mediated (photo-production of biolabile substrates) role in the removal of DOC from sunlit waters. In addition to these removal processes, photochemistry leaves behind a fraction of DOM with modified optical, bulk and molecular composition (Gonsior et al., 2009; Kujawinski et al., 2004; Medeiros et al., 2015; Osburn et al., 2001; Spencer et al., 2009; Stubbins et al., 2010). In the current paper, we focus upon the photo-alteration of deep ocean DOM molecular signatures for a sample collected from North Atlantic Deep Water (NADW).

The photo-lability (i.e., the ease with which a substrate can be degraded) of DOM has been related to optical and molecular properties. For instance, CDOM is preferentially degraded during photo-irradiation experiments (Helms et al., 2008, 2013). The light absorbing properties of CDOM stem from aromatic moieties within the DOM pool (Stubbins et al., 2008; Weishaar et al., 2003), suggesting aromatic signatures should be preferentially photo-degraded relative to non-aromatic ones. Chemical characterization of photo-irradiated DOM bears this out. Multiple lines of evidence, for samples of multiple origin (e.g., terrigenous and marine) and utilizing multiple chemical analyses (e.g., nuclear magnetic resonance spectroscopy, specific compound analysis, and high resolution mass spectrometry), all reveal the preferential photo-degradation of aromatic moieties (Helms et al., 2014; Spencer et al., 2009; Stubbins et al., 2012).

Fourier transform ion cyclotron mass spectrometry (FTICR-MS) brings a major fraction of DOM into our analytical window, providing high accuracy molecular-level information regarding elemental and inferred structural composition that can be related to source (Dittmar and Stubbins, 2014; Kujawinski et al., 2002; Mopper et al., 2007) and has been used to address the photochemical transformations of DOM (Gonsior et al., 2009; Kujawinski et al., 2004; Medeiros et al., 2015; Stubbins et al., 2010). Here we apply FTICR-MS to elucidate the molecular signatures of DOM photo-alteration for a sample of NADW. This sample was previously analyzed for DOC, CDOM and dissolved black carbon photo-degradation (Stubbins et al., 2012). In the current study, FTICR-MS data was used to determine the molecular signatures of the following three photochemically defined pools of DOM and to contrast the nature of these pools with the same fractions observed in Congo River water DOM (Stubbins et al., 2010):

- 1) Photo-resistant DOM: molecular signatures that survive irradiation;
- 2) Photo-labile DOM: molecular signatures that are lost during irradiation, and;
- 3) Photo-produced DOM: molecular signatures that are formed during irradiation.

2. Materials and methods

2.1. Sample collection

Bermuda Atlantic Time Series (BATS) cruise 252 on board the RV Atlantic Explorer (6th to 10th November 2009) was joined to collect

North Atlantic Deep Water (NADW), one of the major global deep ocean water masses. Water masses and their dissolved organic constituent loads undergo modification during transport. For NADW at BATS, DOC concentrations are lower than in NADW near points of deep water formation around Greenland, indicating DOC entrained within NADW at deep water formation sites slowly biodegrades or is otherwise removed as the water mass transits to our sampling site near Bermuda (Hansell and Carlson, 1998). The NADW sample was collected by CTD on the 9th of November 2009 from 3000 m at the BATS site (31°40' N; 64°10' W). Three Niskin bottles were fired at 3000 m. As soon as the CTD was on deck and secure, large surface area 0.2 µm capsule filters were attached (Polycap TC, Whatman) directly to the Niskin bottles' nipples and sample was gravity filtered into a 20 L fluorinated high density polyethylene carboy (Nalgene). The filters and carboy were pre-cleaned by soaking for at least 24 h in acidified ultrapure (MilliQ) water (pH 2 with hydrochloric acid; p.a.), soaking in basic ultrapure water for a further 24 h (0.1 M sodium hydroxide; p.a.), and rinsing with copious volumes of ultrapure water (filters flushed with >20 L; carboy quintuple rinsed). The sample was then stored frozen in the dark at –20 °C onboard RV Atlantic Explorer until she docked in Norfolk, Virginia, USA (19/12/2009). At this point the carboy was collected and taken to Old Dominion University, approximately 10 min drive from the dock, and returned to a –20 °C freezer. From there, the sample was later transported the 9 h to Skidaway Institute of Oceanography (SkIO), Georgia, USA in a large cooler with other frozen samples and placed back in a –20 °C freezer upon arrival. Thus, the sample remained frozen from shortly after collection until defrosting for the irradiation study.

2.2. Irradiations

All analyses, from the irradiation through the extraction and FTICR-MS analysis were conducted in duplicate. On the 20th of September 2010 the thawed sample was transferred to two 2 L precombusted spherical quartz irradiation flasks. A further 4 L aliquot was divided between two 2 L combusted borosilicate flasks, which were then wrapped in aluminum foil. All samples were then placed under a solar simulator fitted with 12 UVA-340 bulbs (integrated irradiance ~25 W m⁻²; Q-Panel), which provide a spectral shape and flux closely approximating natural sunlight from 295 to 365 nm (Stubbins et al., 2008), the main wavelength range for environmental photochemical reactions involving CDOM. The temperature in the solar simulator was kept at approximately 20 °C using a side mounted fan. Sample water temperatures were likely higher as measured temperatures for test samples have been between 25 °C and 30 °C. Duplicate 2 L flasks were taken from the light table after 28 days. One day of irradiation using this solar simulator design is approximate to 1.27 times daily solar irradiance during the winter at 36.89°N or 0.67 times the daily (12 h) irradiance at the equator (Helms et al., 2008; Spencer et al., 2009).

2.3. Fourier transform ion cyclotron resonance mass spectrometry

Duplicate samples were solid phase extracted using PPL Bond Elut (Agilent) resins before analysis by electrospray ionization FTICR-MS in negative ion mode. As reported in Stubbins et al. (2012), 1507 to 1975 mL of acidified NADW seawater was solid phase extracted following the method of Dittmar et al. (2008). The DOC extraction efficiency ranged from 67 to 74% (Stubbins et al., 2012). An ultrapure water sample was also loaded onto PPL, eluted and used as a procedural blank for extraction. The duplicate methanol extracts were diluted 1:1 with ultrapure water and analyzed in negative mode electrospray ionization using a 15 Tesla FTICR-MS (Bruker Solarix) at the University of Oldenburg, Germany. 500 broadband scans were accumulated for the mass spectra. After internal calibration, mass accuracies were within an error of <0.2 ppm. Molecular formulas were assigned to peaks with signal to noise ratios greater than five based on published rules (Koch

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