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# Surface accumulation of low molecular weight dissolved organic matter in surface waters and horizontal off-shelf spreading of nutrients and humic-like fluorescence in the Chukchi Sea of the Arctic Ocean

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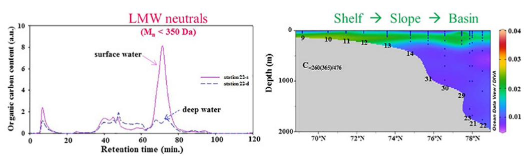
## HIGHLIGHTS

- Spatial distribution of DOM was examined in a highly productive polar sea.
- Low molecular weight ($M_n$ < ~350 Da) DOM molecules tend to be accumulated in surface ocean.
- Horizontal off-shelf spreading of nutrients and humic-like fluorescence was found.
- The study suggests sea ice treat in the Arctic Ocean can potentially accelerate primary productivity and DOC increase.
- It provides a new insight into DOM dynamics and the roles in future polar oceans.

## GRAPHICAL ABSTRACT

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## ABSTRACT

Polar regions play unique roles in global overturning circulation, carbon cycling, and climate change. In this study, seawater dissolved organic matter (DOM) was characterized for the Chukchi Sea in the Arctic Ocean in the summer season. The seawater generally contains high concentrations of dissolved organic carbon (DOC, up to 92 μM C) and tyrosine-like fluorescence (up to 0.21 RU), and it was enriched with heteroatomic molecular formula with nitrogen-containing and sulfur-containing formulas counting 2246 (~41% of total identified molecular formula) and 1838 (~34%), respectively. Significant correlations were observed between salinity and the absorption coefficient at 254 nm, between chlorophyll-*a* and DOC as well as the tyrosine-like component, $C_{270/302}$ ($C_{ex/em}$ maxima), and between biological index and two protein-like components, $C_{275/338}$ and $C_{305/344}$. A comparison between surface waters and close-to-seafloor deep waters suggested a trend of the accumulation of low molecular weight (LMW) fraction (~54–74%, nominal average molecular weight $M_n$ < ~350 Da) in the surface waters. Another interesting finding from spatial data was an obvious horizontal off-shelf spreading of nutrients and humic-like fluorescence. This study sheds novel insights of DOM characteristics and dynamics in the highly productive polar sea.



## 1. Introduction

The Arctic Ocean, being super sensitive to the ongoing climate change, plays pivotal roles in global biogeochemical cycles. Approximately

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1100–1500 Pg of organic carbon is stored in the Arctic soils (Rachold et al., 2004). Moreover, the Arctic Ocean sinks ~5–14% of the total anthropogenic $CO_2$ emission (Bates et al., 2011).

DOM in the Arctic Ocean is known to originate from riverine runoff, coastal erosion, aeolian input, benthic efflux from sediments, sea ice, and autochthonous primary productivity (Stein, 2008; Chen et al., 2016a). In addition, microbes have been reported to play a powerful role in glacial environments (including supra-, en-, and sub-glacial) in the Arctic (Musilova et al., 2017). The biological index (BIX) was found to be positively correlated with temperature as well as protein-like fluorescence in a previous study in the Chukchi Sea of the Arctic (Chen et al., 2017a). With the ongoing sea ice retreating and thinning, recent studies conducted in the Arctic Ocean provided evidence on widespread shift to double algal blooms (both spring and fall, Ardyna et al., 2014; Uchimiya et al., 2016; Chen et al., 2017a) and the ice algae derived DOM contributed by ice-edge upwelling phytoplankton bloom (mostly, *Phaeocystis pouchetii*) (Mundy et al., 2009; Assmy et al., 2017). A fall phytoplankton bloom leading to high protein-like fluorescence is also noteworthy in recent studies on the Chukchi Sea of the Arctic Ocean (Chen et al., 2017a). Furthermore, it was previously reported that humic-like DOM and nutrients could be spread laterally in cold dense subsurface water of the Arctic Ocean (Hioki et al., 2014).

Despite the several DOM studies conducted in the Arctic Ocean (Walker et al., 2009; Guéguen et al., 2012, 2014, 2015; Tanaka et al., 2016; Chen et al., 2017a), they primarily used optical methods or studied the surface waters only, which could limit the full understanding of DOM in the Arctic Ocean. Thus, we investigated here the dynamics of DOM through the entire water column, and also utilized three analytical tools for DOM characterization, including fluorescence excitation emission matrix coupled with parallel factor analysis (EEM-PARAFAC), high-resolution Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS), and size exclusion chromatography with an organic carbon detector (SEC-OCD), which allowed to probe DOM fluorescent and molecular signatures and molecular weight distribution. The Chukchi Sea was chosen as a highly productive sea, which has a DOC production rate of ~35 mmol C $m^{-2}$ $d^{-1}$ (Yun et al., 2016). This Sea is known to be an important source of organic matter in the Western Arctic due to its high primary productivity driven by the nutrient-enriched Bering Shelf Anadyr Water (BSAW) entraining through the Bering Strait (Sakshaug, 2004).

## 2. Materials and methods

### 2.1. Site description and water mass properties

Sampling sites are located in the Chukchi Sea of the Arctic Ocean (Fig.1). The Chukchi Sea is well known for seasonal sea ice cover and high primary productivity. In the Arctic Ocean, water masses usually include a low-salinity Arctic Surface Water (ASW: <50 m), a complex Halocline Intermediate Water (HIW: 50–200 m, Pacific-derived on the Bering Strait side while Atlantic-derived on the Fram Strait side), a warm and saline Atlantic Deep Water (ADW), and a layer of Arctic Bottom Water (ABW > 900 m, Fig. 2).

### 2.2. Field sampling

Hydrographic surveys and seawater sampling were carried out at 12 stations in the Chukchi Sea, using a conductivity-temperature-depth (CTD) and a rosette system holding 24 10 L-Niskin bottles (SeaBird Electronics, SBE 911 plus) aboard the Korean icebreaker R/V *Araon* during the ARA07B (August 6th to 19th, 2016) cruise. The twelve sites in the Chukchi Sea spanned along a shelf to slope and basin gradient with four ice-free sites (Fig.1, red labels) and the remainders were partially ice-covered (blue labels) at the sampling time.

Samples for DOC analysis were drawn from the Niskin bottle by gravity filtration through an inline pre-combusted (at 550 °C for 6 h) Whatman GF/F borosilicate glass fiber filter held in an acid-cleaned (0.1 M HCl) polycarbonate 47 mm filter holder (PP-47, ADVANTEC). The filter holder was attached directly to the Niskin bottle spigot. The filtrate (~250 ml) was collected in an acid-cleaned glass bottle after ~100 ml of seawater was passed through to clean the sampling system. The collected samples were distributed into two pre-combusted 20 ml glass ampoules with a sterilized serological pipette. Each ampoule was sealed with a torch, quick-frozen, and preserved at −24 °C until further analyses in land laboratory within about two months. Samples for inorganic nutrient analyses were pre-filtered in a manner similar to that for DOC, transferred to a 50 ml conical tube and immediately stored in a refrigerator at 2 °C prior to chemical analysis onboard within 3 days.

### 2.3. Onboard analyses

The nutrients were measured onboard after sampling using a four-channel continuous Auto-Analyzer (QuAAtro, Seal Analytical) according

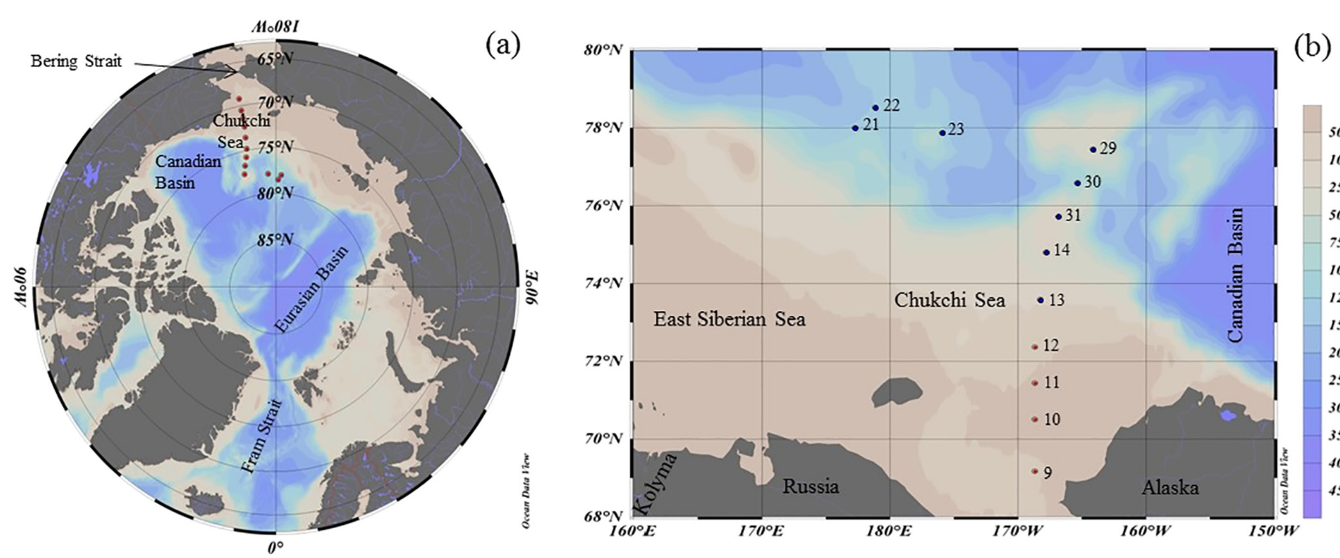


**Fig. 1.** Sampling sites in the Chukchi Sea, Arctic. Ice-free and ice-covered sites are marked with red and blue colors, respectively. The sea ice concentration data from Aug. 6th to Aug. 19th in the Arctic are obtained from http://www.meereisportal.de. The maps were created with Ocean Data View (Schlitzer, 2017). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)