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The potential role of sea ice melt in the distribution of chromophoric dissolved organic matter in the Chukchi and Beaufort Seas

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ABSTRACT

We investigated chromophoric dissolved organic matter (CDOM) in sea ice and the underlying water column in the Chukchi and Beaufort seas of the Pacific Arctic region and its relationship with both physical and biogeochemical parameters. Sea ice, water and melt pond samples were collected as sea ice melted in June–July 2010 and 2011. CDOM absorption was found to be significantly lower in sea ice compared to under-ice waters. In particular, the average CDOM absorption coefficient at 254 nm was approximately four times greater in the underlying water column than in the overlying ice. This indicates that melting sea ice did not contribute to net CDOM at this point in the melt season, but rather diluted CDOM in the under-ice water column. In the 2011 under-ice water column samples, the average CDOM absorption coefficients at 440 nm were twice as high along a transect associated with high phytoplankton biomass, which may have been contributed through subsequent microbial generation of CDOM. Less extensive sea ice cover with melt ponds may also have increased the presence of CDOM owing to increases in light transmission, leading to under-ice phytoplankton blooms and associated microbial production. However, oxygen isotope analysis of these waters with high under-ice phytoplankton biomass also indicates the presence of prior sea ice melt, including potentially sea ice algae and microbes, which could have also contributed to this anomalously high CDOM. These observations suggest that while melting sea ice may not necessarily contribute to increased CDOM concentrations, there are circumstances where CDOM in underlying waters may be higher than expected, either due to enhanced light transmission and higher under-ice production, and/or prior ice melt that provided significant contributions to under-ice CDOM.

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1. Introduction

Arctic seasonal sea ice extent has significantly decreased in recent years (Serreze et al., 2007; Stroeve et al., 2007; Comiso et al., 2008; Perovich et al., 2012). This has been accompanied by an increase in the length of the summer melt season (Markus et al., 2009) and an overall thinning of the ice pack (Maslanik et al., 2007, Kwok and Rothrock, 2009; Maslanik et al., 2011; Comiso, 2012). Arctic sea ice is expected to continue thinning and decreasing in areal extent, but there are large uncertainties as to how this will impact biological and biogeochemical processes in the Arctic Ocean. One uncertainty with this sea ice decline is how and to what extent chromophoric dissolved organic matter (CDOM) in underlying ocean waters will be impacted. CDOM plays an important role in the marine ecosystem by inhibiting light transmittance through the water column and providing a

food source for aquatic bacteria (Moran and Zepp, 1997; Blough and Del Vecchio, 2002; Nelson and Siegel, 2002). Although CDOM has been observed in Arctic sea ice (Belzile et al., 2000; Scully and Miller, 2000; Stedmon et al., 2007a), its distribution is not well known, making it difficult to predict the impact of sea ice decline on biological and biogeochemical processes in the Arctic Ocean.

Sources of CDOM in the ocean include two primary categories: (a) *in situ* (autochthonous) biological production (e.g., Carlson et al., 2002); and (b) inputs of terrestrially-derived (allochthonous) organic matter transported to the ocean by terrestrial runoff. CDOM is defined as the optically active fraction of dissolved organic material (DOM), absorbing ultraviolet (UV) and visible light, and acting as one of the primary regulators of light penetration in the oceanic euphotic zone (Blough and Del Vecchio, 2002; Nelson and Siegel, 2002). In particular, CDOM limits the amount of photosynthetically active radiation (PAR) in the water column, thereby potentially reducing rates of primary production

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(Retamal et al., 2008) but also blocking harmful UV radiation (Williamson et al., 2001). CDOM can also contribute to the heating of surface waters and subsequent melting of sea ice by absorbing shortwave visible radiation (380–760 nm; Kirk, 1988, 1994; Pegau, 2002; Granskog et al., 2007; Hill, 2008). In addition, absorption of light by CDOM can lead to photodegradation of DOM, potentially resulting in a decrease in CDOM absorption of light (i.e., photo-bleaching). Through these photodegradation processes, a pool of DOM can be directly photomineralized to dissolved inorganic carbon, with subsequent outgassing of CO₂ to the atmosphere (Xie and Gosselin, 2005; Belanger et al., 2006; Stubbins et al., 2008; Osburn et al., 2009). In addition, less bio-reactive (refractory) DOM may be broken down into more biologically labile material, allowing it to be more readily respired by bacterioplankton (Moran and Zepp, 1997).

In the polar regions, sea ice can be considered a potential source of CDOM to underlying ocean waters. During ice formation most of the CDOM from the underlying water column is removed from the ice during brine rejection, however, a small fraction of CDOM can be incorporated into the ice and later redistributed to the water column upon sea ice melt (Belzile et al., 2000, 2002; Amon et al., 2004; Dittmar, 2004; Matsuoka et al., 2012). Additionally, CDOM can be produced *in situ* within the ice by sea ice algae (Belzile et al. 2000; Scully and Miller, 2000).

Previous studies of the optical characteristics of CDOM in sea ice include work in the Baltic Sea (Ehn et al., 2004; Granskog et al., 2005; Stedmon et al., 2007a; Uusikivi et al., 2010), the Canadian Arctic (Belzile et al., 2000; Scully and Miller, 2000), and Antarctica (Norman et al., 2011). The magnitude of CDOM absorption in sea ice can be up to two orders of magnitude greater than that found in the adjacent water column in Baffin Bay (Scully and Miller, 2000) and up to four times greater than that found within sea ice brines in Antarctica (Norman et al., 2011). Scully and Miller (2000) concluded that sea ice is a significant source of CDOM during sea ice melt in Baffin Bay and Antarctic sea ice has also been implicated as a potential source of CDOM to ocean waters (Ortega-Retuerta et al., 2010; Norman et al., 2011).

In this study, we investigated CDOM properties of sea ice and the under-ice water column in the Chukchi and Beaufort Seas during sea ice melt in June–July 2010 and 2011. Specifically, we examined: (1) the optical properties of CDOM in the sea ice; (2) how this compares to CDOM in the under-ice water column; and (3) how sea ice melt could affect the distribution of CDOM in the underlying water. In addition to CDOM absorbance, spectral slope parameters were calculated to provide insight on DOM quality including molecular weight (Blough and Del Vecchio, 2002; Helms et al., 2008). Sea ice melt impacts on CDOM were investigated using oxygen isotope analyzes. While sea ice and meteoric water have similar salinities as a result of brine rejection during sea ice formation, fresh water from sea ice melt can be distinguished from meteoric waters because the latter is depleted in the heavier isotopes of oxygen (Dansgaard, 1964). We used the ratios of the oxygen isotopes, ¹⁸O and ¹⁶O, to assess the relative fractions of sea ice melt and meteoric water in under-ice waters, an approach that has been widely used in the Arctic (e.g. Ekwurzel et al., 2001; Cooper et al., 2005). A combination of fluorescence Excitation Emission Matrix (EEM) spectroscopy and Parallel Factor (PARAFAC) analyzes was used to provide additional information about the composition and potential sources of CDOM (Coble 1996; 2007; Stedmon and Bro, 2008). In addition, salinity, chlorophyll-*a* (Chl*a*) and the fluorescent portion of CDOM (FDOM) were used to investigate potential sources of CDOM in the underlying water column.

2. Study sites and methods

2.1. Study area

Ocean water and sea ice samples were collected as part of NASA's ICESCAPE (Impacts of Climate change on the Eco-Systems and Chemistry of the Arctic Pacific Environment) program in the Chukchi and Beaufort Seas during the summer melt season in June and July of 2010 and 2011 (Cruises HLY1001 and HLY1101 on the US Coast Guard Cutter (USCGC) *Healy*; Fig. 1). The overarching goal of this program was to better understand the impacts of climate change on the ecology and biogeochemistry of this biologically productive region through multidisciplinary observations of the biological, chemical, physical and optical properties of both the sea ice and the upper ocean during the summer melt season.

Sea ice and water samples were collected June 25–July 11, 2010 at 10 ice stations clustered north of Barrow, Alaska (Fig. 1). Samples were additionally collected at 9 ice stations distributed along three north-south ship transects between July 4–19, 2011 (Fig. 1). The westernmost transect (Transect 1) was located on the continental shelf of the Chukchi Sea in an area of high under-ice primary productivity (Arrigo et al., 2012, 2014), the central transect (Transect 2) crossed the shelf-basin interface in the Chukchi Sea, and the easternmost transect (Transect 3) extended into the Canada Basin of the Arctic Ocean from the shelf in a region impacted by river runoff, primarily from the Colville River.

2.2. Sampling

At each station, under-ice ocean water samples were collected by hand deploying a 2 L Kemmerer water sampler through holes drilled in the sea ice. Samples were collected at six depths below the ice: 0 m (ice–water interface), 1 m, 5 m, 10 m, 20 m, and 30 m. Additional water was also collected from a representative melt pond (from the sea ice surface) at each station. Two ice cores were taken at every site: one from bare ice and the second from below a melt pond. All ice cores were sub-sectioned into 10 cm increments and melted shipboard for subsequent analysis. Both water and melted sea ice samples were analyzed for salinity, CDOM, and δ¹⁸O values. Additionally, under-ice waters from 2011 were analyzed for FDOM and Chl*a*. Salinity measurements were made shipboard using a Guildline Autosol salinometer, while Chl*a* measurements were made shipboard using a Turner Designs 10 AU field fluorometer. Samples for δ¹⁸O were taken directly from the water sampler and melted ice. Samples for CDOM and FDOM (the fluorescent portion of CDOM) were filtered using pre-rinsed 0.2 μm Whatman Nuclepore polycarbonate track-etched membranes immediately after sampling. CDOM was determined shipboard, while samples for δ¹⁸O (left unfrozen) were later analyzed at the University of Maryland Center for Environmental Science. FDOM was frozen and later analyzed on a spectrofluorometer. We note that ideally FDOM would have been measured shipboard within 24 h of sampling (Mitchell et al., 2003), however this was not practical due to the ship's ice breaking activities and resulting interference with the long integration time necessary to measure low FDOM intensity. For these reasons, samples were frozen and measured ashore.

2.3. Analyses

2.3.1. CDOM

After filtering, CDOM samples were stored in the dark at 4 °C in acid washed (10% HCl) pre-combusted (450 °C for 6 h) foil-covered Qorpak clear glass bottles (Bridgeville, Pennsylvania, USA) and analyzed within 24 h. CDOM absorbance was measured using a Shimadzu UV-1800 UV-visible spectrophotometer at 1 nm

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