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The nature of colored dissolved organic matter in the southern Canada Basin and East Siberian Sea

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ABSTRACT

Distributions of colored dissolved organic matter (CDOM) in the upper 400 m of the southern Canada Basin and East Siberian Sea were determined using an in situ WETStar fluorometer and fluorescence spectroscopy during cruises in 2008 as part of the Canada/US Joint Ocean Ice Study and Japan's International Polar Year program. Despite the low CDOM range (0.009–0.069 r.u.) observed in the upper 400 m of the study area, our results show that CDOM can be quantified from in situ DOM fluorescence sensor measurements. Unlike DOC concentrations, which are known to decrease with increasing depth, a pronounced mid-depth CDOM maximum was associated with the Pacific-derived winter water throughout our study area. Using parallel factor analysis (PARAFAC) to resolve dominant fluorophore components in fluorescence excitation–emission matrices (EEM), we identified three humic-like and two proteinaceous components. The nature and origin of these five fluorophores were investigated based on their fluorescent characteristics as well as their vertical and geographical distributions. The lowest terrestrial humic-like signals in the surface waters were mostly due to photochemical processes, whereas the highest microbial/marine humic-like signal revealed interactions with sediment during the formation of Pacific-origin haloclines over the Arctic shelves. The humic-like fluorophores dominated DOM fluorescence in the Westernmost region in the East Siberian Sea whereas the contribution of protein-like fluorophores was predominant elsewhere. The significant difference in CDOM composition between East and West of the 180° meridian suggests the presence of a front that divides our study area into the Eastern Chukchi—Beaufort and East Siberian sides. This indicates a change in water circulation, and that more than one DOM source affects our study area. Unlike proteinaceous material, the humic-like compounds varied significantly in the halocline. Ten to 20 percent enrichment was observed in terrestrially-derived DOM in the two Pacific-derived haloclines relative to the Atlantic-derived lower halocline. The application of PARAFAC modeling on fluorescent DOM is shown to be an important tool to investigate the dynamics and transport of allochthonous DOM in the Arctic Ocean.

1. Introduction

Aquatic dissolved organic matter (DOM) is a complex mixture of soluble organic compounds derived from both terrestrial and aquatic sources. DOM plays an important role in the biogeochemistry of carbon, nitrogen and phosphorus; and in the mobility and fate of inorganic and organic pollutants such as heavy metals (Koukal et al., 2003; Guéguen et al., 2004). Colored DOM (CDOM), the light-absorbing fraction of the DOM pool, represents a significant fraction of dissolved organic carbon (DOC) (from 1% to 10%; Coble, 2008). Much of the DOM pool is resistant to microbial activity and makes up a large part of CDOM (Hansell and Carlson, 2002). The optical properties of CDOM, and particularly its fluorescence properties, have been used to distinguish compositional characteristics and discriminate between terrestrial and marine DOM sources (Coble, 1996; Del Castillo et al., 2000; Blough and Del Vecchio, 2002). Recent advances in fluorescence spectroscopy have resulted in the development of excitation–emission matrix fluorescence (EEM) (Coble, 1996). EEMs are obtained by concatenating successive emission spectra at a series of excitation wavelengths and can be used to discriminate among different fluorophore classes of terrestrial, autochthonous and anthropogenic origins according to their excitation/emission maxima (Coble, 1996; Parlanti et al., 2000). It may be difficult

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to assess the dynamics of DOM based on the EEM peak-picking technique because locations of individual peaks are sensitive to physical and chemical conditions (Coble, 1996). However, the characterization of CDOM fluorescence has improved with the application of a multivariate modeling approach called parallel factor analysis (PARAFAC) (Stedmon et al., 2003; Stedmon and Bro, 2008), which allows EEMs to be decomposed into individual fluorescent components. This new approach has been successfully applied to study variability in CDOM composition in coastal and open ocean systems (e.g. Stedmon and Markager, 2005a, 2005b; Murphy et al., 2008; Yamashita et al., 2008; Kowalczuk et al., 2009; Guéguen et al., in press).

In this study, we apply PARAFAC to EEMs to characterize CDOM in samples collected from the East Siberian, Chukchi and Beaufort seas. Upper Canada Basin waters are highly stratified due to the combined effects of river inflow, seasonal ice melt and inputs of relatively less saline Pacific-origin waters (Yamamoto-Kawai et al., 2008). There are three main layers, differentiated on the basis of salinity (S): a low-salinity surface layer, a complex halocline and a warm Atlantic layer. The surface layer is influenced by runoff, sea-ice formation and melt and surface exchange processes (Guéguen et al., 2005, 2007; Walker et al., 2009). Despite a high angle of incidence from the sun and the existence of sea ice, the photochemical transformation of DOM may also occur in the surface Arctic Ocean (Benner et al., 2005; Bélanger et al., 2006). This would influence greatly DOM composition as photoirradiation decreases humic-like fluorescence (Nieto-Cid et al., 2005). The halocline, found between depths of about 50–200 m, consists mainly of seasonal influxes of Pacific-origin waters modified by heat exchange, ice formation and melting, biological production and interaction with sediment. Summer and winter modifications produce the upper halocline or Bering Sea Summer Water (BSSW, $S\sim32.4$) and middle halocline or Bering Sea Winter Water (BSWW, $S\sim33.1$), respectively (Coachman and Barnes, 1961). BSSW occupies the central Chukchi Sea and is assumed to be transported into the Canada Basin interior by the Beaufort Gyre, forming a temperature maximum at $S\sim32.4$ (Shimada et al., 2001; Steele et al., 2004). Beneath the middle halocline lies the Atlantic-derived lower halocline ($S\sim34.4$; Jones and Anderson, 1986; Woodgate et al., 2005), which in turn overlies the warm Atlantic layer found below ~350 m.

The goal of this study was to determine how surface and halocline waters differ in CDOM concentration and composition and how various sources of water contribute to the fluorescence signal. The results illustrate how PARAFAC analysis of fluorescence spectra can be used to describe the nature of CDOM and demonstrate its potential to characterize surface and halocline waters in the Arctic Ocean.

2. Methods

2.1. Sampling

CDOM samples were collected in the Beaufort, Chukchi and East Siberian seas during cruises in summer/fall 2008 as part of the Canada/US Joint Ocean Ice Study (July 17 – August 21, 2008) and Japan's International Polar Year program (August 15 – October 9, 2008). Seawater samples were collected in Niskin bottles mounted on a rosette together with a conductivity–temperature–depth profiler. Sample collection was confined to the upper 400 m of the water column, from the surface layer to the lower halocline.

Immediately after sampling, the samples were filtered through precombusted (450 °C for 4 h) GF/F filters. The filtrate was stored in precombusted (550 °C for 5 h) amber glass bottles with acid washed Teflon-lined caps at 4 °C until analysis in the laboratory (<6 months). Bacterial growth, and its impact on CDOM fluorescence, was probably limited as CDOM composition and intensity were similar to a previous Arctic Ocean study in which samples were frozen until analysis (Walker et al., 2009).

2.2. CDOM fluorescence measurements

Fluorescence was measured using a Fluoromax-4 Jobin Yvon spectrofluorometer equipped with two monochromators for both the excitation light source and the emission detector. Excitation–emission matrices (EEMs) were generated for each sample over excitation wavelength range of 260–460 nm and emission wavelengths covering 270–518 nm, both in 5-nm increments. All measurements were made at 20 °C using a thermostatted cell holder. The water Raman peak (Ex 350 nm) of fresh Milli-Q water was collected daily to monitor instrument performance and stability. We observed no significant variation in the Raman water fluorescence peak intensity during the investigation ($<2\%$). The recorded spectra were corrected for the instrumental response characteristics (Ewald et al., 1993; De Souza-Sierra et al., 1994). Milli-Q water was used as a blank and subtracted from sample spectra. Absorbance values were lower than 0.05 at 260 nm for all samples so that re-absorption and inner filter effects were minimized. This also allowed operation within the linear range of the fluorescence intensity–concentration relationship (Ewald et al., 1984). Finally, the fluorescence intensity was normalized to the area under the Milli-Q water Raman peak (Lawaetz and Stedmon, 2009) and reported in equivalent water Raman units (r.u.).

2.3. In situ CDOM fluorescence

High-resolution vertical profiles of CDOM fluorescence (WET Labs WETStar) were also collected at each station. The raw voltage from the WETStar fluorometer (DOM-FL; Ex/Em 370/460 nm) was compared to the identical CDOM fluorescence emission spectra of filtered samples acquired on the Fluoromax-4 Jobin Yvon fluorometer (Ex/Em 370/460 nm). Discrete samples were collected from the CTD-rosette to assess the stability and linearity of the CDOM sensor in the upper 400 m of the water column.

2.4. PARAFAC modeling

Fluorescence EEMs were modeled using parallel factor analysis (PARAFAC), which decomposes complex mixtures of CDOM fluorophores into their main components (Stedmon et al., 2003). Analysis was carried out in Matlab using the DOMFluor toolbox (Stedmon and Bro, 2008). The model was constrained to non-negative values and run for three to ten components. The appropriate number of components was determined by a split-half analysis and Tucker congruence coefficient analysis (Stedmon et al., 2003; Stedmon and Bro, 2008). A five-component model was found to be sufficient to describe the dataset. The percent contribution of a given component was calculated as the ratio of the given component fluorescence intensity to the total component fluorescence intensity (i.e. $C1\%=C1/(C1+C2+C3+C4+C5)$) calculated using DOMFluor (Stedmon and Bro, 2008).

3. Results

3.1. Hydrographic data

The temperature–salinity (T–S) diagram demonstrates the existence of several water masses over the sampling area