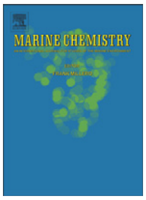
Marine Chemistry 177 (2015) 288–297

Contents lists available at ScienceDirect

Marine Chemistry

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



Conservation of dissolved organic matter molecular composition during mixing of the deep water masses of the northeast Atlantic Ocean

Roberta L. Hansman [a,*], Thorsten Dittmar [b,c], Gerhard J. Herndl [a,d]

[a] Department of Limnology and Oceanography, University of Vienna, Vienna, Austria
[b] Research Group for Marine Geochemistry (ICBM-MPI Bridging Group), Institute for Chemistry and Biology of the Marine Environment (ICBM), Carl von Ossietzky University of Oldenburg, Oldenburg, Germany
[c] Max Planck Institute for Marine Microbiology (MPI), Bremen, Germany
[d] Department of Biological Oceanography, Royal Netherlands Institute for Sea Research (NIOZ), Den Burg, The Netherlands

ARTICLE INFO

Article history:
Received 20 January 2015
Received in revised form 21 May 2015
Accepted 1 June 2015
Available online 4 June 2015

Keywords:
Marine dissolved organic matter
FT-ICR-MS
North Atlantic
Carbon cycle

ABSTRACT

Characterizing the composition of marine dissolved organic matter (DOM) is important for gaining insight into its role in oceanic biogeochemical cycles. Using Fourier transform ion cyclotron resonance mass spectrometry, we analyzed the molecular composition of solid phase extracted (SPE) DOM from the northeast Atlantic to investigate the specificity of the DOM pool of the individual major water masses of the North Atlantic. All 272 measured samples from depths ranging from 87 to 5609 m and latitudes from 24°N to 68°N shared 96% similarity (on a Bray–Curtis scale) in their DOM composition. Small variations between subsurface and deep samples and among latitudinal groupings were identified, but overall, water mass specific SPE-DOM composition was not apparent. A strong correlation between a calculated degradation index and water mass age indicates variability in portions of the DOM pool, and ocean-scale differences were observed between the North Atlantic and deep North Pacific. However, within the deep northeast Atlantic, conservative mixing primarily drives the molecular composition of SPE-DOM.

1. Introduction

With an inventory of 662 Pg C, marine dissolved organic matter (DOM) is one of the largest active pools of carbon on the planet and is comparable in size to atmospheric CO_2 (Hansell et al., 2009; Hedges, 1992). Produced mainly by primary production in surface waters (Carlson, 2002), DOM serves as the dominant substrate for heterotrophic microbes throughout the water column (Azam et al., 1983). Marine DOM can be described by its reactivity and age along a continuum ranging from labile to refractory and on timescales of hours to thousands of years (Follett et al., 2014; Hansell et al., 2012; Kirchman et al., 1991). Though the majority of the marine DOM pool is thought to be recalcitrant, gradients in reactivity exist vertically throughout the water column and laterally in the open ocean (Hansell, 2013; Hansell et al., 2012). Abiotic processes such as photo-degradation in surface waters contribute to these gradients, as well as both the production and remineralization of marine DOM by microbial communities throughout the water column.

Characterizing marine DOM has been a challenge for many years, primarily due to its complexity and low concentration relative to the inorganic salts present in seawater. The composition of parts of the DOM pool has been discerned by quantifying specific biochemical groups (e.g., amino acids, carbohydrates) and/or size classes using several techniques such as ultrafiltration, NMR, and HPLC (Aluwihare et al., 1997; Benner, 2002; Benner et al., 1992; McCarthy et al., 1998; Pakulski and Benner, 1994), but the molecular structure of the majority of marine DOM remains elusive. Recently, ultrahigh resolution Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS) has been used with electrospray ionization (ESI) to characterize marine DOM at a molecular level (Chen et al., 2014; Dittmar and Paeng, 2009; Flerus et al., 2012; Hertkorn et al., 2006; Koch et al., 2005; Kujawinski et al., 2009; Medeiros et al., 2015). Mass accuracies within 1 ppm allow for the assignment of elemental formulas to thousands of peaks resolved from marine DOM, establishing a molecular fingerprint for each particular seawater sample. Though still subject to the limitations of the method used to isolate marine DOM, FT-ICR-MS provides another useful tool available for further characterizing the composition of the oceanic DOM pool.

The North Atlantic is comprised of several well-characterized water masses with distinct physical and chemical attributes (van Aken, 2000a, b). These include cold and typically less saline Lower Deep Water (LDW) from the south, Iceland–Scotland Overflow Water (ISOW) and Labrador Sea Water (LSW) from the north, and warm salty Mediterranean Sea Outflow Water (MSOW) emanating from the Strait of Gibraltar (Table S1). The North Atlantic is also the site of North Atlantic Deep Water (NADW) formation, where cold and saline surface water

---

[*] Corresponding author at: Department of Limnology and Oceanography, University of Vienna, Althanstrasse 14, 1090 Vienna, Austria.
E-mail address: rhansman@gmail.com (R.L. Hansman).

http://dx.doi.org/10.1016/j.marchem.2015.06.001

sinks into the deep ocean's interior in the Greenland–Iceland–Norwegian Sea. The formation of NADW leads to the export of DOM from the euphotic layer to meso- and bathypelagic depths where microbes remineralize a portion of this DOM as it is transported southward in the NADW. These processes lead to prominent vertical and latitudinal gradients in dissolved organic carbon (DOC), ranging from up to 80 μM in surface waters to 40 μM in the deep North Atlantic (Carlson et al., 2010). From a biological perspective, studies have also shown that distinct microbial communities and activities exist within the water masses and depth layers of the North Atlantic (Agogué et al., 2008, 2011; Sintes et al., 2013; Varela et al., 2008a,b). The northeast core of NADW (NEADW) is comprised primarily of four source water types: ISOW, LSW, LDW, and MSOW (Table S2).

In this study we used FT-ICR-MS to characterize solid-phase extracted (SPE) marine DOM in the northeast Atlantic, focusing primarily on the deep waters below 200 m. We hypothesized that the molecular composition of SPE-DOM would exhibit water mass specific signatures, shaped by the combination of physical, chemical, and biological attributes that are unique to each distinct depth layer. We further focused on specific components of our data, using a degradation index (Flerus et al., 2012) to evaluate aging of the DOM pool, and on a subset of samples to investigate the impact of water mass mixing on the molecular composition of DOM within the core of NEADW.

2. Methods

2.1. Sampling

Samples were collected from 46 stations spanning a transect from approximately 67°N to 24°N in the eastern basin of the North Atlantic as part of the Microbial Ecology of the Deep Atlantic (MEDEA) project (Fig. 1). The stations were sampled during two cruises on the RV *Pelagia*: MEDEA-1 (49°N to 24°N in October and November 2011) and MEDEA-2 (49°N to 67°N in June and July 2012). Seawater was collected in 25-L Niskin bottles from generally six depths per station corresponding to identified water masses determined primarily from potential temperature and salinity data (van Aken, 2000a,b) or distinct physical-chemical features in the water column (Table S1). Conductivity (salinity), temperature, pressure, and oxygen (SBE 43, Seabird) were measured using a Seabird CTD-system mounted on the rosette. Potential temperature (θ) and apparent oxygen utilization (AOU) were calculated using Ocean Data View 4.6.2 (Schlitzer, 2013).

2.2. Nutrients and dissolved oxygen

Concentrations of nitrate and silicate were measured on a continuous flow auto-analyzer (AxFlow Bran + Luebbe Traacs800) onboard following JGOFS recommended protocols (Gordon et al., 1993). Dissolved oxygen concentrations from the CTD sensor were checked and calibrated via Winkler titrations. Samples were collected for DOC concentrations, but unfortunately contamination and analysis problems resulted in unreliable data.

2.3. SPE-DOM and FT-ICR-MS

SPE-DOM was obtained from 5 L of unfiltered seawater after acidifying (pH 2 with 25% HCl) and loading it onto commercially available modified styrene divinyl benzene polymer cartridges (PPL, Agilent) (Dittmar et al., 2008). As the contribution of particulate material to the total organic matter pool in the open ocean has been shown to be small and essentially negligible in the deep ocean (i.e., <4% in the Sargasso Sea water column; Hansell and Carlson, 2001; Kaiser and Benner, 2009), these unfiltered samples were presumed to be predominantly organic matter in the dissolved phase (DOM). Following extraction, cartridges were rinsed with acidified ultrapure water, dried under nitrogen, and eluted with 8 mL methanol into amber glass vials that were then stored at −20 °C. Resulting SPE-DOM samples were diluted to approximately 15 ppm in 1:1 methanol:ultrapure water and run in negative ion mode on a 15 Tesla Solarix Fourier-transform ion cyclotron resonance mass spectrometer (FT-ICR-MS; Bruker Daltronics) with an electrospray ionization source (Bruker Apollo II).

SPE-DOM from large volumes of North Equatorial Pacific Intermediate Water (NEqPIW) collected at 670 m depth off Kona, Hawaii (Green et al., 2014), was used as an in-house reference sample (Osterholz et al., 2014; Riedel and Dittmar, 2014). This reference sample was analyzed by FT-ICR-MS every day that MEDEA cruise samples were analyzed, and was used to assess and correct for instrument variability over time.

2.4. Data analysis

The Data Analysis software package (Bruker Daltronics) was used to calibrate FT-ICR-MS spectra with an internal calibration list, and in-house Matlab routines were used to process the resulting mass-to-charge (m/z), resolution, and intensity for each peak in all samples. A method detection limit (MDL; Riedel and Dittmar, 2014) was established and used to filter FT-ICR-MS data. Masses present in only one sample were removed as well as those with a maximum signal-to-noise ratio less than four across all samples. Peaks present in less than 20% of samples that had a maximum signal-to-noise ratio less than 20 were also removed. Data were then normalized to the sum of all peak intensities with signal-to-noise ratios greater than five in each sample. Molecular formulas were assigned following the guidelines established in Koch et al. (2007) using the elements C, H, O, N, S, and P. Molecular indices were calculated for each assigned molecular formula to assess the degree of unsaturation (double-bond equivalents, DBE) and aromaticity (aromaticity index and modified aromaticity index, AI and AI_{mod}) (Koch and Dittmar, 2006). The formulas for these calculations are included in the Supplementary Material.

The degradation index (I_{deg}) was calculated for each sample with the formula developed by Flerus et al. (2012) that uses the intensities of ten compounds that correlated strongly either negatively or positively with the radiocarbon age of the DOM extracts in their study. The formula and peaks used for this calculation are included in the Supplementary Material (Table S3).

Multivariate statistics including principal component analysis (PCA) and canonical analysis of principal coordinates (CAP) (Anderson and Willis, 2003) were performed using the vegan package (Oksanen et al., 2013) in R (R Core Team, 2014). Distance matrices (Euclidean for PCA, Bray–Curtis for CAP) were calculated using the normalized peak intensities described above. As a constrained ordination method, CAP was used to test for associations between SPE-DOM molecular composition and other environmental factors, including sample depth and latitude.

2.5. Mixing model

The contribution of four specific water types forming the NEADW sampled during the MEDEA cruises was calculated using the model presented in Reinthaler et al. (2013). Briefly, a set of linear mixing equations conserving potential temperature (θ), salinity (S), and silicate concentration (SiO_4) were solved with the additional constraint that all contributions from the four water types must total to 100%. The parameters used in the model for the MSOW (Álvarez et al., 2004), LDW, LSW, and ISOW end-members are listed in Table S2. To test whether the molecular composition of SPE-DOM is a conservative parameter in the NEADW core, the resulting contributions of each water type to the NEADW samples were then used to calculate expected FT-ICR-MS spectra for each sample collected within the NEADW using the average SPE-DOM molecular composition from 4 to 6 samples of identified end-members. This calculated data set was then compared to the actual SPE-DOM molecular compositions we measured in NEADW samples.