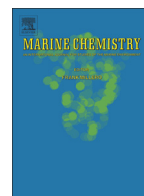




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Spectroscopic characterization of oceanic dissolved organic matter isolated by reverse osmosis coupled with electro dialysis

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ABSTRACT

Oceanic dissolved organic matter (DOM) is one of the largest pools of reduced carbon on Earth, yet DOM remains poorly chemically characterized. Studies to determine the chemical nature of oceanic DOM have been impeded by the lack of efficient and non-fractionating methods to recover oceanic DOM. Here, a DOM fraction (~40 to 86% recovery) was isolated using reverse osmosis/electrodialysis (RO/ED) and analyzed by solid-state ¹³C nuclear magnetic resonance (NMR) spectroscopy. Samples were obtained from biogeochemically distinct environments: photobleached surface gyre, productive coastal upwelling zone, oxygen minimum, North Atlantic Deep Water, and North Pacific Deep Water. A ubiquitous 'background' refractory carbon pool was apparent throughout the ocean and dominated in the deep Pacific Ocean. Advanced NMR spectral editing revealed that condensed aromatic and quaternary anomeric carbons contribute to this deep refractory DOC pool, the quaternary anomeric carbons being a newly identified and potentially important component of bio-refractory carbohydrate-like carbon. Additionally, our results support the multi-pool (e.g. 3-pool: labile, semi-labile, and refractory) conceptual model of marine DOM biogeochemistry. Surface samples, hypothesized to be enriched in labile and semi-labile DOM, were enriched in carbohydrate-like material consistent with prior studies. High carboxyl signals in the deep Pacific support the hypothesis that a major fraction of the refractory pool consists of carboxyl-rich alicyclic molecules (CRAM).

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1. Introduction

The oceans contain approximately 662 Pg-C of dissolved organic carbon (DOC) (Hansell et al., 2009), a pool on the same order as atmospheric CO₂ (860 Pg-C; Forster et al., 2007). Oxidation of 1% of the

oceanic DOC pool would exceed the annual flux (ca. 2000) of anthropogenic CO₂ (Hedges, 2002). Despite its quantitative importance, only a small fraction of marine dissolved organic matter (DOM) has been identified (Repeta, 2015), hindering our understanding of DOM sources and cycling (Dittmar and Stubbins, 2014; Hedges, 2002). One impediment to the development of a comprehensive overview of ocean DOM composition has been the lack of efficient and non-fractionating methods of DOM isolation and salt removal (Mopper et al., 2007).

The two most widely used DOM isolation techniques are solid phase extraction (SPE) (Dittmar et al., 2008; Leenheer, 1981; Leenheer, 2009) and ultrafiltration (UF) (Benner et al., 1992; Swift, 1985). In both methods, a major fraction of ocean DOM is lost during processing resulting in DOC recoveries that range from 17–74% for SPE and 13–38% for UF (Benner et al., 1997; Hertkorn et al., 2013; Mopper et al., 2007; Stubbins et al., 2012b). In addition, as these methods isolate DOM based upon either an apparent size cutoff (UF) or chemical affinity for a resin (SPE), they have failed to produce a representative DOM isolate (Mopper et al., 2007). A system was recently developed that combines concentration of DOM by reverse osmosis and de-salting by electro dialysis (RO/ED) (Gurtler et al., 2008; Koprivnjak et al., 2006; Vetter et al., 2007). Further study has shown that when directly

Abbreviations: ALOHA, A Long-term Oligotrophic Habitat Assessment field site (22° 45' N, 158° W); CDOM, chromophoric (or colored) dissolved organic matter; CP, cross polarization; Cq, quaternary carbon(s); CSA, chemical shift anisotropy; DOC, dissolved organic carbon; DOM, dissolved organic matter; DP, direct polarization; ED, electro dialysis; HS, humic substances; ISOW, Iceland/Scotland overflow water; LCPW, lower circumpolar water; MAS, magic angle spinning; NADW, North Atlantic deep water; NMR, nuclear magnetic resonance; POM, particulate organic matter; ppm, NMR chemical shift frequency in parts per million; RO, reverse osmosis; SPE, solid phase extraction; SUVA, specific UV absorbance; TOSS, total suppression of spinning sidebands; UDOM, DOM retained by ultrafiltration; UF, ultrafiltration.

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compared with SPE, RO/ED exhibits DOC yields that are typically higher and provides isolates that are more representative of the original organic matter (Green et al., 2014; Helms et al., 2013; Koprivnjak et al., 2009).

Mao et al. (2012) and Koprivnjak et al. (2009) applied solid-state CP/MAS ^{13}C NMR and solution ^1H NMR to RO/ED isolates collected in the North Atlantic and observed differences between DOM isolated from a regional transect across the Georgia Bight to the Gulf Stream. The NMR spectra of RO/ED isolates appeared to represent an intermediate of DOM isolated by UF and DOM isolated by XAD, suggesting that RO/ED isolates a more representative fraction of the DOM than these methods. The latter conclusion is also supported by the molar C/N ratios and absorption spectral slopes of RO/ED isolated DOM being more consistent with the original seawater DOM (Green et al., 2014; Helms et al., 2013; Koprivnjak et al., 2009).

Studies of SPE and UF DOM isolates have increased knowledge of the reactivity and cycling of organics in the ocean. For example Hedges et al. (1992) used solid-state cross polarization/magic angle spinning (CP/MAS) ^{13}C nuclear magnetic resonance (NMR) spectroscopy to investigate the bulk structural characteristics of humic substances (HS) extracted using XAD from two sites in the Pacific Ocean (DOC recovery ~10%), while Benner et al. (1992) used CP/MAS NMR to characterize UF isolated DOM (UDOM) from three depths in the North Pacific Ocean (DOC recoveries: 22–33%). DOM isolated from the deep ocean contained more aromatic and/or olefinic carbon than surface ocean DOM and deep-ocean UDOM was enriched in carbohydrate-like carbons and depleted in unsubstituted alkyl carbons relative to deep-ocean HS (Benner et al., 1992; Hedges et al., 1992). N. Pacific UDOM was enriched in carbohydrates (oligo- and poly-saccharides) relative to deep and even mesopelagic UDOM (Benner et al., 1992), a trend not seen for HS (Hedges et al., 1992). More recently, Hertkorn et al. (2013) analyzed SPE-DOM from various depths in the South Atlantic Ocean (DOC recovery ~40%) using NMR and mass spectrometry concluding that, in addition to the prevalence of aliphatic cyclic moieties among carboxylic rich molecules, there is 1) high diversity in aliphatic branching patterns, 2) progressive oxygenation of aromatic C and deoxygenation of aliphatic C in the ocean interior, 3) significant evidence for methylated carbohydrates and both pyranose and furanose sugar derivatives, and 4) evidence of a ubiquitous background DOM including carboxylic rich alicyclic molecules (CRAM) and thermogenic condensed aromatic carbon at all depths.

In addition to CP/MAS, complementary and improved solid-state ^{13}C NMR methods have been developed and applied to natural organic matter. Mao et al. (2011) demonstrated a systematic approach for characterizing humic substances by advanced solid-state NMR techniques. These techniques were used here to characterize the bulk chemical composition of five globally distributed RO/ED-DOM. Previous studies of RO/ED-DOM from specific oceanic regions explored local biogeochemical processing (Koprivnjak et al., 2009; Mao et al., 2012). The current study sampled carefully selected oceanic water masses within the Atlantic and Pacific Oceans that fall along the thermohaline circulation pathway and a global gradient in DOM quality. The RO/ED isolates analyzed here provide in-depth structural characterization of the RO/ED-DOM within productive upwelling zones, an oligotrophic tropical gyre, within an oxygen minimum, and within the deep waters of the North Atlantic and North Pacific Oceans.

2. Material and methods

2.1. Sample collection and DOM isolation by RO/ED

Three Atlantic Ocean and two Pacific Ocean water samples were collected aboard R/V Oceanus and R/V Kilo Moana, respectively. The samples include (i) surface water from the Mauritanian upwelling (5 m; 20.161°N, 17.406°W), (ii) North Atlantic oxygen minimum zone (415 m; 18.995°N, 21.487°W), (iii) North Atlantic deep water (3000 m; 18.485°N, 23.397°W), (iv) a surface sample from station

ALOHA in the North Pacific (5 m; 22.450°N, 158.00°W), and (v) a deep sample from station ALOHA (3500 m; 22.450°N, 158.00°W).

The Mauritanian upwelling is an area of high primary production and represents waters impacted by fresh algal DOM enriched in labile and/or semi-labile DOM (Carlson, 2002; Reintaler et al., 2008; Teira et al., 2001). The 415 m North Atlantic RO/ED-DOM from the oxygen minimum layer was expected to contain DOM that is degraded during and after export to the ocean interior from surface waters or released during the degradation of POM in the nearby shelf sediments (Carlson, 2002; Hansell, 2002; Hansell and Carlson, 2001). The 3000 m North Atlantic sample was representative of the Iceland–Scotland overflow water (ISOW), which is a component of North Atlantic Deep Water (NADW) (Hernes and Benner, 2006; LeBel et al., 2008). ISOW forms in the sub-polar North Atlantic before sinking to depths of ~2500 to 3000 m and flowing southward. The surface water sample collected at Station ALOHA (5 m North Pacific sample) represents oligotrophic surface waters that cover the majority of Earth's surface and is largely dominated by semi-labile (Carlson, 2002) and extensively photobleached DOM (Kitidis et al., 2006; Nelson et al., 2010; Siegel et al., 2005). The 3500 m North Pacific sample collected at Station ALOHA represents Lower Circumpolar Water (LCPW) (Johnson and Toole, 1993), which exhibits old apparent ^{14}C DOC ages (~6000 y) (Williams and Druffel, 1987), suggesting that DOM from this water mass consists largely of highly-degraded and refractory DOM that resists degradation over multiple ocean overturn cycles (Hedges et al., 1997).

Sample volumes ranging from 142 L to 473 L were collected using Niskin bottles (General Oceanics) from which they were sterile-filtered directly through pre-cleaned 0.1 μm capsule filters (Whatman, PolycapTM TC). The RO/ED method is described in detail elsewhere (Green et al., 2014; Vetter et al., 2007). Samples were desalted by ED using anion and cation exchange membranes (Selemon AMV/CMV, AGC, Japan) and concentrated by RO (FilmTec TW30-4021, Dow, USA). Samples were recirculated through both RO and ED systems until a sufficiently low conductivity (<50 $\mu\text{S cm}^{-1}$) and volume (~5 L) were obtained. Pacific Ocean samples were frozen shipboard and processed on Hawaii within 9 days. All other sterile-filtered samples were refrigerated before starting RO/ED within 6 h. Sample handling times ranged from 6.5 to 32.2 h after which RO/ED isolates were frozen immediately. Each sample was freeze-dried (without further treatment) for analysis by solid-state NMR.

2.2. UV-visible spectroscopy and dissolved organic carbon analysis

Absorption spectra of chromophoric dissolved organic matter (CDOM) were collected for seawater and isolated samples using an Agilent 8453 diode array spectrophotometer with a 1 cm, 5 cm or 10 cm pathlength quartz cuvette (Helms et al., 2008). Data output from the spectrophotometer were in the form of dimensionless absorbance or optical density (OD) and were subsequently converted to the Napierian absorption coefficient, a (m^{-1} ; Hu et al., 2002). Spectral slope (S) and slope ratio (S_R) were calculated (Helms et al., 2013). DOC was measured as non-purgeable organic carbon using high-temperature catalytic combustion by high temperature combustion (720 °C) on a Shimadzu TOC-VCPH (Shimadzu Scientific Instruments; Chen et al., 2014a). Specific UV absorbance (SUVA) was calculated by dividing decadic absorbance in units of m^{-1} by the DOC concentration in units of mg C L^{-1} (Weishaar et al., 2003).

2.3. Solid-state ^{13}C NMR

NMR experiments were performed using a 400 MHz (^1H) Bruker Avance II with a dual resonance probe. Samples were packed in 4 mm diameter zircon NMR tubes with Kel-F rotor caps (Bruker-Biospin). A detailed description of NMR methods is given in Supplementary Material. Briefly, semi-quantitative compositions of the RO/ED-DOM were investigated using ^{13}C cross polarization/total sideband suppression

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