Deep–Sea Research Part II 144 (2017) 104–111

Contents lists available at ScienceDirect

Deep–Sea Research II

journal homepage: www.elsevier.com/locate/dsr2

Optical properties and molecular diversity of dissolved organic matter in the Bering Strait and Chukchi Sea

Michael Gonsior[a,*], Jenna Luek[a], Philippe Schmitt-Kopplin[b,c], Jacqueline M. Grebmeier[a], Lee W. Cooper[a]

[a] University of Maryland Center for Environmental Science, Chesapeake Biological Laboratory, Solomons, USA
[b] Helmholtz Zentrum München, Analytical BioGeoChemistry, Neuherberg, Germany
[c] Technische Universität München, Analytical Food Chemistry, D-85354 Freising-Weihenstephan, Germany

ABSTRACT

Changes in the molecular composition of dissolved organic matter (DOM) and its light absorbing chromophoric component (CDOM) are of particular interest in the Arctic region because of climate change effects that lead to warmer sea surface temperatures and longer exposure to sunlight. We used continuous UV–vis (UV–vis) spectroscopy, excitation emission matrix fluorescence and ultrahigh resolution mass spectrometry during a transect from the Aleutian Islands in the Bering Sea to the Chukchi Sea ice edge through Bering Strait to determine the variability of DOM and CDOM. These data were combined with discrete sampling for stable oxygen isotopes of seawater, in order to evaluate the contributions of melted sea ice versus runoff to the DOM and CDOM components. This study demonstrated that high geographical resolution of optical properties in conjunction with stable oxygen ratios and non-targeted ultrahigh resolution mass spectrometry was able to distinguish between different DOM sources in the Arctic, including identification of labile DOM sources in Bering Strait associated with high algal blooms and sampling locations influenced by terrestrially-derived DOM, such as the terrestrial DOM signal originating from Arctic rivers and dirty/anchor sea ice. Results of this study also revealed the overall variability and chemodiversity of Arctic DOM present in the Bering and Chukchi Seas.

1. Introduction

More than 97% of organic carbon in the ocean is present as dissolved organic matter (DOM), which is also one of the most dynamic components of the global carbon cycle. The amount of carbon in DOM (620 gigatons C) approximately equals that of carbon in the atmosphere (CO_2) (Hansell and Carlson, 1998; Hansell et al., 2009) and represents a transient pool of organic carbon. Hence, a shift in its molecular composition as well as in distribution patterns of DOM can have large effects on the Earth's carbon cycling. The Arctic Ocean is surrounded by landmasses and the ratio of the discharge of freshwater to ocean surface area is the highest of all oceans. Rivers draining into the Arctic Ocean contribute about 10% of global freshwater to the marine system and are the major factor in maintaining the stratification of the Arctic surface water. Arctic rivers also contain on average 2.5 times more DOM compared to temperate rivers with the same discharge volume (Raymond et al., 2007). As a direct result, the Arctic Surface Ocean contains exceptionally high levels of terrigenous DOM (Dittmar and Kattner, 2003).

Previous research indicates that microbial degradation rates of terrigenous DOM are low in the Arctic (Dittmar and Kattner, 2003). Chromophoric DOM (CDOM) photo-oxidation in the Arctic Ocean has also been considered relatively inefficient because photo-labile lignin derivatives, as tracers for terrigenous CDOM, persist in the high-molecular weight DOM fraction (Benner et al., 2005). This finding is not surprising given the extensive ice cover and low light regime over much of the year. As a result, the two major removal pathways of terrigenous DOM (microbial- and photo-degradation) are likely limited in the Arctic and this limitation in turn contributes to the exceptionally high concentration of terrigenous DOM.

Despite temporal and spatial variability in ice cover in the Chukchi and Beaufort Seas, higher absorption and lower spectral slopes have been observed below 20 m, which is consistent with photobleaching (Matsuoka et al., 2015). These low spectral slopes were also significantly correlated with high bacterial production and abundance, indicating the importance of the microbial community in altering CDOM (Matsuoka et al., 2015).

The seasonal sea ice cover of the Arctic Ocean is decreasing in an unexpectedly fast manner and if the scenario of an ice-free Arctic

* Corresponding author.

http://dx.doi.org/10.1016/j.dsr2.2017.01.003
Received 6 April 2016; Received in revised form 4 November 2016; Accepted 2 January 2017
Available online 04 January 2017

Ocean in 2040 (Serreze et al., 2007) becomes reality, then the current limitations on terrigenous DOM degradation due to sea ice cover will likely no longer be limiting. To make the situation more dramatic, the summer decrease in sea ice cover in the Arctic also has a substantial positive feedback effect on Arctic warming (ice-albedo feedback) itself and hence on terrestrial Arctic environments up to 1,500 km inland (Lawrence et al., 2008). Inland warming may cause changes in the supply of DOM to the Arctic Ocean and the resulting changes in Arctic carbon cycling will ultimately have unforeseen impacts within the Arctic and beyond.

Despite the importance of terrigenous DOM as a major player in the Arctic ecosystem, the molecular composition of Arctic DOM is poorly characterized and a link between the light-absorbing chromophoric DOM (CDOM) and the overall molecular composition of DOM remains largely unresolved. However, recent measurements of total dissolved amino acids and dissolved organic carbon (DOC) indicate that bioavailable DOM may be accumulating in the Chukchi Sea (Shen et al., 2012).

Attempts have also recently been made to link optical properties and the molecular signatures in boreal rivers that have been determined by ultrahigh resolution Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS). For example, correlations between fluorescent DOM (FDOM) followed by Parallel Factor Analysis (PARAFAC) and molecular formulas have been demonstrated (Stubbins et al., 2014). Thus far, Arctic DOM in the Lena delta has been characterized by FT-ICR-MS (Dubinenkov et al., 2015) and significant differences were also found among different DOM sources, and arctic fjords in the Svalbard archipelago (Osterholz et al., 2014), where DOM appeared to be turned over quickly. Excitation emission matrix fluorescence coupled with PARAFAC (EEM-PARAFAC) has been used to describe the variability of fluorescence with respect to Arctic water masses (Dainard and Guéguen, 2013; Guéguen et al., 2011), and has indicated a strong correlation between CDOM originating from Arctic rivers with DOC concentrations and lignin phenols (Walker et al., 2013).

In this study, we bring these developing organic material characterization tools to a transect we sampled from the Aleutian Islands in the Bering Sea to the Chukchi Sea ice edge through Bering Strait. The overall aim of our study was to characterize the optical properties of DOM using UV–vis and fluorescence spectroscopy. We tracked specific sources of DOM by using reference and comparison optical signatures associated with the molecular composition of DOM determined by a 12 Tesla FT-ICR-MS instrument.

This sampling effort traversed the Arctic waters most influenced by inflows of nutrient rich waters through the Bering Strait. Additionally, we were able to sample in the vicinity of melting sea ice visibly entrained with sediments, which afforded the opportunity to examine the potential influence of these sediments on the DOM pool during sea ice melt. It has been suggested that DOM associated with sea ice can be significantly different at the molecular level relative to surface seawater in the Chukchi Sea, specifically with respect to the proteinaceous component of DOM (Longnecker, 2015), so we also sought to explore the impacts of this DOM source as part of this continuous shipboard sampling effort. We assessed sea ice melt contributions in part by using the stable oxygen isotope composition of surface water samples collected during the cruise; the freshwater component of melted sea ice differs significantly in isotopic composition from runoff from meteoric sources (Strain and Tan, 1993).

2. Materials and methods

2.1. Sampling

10 L water samples for the solid-phase extraction were collected from the high flow seawater system aboard the USCGC Healy along a transect from the Aleutian Islands (Dutch Harbor, across the Bering Strait and Chukchi Sea to Barrow, Alaska. Water samples for the oxygen isotope measurements were collected from a 24 Niskin bottle CTD profiler. All grab samples used in this study were collected at 3–5 m depth.

2.2. Chlorophyll a measurements

250 mL water samples were collected from the Niskin bottles, typically at six depths within the water column. Water was filtered through Whatman GFF filters, and filters were briefly frozen to fracture cell membranes. Following a 24 h incubation of the filters in the dark in 10 mL of 90% acetone at 4 °C, the 90% acetone was decanted and the water column chlorophyll a was determined shipboard using a Turner Designs AU-20 fluorometer (non-acidfication or Welschmeyer method; see Cooper et al. 2012, 2013 for further details). Certified chlorophyll a standards were used to calibrate the fluorometer.

2.3. Ultraviolet–Visible (UV–vis) spectroscopy

The seawater system aboard the USCGC Healy was used to collect water and a small flow was continuously filtered through a 0.2 µm cartridge filter. An ocean optics UV/Vis spectrophotometer with an integrated light source (JAZZ System) was then attached to a capillary wave guide of 50 cm path length to measure the UV/Vis absorbance between 240–750 nm which was fed by the filtered seawater. The raw absorbance was converted into apparent absorption coefficients (Gonsior et al., 2008) and all data was normalized to zero absorbance at wavelength 700 nm to account for remaining scattering. Data gaps were removed and data was synchronized with the ship's global positioning system in order to map the analyzed data.

2.4. Solid-phase extraction of DOM

A previously described solid-phase extraction procedure (Dittmar et al., 2008) was used to isolate DOM from the water using Agilent Bond Elut PPL solid-phase extraction (SPE) cartridges filled with 1 g of a functionalized styrene-divinylbenzene polymer (PPL) resin. This resin has high extraction efficiency for DOM (≈60%) and recovers quantitatively the CDOM component. Briefly, after the conditioning of the Agilent PPL cartridges with 10 mL pure methanol (Sigma Aldrich LC-MS Chromasolv), the filtered (GF/F Whatman glass fiber filter) water samples (10 L) were first acidified (pH 2 with conc. HCl) and then gravity-fed to the cartridge. The cartridge was washed with 10 mL acidified pure water, dried and the isolated DOM was then eluted off the cartridge using 10 mL methanol.

2.5. Excitation emission matrix fluorescence and PARAFAC modeling

One ml of the solid-phase extracted DOM (SPE-DOM) was dried under vacuum and then re-dissolved in pure water. The aqueous sample was then used to determine the EEM spectra. EEMs were determined using a Horiba Aqualog fluorometer between 200–600 nm emission wavelengths and between 240–600 nm excitation wavelengths at 3 nm intervals. The spectra was corrected for Raleigh and Raman scattering and inner filter effects and normalized to a 1 ppm quinine sulfate reference material (Starna ®). The DrEEM toolbox was used in this study to develop a PARAFAC model (Murphy et al., 2013). Several PARAFAC component models (3–6 components) were developed, but only the 4 component model was satisfactory and most suitable for the data set and could be validated (split-half validation, Supplementary online material: Fig. S1) with a core consistency of 90.6% and 99.2% of the variance was explained by this 4 component PARAFAC model.