SUMMER CDOM OPTICAL PROPERTIES IN THE WESTERN ARCTIC UNDER LOW SEA ICE CONDITIONS

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ABSTRACT

Background: Dissolved organic matter (DOM) constitutes the largest pool of reduced organic carbon in the ocean and plays an important part in the global carbon cycle. The Arctic Ocean, with about 1% of the global ocean volume receives about 10% of the global river discharge. Under climate change, increased discharge from the Arctic rivers could significantly affect the carbon cycle in the Arctic Ocean. The colored or chromophoric DOM or CDOM is the fraction of DOM that absorbs light in the ultraviolet and visible wavelength and is a major light absorbing constituent in the ocean that influences light penetration and thus biological productivity. Through its influence on the water leaving radiance or the light field it also affects satellite ocean color chlorophyll algorithms. CDOM also fluoresces and its fluorescence properties have been studied using excitation-emission matrix spectroscopy (EEMs). The fluorescent constituents of DOM can include humic and protein substances (Coble 1996; 1997; Mopper and Schultz 1993). Humic substances are mostly of terrestrial origin, but humic-like fluorescent material of marine origin is also present in aquatic systems (Coble 2007).

CDOM is produced in situ by biological production (authochthonous) or transported from terrestrial sources (allochthonous), and removed by photochemical degradation or physical processes such as circulation and mixing (Hansell and Carlson 2002; Blough and Del Vecchio 2002; D'Sa and DiMarco 2009; D'Sa 2008; Nelson and Siegel 2013). CDOM absorption properties including spectral slopes have been used to gain insights into CDOM source, and photooxidative state (Blough and Del Vecchio 2002; Helms et al. 2008). Studies have reported on the DOM/CDOM absorption properties in the Arctic (Wheeler et al. 1997; Gueguen et al. 2005; 2011) and the rivers have been found to be an important source of DOM/CDOM to the Arctic Ocean. Fluorescence measurements have also been reported for the Arctic and both humic-like and protein like substances have been detected (Gueguen et al. 2005). Only limited studies have been reported for the Western Arctic (Gueguen et al. 2005). In this study we report on the DOC and CDOM optical properties of absorption and fluorescence in the Western Arctic region during summer of 2012 when the extent of Arctic sea ice was the lowest recorded.

Data and Methods: Field samples were obtained during a field campaign in the Western Arctic onboard the Korean Ice Breaker Araon between 31st July – 10th August 2012. Hydrographic data were collected using a Sea-Bird CTD and water samples were collected at every station during the CTD casts from Niskin bottles attached to a Carousel rosette sampler. Samples were obtained at three depths – surface, at chlorophyll fluorescence maximum and at depths below the maximum where chlorophyll fluorescence signals were low. Samples were filtered immediately through 0.2 µm nylon membrane filters under low vacuum and stored at 4°C in acid cleaned, pre-combusted amber colored bottles until processed for DOC concentrations and CDOM absorption in the laboratory. Absorbance measurements of CDOM were obtained on a Perkin-Elmer Lambda 850 spectrophotometer and the absorption coefficients were calculated using the standard equation (D'Sa et al. 2006) after correction of the absorbance data at 700 nm over a 10 nm interval. CDOM absorption coefficient at 355 nm (a_g355) (m^{-1}) was used as a quantitative parameter of CDOM and the spectral slope for the interval of 275-295 nm ($S_{275-295}$) (μm^{-1}) was calculated according to Helms et al. (2008). EEMs were obtained using a Fluoromax 4 Jobin Yvon fluorometer by scanning emission spectra from 290 to 550 nm at 5 nm intervals while exciting every 5 nm between 250 to 450 nm. Instrument corrections and normalization were carried out according to method described in Singh et al. 2010. DOC measurements were made on a Shimadzu TOC 5000A (with ASI-5000A autosampler).

Preliminary results and discussion: Surface chlorophyll concentrations were generally low with some elevated concentrations off the Alaska coast and the Antarctic Basin (Fig. 1a). Mean DOC concentrations for the average three depths for all the stations sampled were 133.24±32.50 µMol and varied over the range 47.91-248.10 µMol (Fig. 1b). Although, high concentrations of DOC in the northern-western stations in the Arctic Basin were coincident with elevated levels of phytoplankton chlorophyll concentrations (Fig. 1a, b), patterns differed at most other locations.

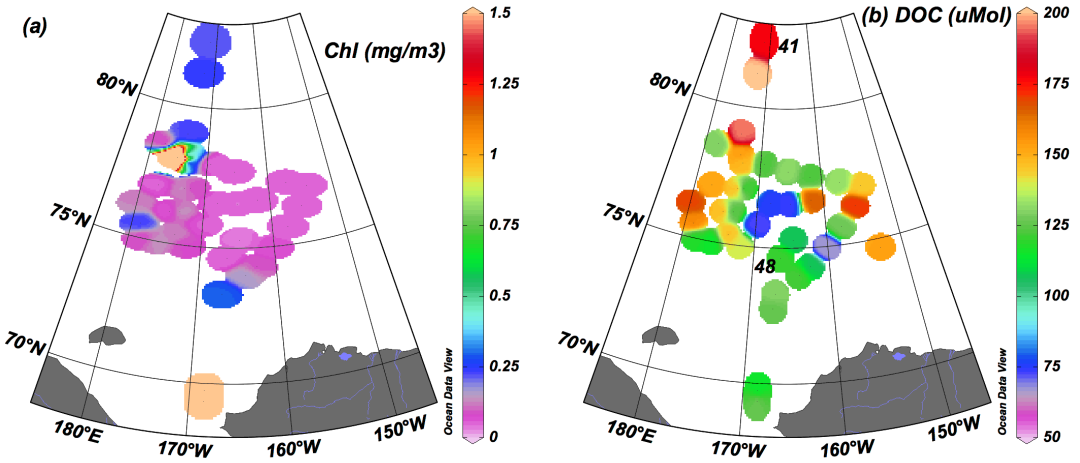

Figure 1. (a) Surface spatial distribution of phytoplankton chlorophyll (mg m^{-3}), (b) DOC concentrations (µMol L^{-1}).

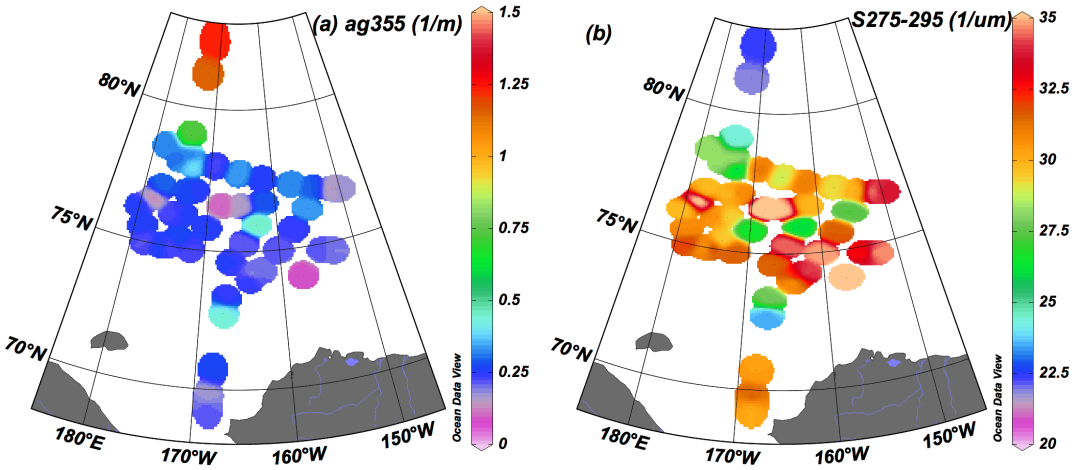

Figure 2. Surface spatial distribution of (a) CDOM absorption coefficient at 355 nm, $a_g(355)$ m^{-1}, (b) spectral slope $S_{275\text{-}295}$ (μm^{-1}).

The mean absorption coefficient at 355, a_g355 was 0.361±0.282 m^{-1}, and varied from 0.053 to 2.03 m^{-1}. Most values of a_g355 were <0.6 m^{-1} with the northern stations having relatively high amount of CDOM. The spectral slope $S_{275\text{-}295}$ in the surface waters of the western Arctic was relatively high suggesting the photodegration of CDOM (Fig. 2b). Howeve, the low $S_{275\text{-}295}$ at the northern stations (e.g., station 41) in the Arctic Basin suggested that surface waters at these high latitudes were not photooxised likely due to reduced solar radiation or recent melt of the sea ice. a_g355 increased with increasing DOC concentrations however the relationship appeared non-linear (Fig. 3a). The relationship between a_g355 and the spectral slope $S_{275\text{-}295}$ revealed two trends (Fig. 3b). One trend was for a_g355 values < 0.5 m^{-1}, and the other was for higher absorption values. These will be examined together with salinity and temperature for linkages to water masses in the western Arctic Ocean.

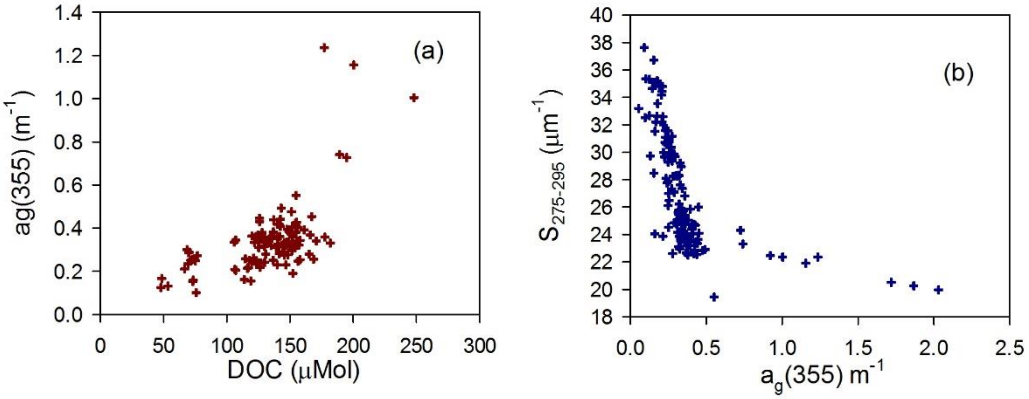

Fig. 3. Relationship between (a) DOC and a_g355, (b) a_g355 and spectral slope S

EEMs plots for two end members are shown as examples of typical fluorescence observed for the various stations sampled during the cruise (Fig. 4). The EEMs plot shown in Figure 4-left corresponds to station 48 that is located in the Chukchi shelf (station location shown in Figure 1b). At this location the EEMs spectra shows maximum emission fluorescence intensity corresponding to peak 'T' or protein-like tyrosine amino acids, and is due to relatively fresh DOM (Coble 1996; Stedmon et al. 2003). There are also peaks of smaller intensities corresponding to the humic-like 'A' peak that can be related to terrestrial source of humic material. Other two lower fluorescence intensity peaks that can be observed are the 'C' and the 'M' peaks. These peaks correspond to terrestrial 'C' and marine 'M' source of humic-like material (Coble 1996; Singh et al. 2010).

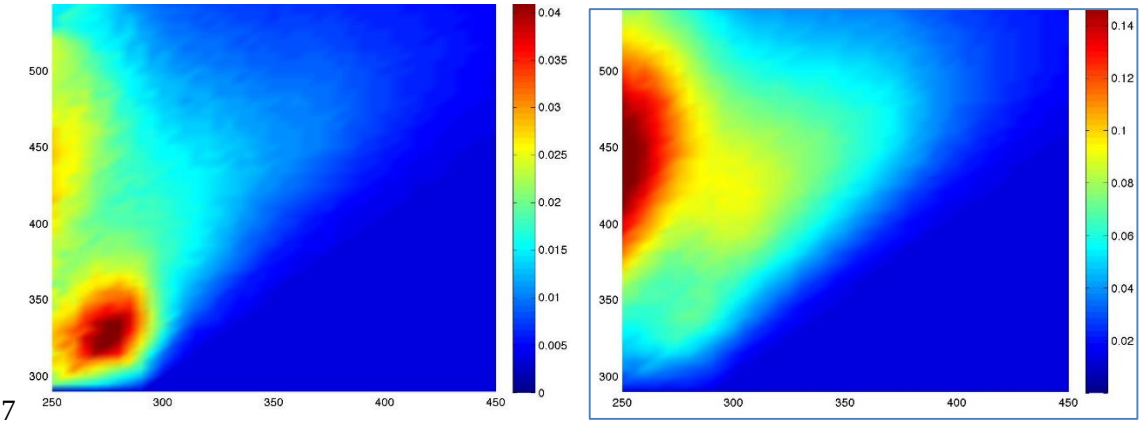

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Fig. 4. Plots of EEM spectra for surface samples at station 48 (Chukchi shelf) and station 41 (Arctic Basin). Locations of these two stations are shown in Figure 1b.

In contrast, the EEMs fluorescence at a station in the Arctic Basin (Fig. 4-right; station 41) is almost four times as intense as that at station 48 in the Chukchi shelf. The Arctic Basin surface water appears to be dominated by the 'A' and 'M' peaks. A strong terrestrial influence is observed in the most northern station 41.The EEMs data set will be further analyzed using parallel factor analysis (PARAFAC), which allows for the chemical identification of the CDOM fluorophores (Stedmon et al. 2003).

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