



High abundance of protein-like fluorescence in the Amerasian Basin of Arctic Ocean: Potential implication of a fall phytoplankton bloom



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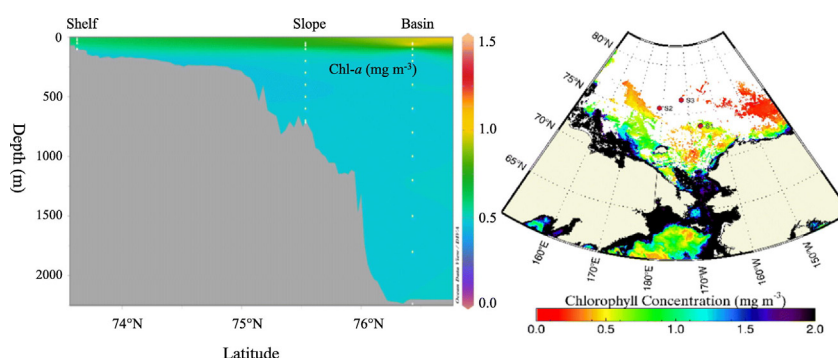
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HIGHLIGHTS

- Importance of CDOM dynamics in the fast-changing Arctic ecosystem is highlighted.
- Optical properties of DOM were spatially examined in the Arctic Ocean area.
- High levels of protein-like fluorescence were newly found in the region.
- All observed data including remote sensing data supported fall phytoplankton bloom.
- A lateral spreading of nutrients and DOM was suggested along shelf-slope-basin.

GRAPHICAL ABSTRACT



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ABSTRACT

The seawater samples from the Chukchi and East Siberian Seas were collected along a shelf-slope-basin gradient and analyzed for chromophoric and fluorescent DOM (i.e., CDOM and FDOM, respectively). Unexpected high protein-like FDOM (0.35 ± 0.40 and 0.24 ± 0.34 RU for peaks B and T, respectively) levels were identified, which corresponded to 1–2 orders of magnitude higher than those documented by previous reports. This unique phenomenon could be attributed to a fall phytoplankton bloom. The seawater chl-*a* data, estimated from in situ fluorescence measurements and satellite remote sensing data, showed the subsurface chl-*a* maximum of up to 1.52 mg m^{-3} at ~25–70 m depths and the surface monthly average values (August 2015) up to 0.55 to 0.71 mg m^{-3} , which fall in the range of ~0.5–2.0 mg m^{-3} during fall phytoplankton blooms in this area. Meanwhile, the depth profile of DOM parameters revealed subsurface maxima of protein-like fluorescence peaks along the shelf-slope gradient. The positive correlations between the protein-like peaks and biological index implied the lateral transport of DOM and nutrients from the shelf to the slope and basin. Despite still being a largely ice-covered environment, potential shifts in the ecosystem appear to make progress in response to changing climate in the Arctic Ocean.

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1. Introduction

The Arctic Ocean, which receives ~10% of global river discharges, occupies only <1% of the global ocean volume (Stein, 2008 and reference therein). It has a large drainage basin area of 9.5×10^6 km², which contains 1100–1500 Pg C soil organic carbon including a large stock of permafrost (Rachold et al., 2004; Hugelius et al., 2014). Currently, the fluvial input transports about 25–36 Tg C yr⁻¹ of dissolved organic carbon (DOC) and 12 Tg C yr⁻¹ of particulate organic carbon (POC) into the Arctic Ocean (Rachold et al., 2004; Raymond et al., 2007; Holmes et al., 2012). As such, it plays a pivotal role in regional and global carbon budget and cycle.

Ongoing climate change accelerates terrestrial organic matter inputs of modern plant litter leachates during the spring freshet as well as during winter base flow when aged and degraded materials prevail (Stedmon et al., 2011). Moreover, the Arctic perennial sea ice cover has been declining at a rate of 9% per decade (Comiso, 2002). Global warming has also advanced sea ice melting in spring and delayed sea ice formation in fall at the seasonal ice coverage area. Multiple previous studies have proved that the extent and the concentration of the sea ice were closely related to the Arctic phytoplankton biomass, in which phytoplankton production was usually high along retreating ice edges where nutrients can be replenished by wind- or storm-driven water column vertical overturn (Wang et al., 2005; Perrette et al., 2011). Increase in the intensity and frequency of storms can lead to more episodic vertical mixing events (Inoue et al., 2015; Nishino et al., 2015). Furthermore, Ardyna et al. (2014) have observed via remote sensing that recent retreat of Arctic Ocean sea ice has triggered a shift from single spring bloom to double blooms (both spring and fall, a typical pattern at temperate latitudes) in some regions, which has been supported by a recent in situ measurement evidence in the Chukchi Shelf (Uchimiya et al., 2016). Given the large stock of organic carbon in this area and the pace of the climate change, it is urgent to better understand the characteristics and dynamics of dissolved organic matter (DOM) in this area in an era of rapidly changing Arctic.

To date, previous reports on the DOM optical characteristics in this region have primarily focused on the Arctic rivers (Spencer et al., 2009; Walker et al., 2013; Cory et al., 2014; Mann et al., 2016). These studies generally found that terrestrial humic-like fluorescent DOM (FDOM) dominated the optical properties of DOM in the Arctic Rivers. In the Arctic Ocean, Guéguen et al. (2012, 2014, 2015) carried out a series of seawater chromophoric DOM (CDOM) and FDOM investigations in the Amerasian Basin and Canadian Arctic Archipelago areas. The main findings include the depth- and basin-dependent patterns of optical DOM properties and significant correlations of terrestrial humic-like FDOM components with apparent oxygen utilization (AOU).

The optical methods based on ultraviolet-visible spectroscopy (UV-Vis) and fluorescence excitation-emission matrix (EEM) have the advantages of fast, sensitive, and solvent-free with small sample volume needed. These techniques have been successfully applied to trace DOM dynamics in various ecosystems in previous studies (Coble et al., 1998; Spencer et al., 2009; Walker et al., 2009, 2013; Chen et al., 2010; Stedmon et al., 2011; Hur and Cho, 2012; Guéguen et al., 2012, 2014, 2015; Mann et al., 2016; Chen and Jaffé, 2016).

In this study, we aimed to examine the optical characteristics of the Arctic seawater DOM for a time period from the late August and early September in the Chukchi and East Siberian Seas in the Arctic Ocean. The Chukchi Sea, downstream of the nutrient-enriched Pacific-sourced water, is the only area of inflowing water to the Arctic Ocean. This area is relatively less investigated for DOM studies. Furthermore, the sampling time of this study fell into the fall season, which can capture the DOM characteristics derived from the potential fall phytoplankton bloom in the Arctic Ocean, as suggested by previous satellite remote sensing (Ardyna et al., 2014) as well as a recent in situ observation in Chukchi Shelf (Uchimiya et al., 2016). All these situations are of benefit

in inferring the potential origins and environmental factors shaping the seawater DOM characteristic in the study area.

2. Materials and methods

2.1. Sites description

Sampling sites were located in the shallow Chukchi Shelf (site JPC-1a or site S1), East Siberia Continental Slope (site JPC-3 or site S3), and Chukchi Basin (site JPC-4 or site S4) of the Arctic Ocean (Fig. 1). The locations and the site descriptions are summarized in Table S1. The modern Chukchi Sea is a marginal sea with seasonal ice cover, and it has an expansive shallow continental shelf and an extremely high primary productivity (Sakshaug, 2004). This high productivity is driven by light availability during seasonal open water condition and enriched nutrients replenished by Bering Shelf Anadyr Water (BSAW) entraining through the Bering Strait. The Bering Sea Water (BSW) and the Alaskan Coastal Water (ACW) dominate the Chukchi Sea circulation (Grebmeier et al., 1988). The BSW is a mixture of nutrients-enriched BSAW and nutrients-poor ACW (Grebmeier et al., 1988). The East Siberia Sea receives riverine discharge from the Kolyma and Indigirka rivers. Two major current systems, namely the Beaufort Gyre and the Transpolar Drift, dominate surface water circulation in the Arctic Ocean. The Beaufort Gyre occupies most of the Amerasian Basin, in which our study sites are located, while the Transpolar Drift is dominant in the Eurasian Basin. A switching between cyclonic and anticyclonic Beaufort Gyre was also observed (Morison et al., 2012). The direction and strength of the currents, however, may be affected by the Arctic Oscillation and El Niño–Southern Oscillation, which could lead to large inter-annual variations (Thompson and Wallace, 1998; Liu et al., 2004). As sites S3 and S4 were partially sea ice-covered, only site S1 was ice-free at the time of sampling from August 30th to September 5th, 2015.

2.2. Sampling

The samples were collected between late August to early September 2015 during the ARA06C Expedition. Both seawater and sediment pore waters were collected and the data on pore water study has been reported in a separate paper (Chen et al., 2016). The daily sea ice map and the concentration in the Arctic can be found elsewhere (www.meereisportal.de). Seawater sampling was carried out using a CTD/rosette system holding 24-10L Niskin bottles (SeaBird Electronics, SBE 911 plus) aboard the Korean icebreaker R/V *Araon* during the ARA06C cruise. For partially sea ice-covered sites S3 and S4, we tried to find non-ice covering area to get seawaters or broke the thin sea ice by the ice breaker. The in situ fluorescence data (Ex/Em: 470 nm/695 nm) was monitored while sampling for chl-*a* estimation. The seawaters were sampled with acid-cleaned syringes and filtered with a pre-cleaned in-line 0.20 μm disposable polytetrafluoroethylene filter (Advantec). The seawater aliquots were transferred into acid-cleaned Nalgene® high density polyethylene bottles for onboard, DOM, and nutrients analyses. The samples for DOM analyses were immediately stored in a freezer to avoid potential biodegradation on the long journey from Arctic back to land-based lab. It is noteworthy that freezing/thawing samples may have potential effects on DOM fluorescence signals due to susceptibility of humic-like fraction removal from solution (Thieme et al., 2016). Stedmon and Markager (2001) recommended to sterile filter samples through 0.2 μm filters followed by storage in cool and dark in the fridge to keep DOM samples for spectroscopic analysis, which can made them stable for time period of several weeks. However, when longer storage time ranges are needed (such as on a scale of months, especially when sampling from polar regions), freezing has been a common practice for marine sample preservation (Walker et al., 2009; Stedmon et al., 2011; Logvinova et al., 2015). As such, same or similar sample storage methods are needed to facilitate ease of comparison. The samples for onboard analyses (chl-*a* fluorescence and

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