CDOM FLUORESCENCE OF THE LAPTEV SEA AND EAST SIBERIAN SEA SURFACE WATERS

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ABSTRACT

This study is focused on CDOM fluorescence of the Laptev Sea and East Siberian Sea surface waters. The preliminary results are based on ten samples collected along three transects from the estuarine regions of Khatanga, Kolyma and Indigirka rivers to the continental slope. Fluorescence spectra were recorded in wide ranges of excitation (230-550 nm) and emission (240-650 nm) wavelengths. Humification and biological/autochthonous indices were calculated in order to determine the degree of maturation of DOM and autochthonous biological activity in water. “Blue shift” parameters of CDOM fluorescence ($\Delta_{270\text{-}310}$; $\Delta_{355\text{-}310}$) for the runoff-influenced surface waters were estimated as (26 nm; 33 nm), (24 nm; 40 nm), and (25 nm; 36 nm) for the Khatanga, Indigirka, and Kolyma transect, respectively. Desalinated surface waters of the Laptev Sea were found to be under a strong influence of humic substances, while in case of East Siberian Sea surface waters CDOM is characterized by a predominance of an autochthonous component. Evolution of CDOM fluorescence within the Laptev Sea and East Siberian Sea shelf is considered.

KEYWORDS

CDOM fluorescence, HIX, BIX, Laptev Sea, East Siberian Sea.

INTRODUCTION

Currently, optical techniques are widely used for studying the origin and dynamics of dissolved organic matter (DOM) (1,2). They are based on the ability of the coloured fraction of DOM (CDOM), in particular, fluorescent DOM, to absorb ultraviolet (UV) light and to emit UV and visible light. A typical spectrum of UV-excited fluorescence of natural DOM involves two superimposed bands: the first one has a maximum at 300-350 nm and is due to emission of proteins, aromatic amino acids, and phenolic compounds; the second one is due to fluorescence of humic substances (HS) in the blue spectral range 380-480 nm (3,4). The composition and ratios of DOM components differ from one aquatic area to another affecting the fluorescence and absorption properties of natural waters. The multiplicity of fluorophores comprising natural DOM (3) leads to the dependence of the position of the fluorescence maximum on excitation wavelength (5). In particular, it was demonstrated that the fluorescence maximum appears to be blue-shifted when DOM is excited at 310 nm compared to an excitation at 270 nm. Further increase of the excitation wavelength results in a shift of the emission maximum towards longer wavelengths again. This phenomenon was called “blue shift” and is usually characterized by differences in the position of fluorescence spectra maxima excited at 270 nm, 310 nm and 355 nm, $\Delta_{270\text{-}310}$ and $\Delta_{355\text{-}310}$ (6).

A high HS content is typical for Siberian rivers (7,8), which makes it possible to use the peculiar features of riverine DOM fluorescence to reveal the occurrence of terrigenous DOM in the Arctic Basin. CDOM of the large Arctic rivers has been the focus of numerous studies. Most of them were carried out for Ob, Yenisei, and Lena rivers, since they cause the largest DOM discharge into the Arctic Ocean (2,9). Nevertheless, the data on CDOM optical properties are still fragmentary. One of the least studied water area of the Eurasian Arctic shelf is the East Siberian Sea. A detailed study of the optical properties of DOM, including the absorption and investigation of Parallel Factor

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Analysis (PARAFAC) fluorescence components, was carried out in the Kolyma River. Samples were collected near the Chersky village during the spring flood to study the conversion of DOM releasing from permafrost (10). Another study was performed outside the continental slope (11). Within the shelf area of the East Siberian Sea such studies have not been conducted. Another poorly understood area is the western part of the Laptev Sea affected by Khatanga River runoff.

The goal of the present study was to examine the fluorescence of CDOM in the upper water layer of the Laptev and East Siberian seas. Special attention was paid to the estuarine regions of Khatatga, Indigirka, and Kolyma rivers. A detailed analysis of the luminescence properties of HS was performed. Excitation/emission matrices as well as humification and biological/autochthonous indices were used to investigated the spreading of desalinated waters along the transects, and to reveal the presence of labile autochthonous DOM in surface waters.

SAMPLING AND METHODS

Water samples were collected from the surface layer during the 69th cruise of R/V *Akademik Mstislav Keldysh* in September 2017. The hydrological stations were located along three transects from the estuarine regions of Khatanga, Kolyma and Indigirka rivers to the continental slope, Figure 1. Additionally, sea ice was sampled at station 5607. These waters are of particular interest since they allow studying CDOM optical properties across salinity gradients 3.5-30.1 (Khatanga), 15.1-30.0 (Indigirka), and 17.0-29.3 (Kolyma).

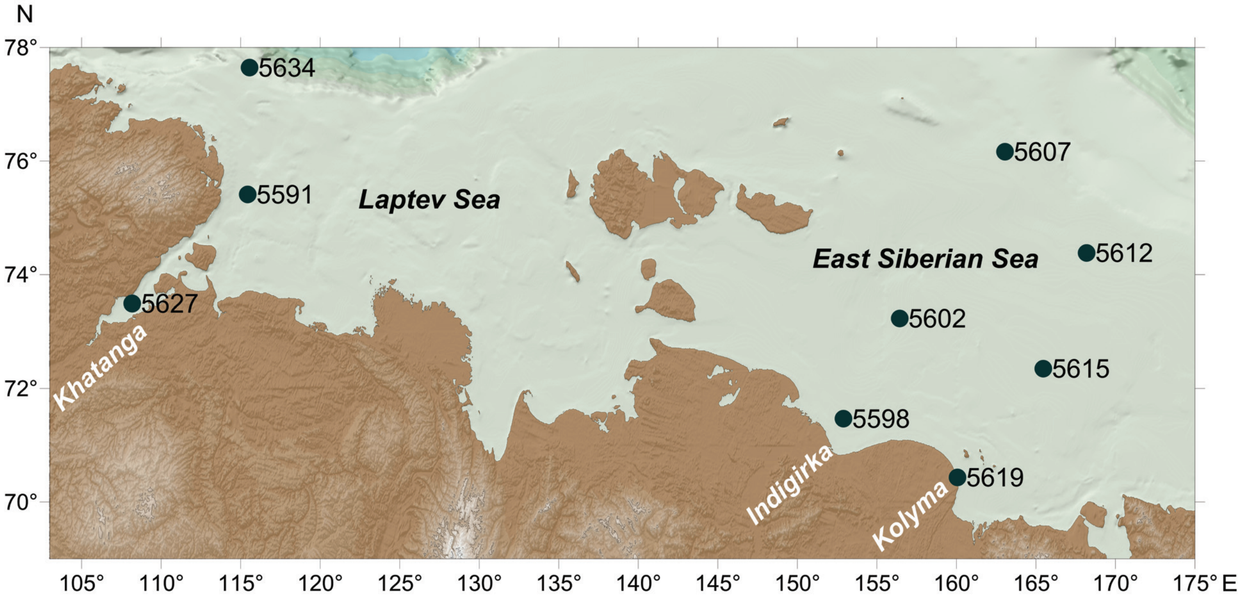

Figure 1: Location of hydrological stations in the 69th cruise of R/V Akademik Mstislav Keldysh, September 2017.

Seawater samples were filtered using precombusted Whatman GF/F filters with a pore size of 0.7 µm. The filtrate was stored in dark glass vials at 4°C until further analysis. Fluorescence measurements were performed in standard 1 cm quartz cuvettes with a Fluorat-02-Panorama spectrofluorometer (Lumex Instruments) equipped with a Xenon flash lamp as the light source, and a PMT detector. The software allows registration of raw spectra as well as data corrected by excitation source intensity and/or response function. We registered fully corrected spectra to enhance the measurement accuracy. The accuracy of excitation and detection wavelength settings was ascertained on the basis of Xe atomic line position and estimated as ±1 nm. The spectral resolution of the monochromators is 15 nm.

Emission scans were acquired at excitation wavelengths (λ_{ex}) from 230 to 550 nm at 5 nm intervals and emission wavelengths from λ_{ex}+10 nm to 650 nm at 1 nm intervals. Humification (*HIX*) and biological/autochthonous (*BIX*) indices were calculated according to the following relations:

$$HIX = \frac{\sum I_{em,435-480}}{\sum I_{em,300-345}}$$

at λ_{ex}=254 nm (12), and

$$BIX = \frac{I_{em,380}}{I_{em,430}}$$

at λ_{ex}=310 nm (13).

"Blue shift" parameters of CDOM fluorescence spectra, $\Delta_{270\text{-}310}$ and $\Delta_{355\text{-}310}$, were defined as shifts of the maxima of emission spectra while excited at 270 nm, 310 nm, and 355 nm, as suggested in (14).

RESULTS AND DISCUSSION

CDOM fluorescence spectra for the samples from the estuarine stations 5598, 5619, and 5627, Figure 2, as well as from the stations 5602 and 5591 comprise a single band in the visible spectral region with a maximum at 400-500 nm attributed to HS. The maximum position of this band depends on the excitation wavelength. "Blue shift" parameters of fluorescence spectra for the regions most influenced by fresh water runoff were well-defined and estimated as $\Delta_{270\text{-}310}$ = 26 nm and $\Delta_{355\text{-}310}$ = 33 nm (station 5627, Khatanga transect, salinity 3.5 psu), $\Delta_{270\text{-}310}$ = 24 nm and $\Delta_{355\text{-}310}$ = 40 nm (station 5598, Indigirka transect, salinity 15.1 psu), $\Delta_{270\text{-}310}$ = 25 nm and $\Delta_{355\text{-}310}$ = 36 nm (station 5619, Kolyma transect, salinity 17.0 psu). The $\Delta_{270\text{-}310}$ parameters are in a good agreement with the ones reported for the White Sea (24-25 nm) (14) and 2-4 nm lower than the data obtained for the desalinated waters of the Kara Sea (15). Otherwise the $\Delta_{355\text{-}310}$ parameters exceed the values obtained earlier in (14,15) by 4-22 nm.

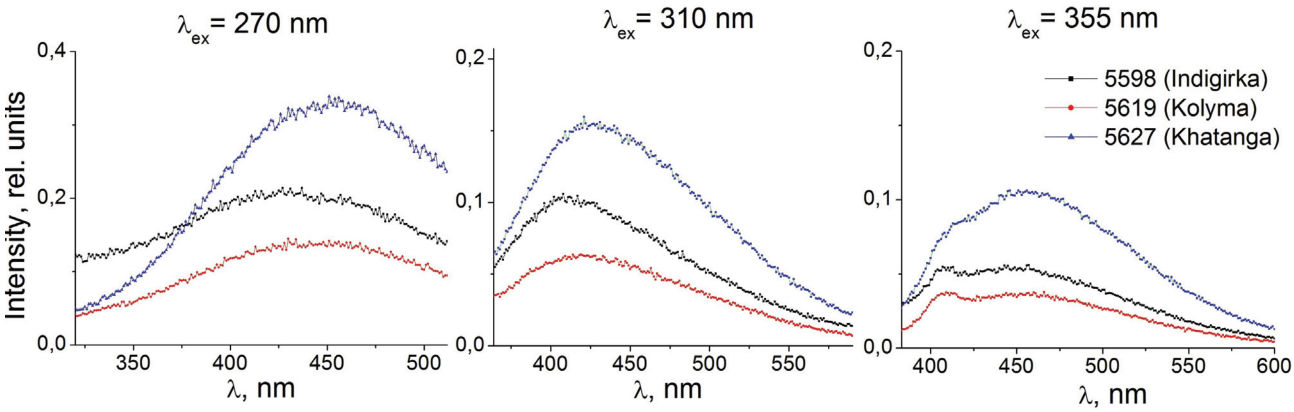

Figure 2: Fluorescence spectra of CDOM from the stations 5598, 5619 and 5627 at excitation wavelengths 270, 310 and 355 nm.

Fluorescence of HS for the rest of the samples was less intense and disappeared completely for the CDOM of melted sea ice. In case of these DOM samples the fluorescence intensity maximum moved towards 350 nm indicating the predominance of protein-like autochthonous CDOM. The "blue shift" parameter $\Delta_{270\text{-}310}$ of the fluorescence spectrum is not defined in this case, while $\Delta_{355\text{-}310}$ varied from 43 to 59 nm.

For all transects we observed a gradual decrease of fluorescence intensity, and, hence, the content of terrestrial DOM, from the estuarine zones to the continental slope, with the maximum intensity of HS fluorescence recorded at the station 5627 (0.33 rel. units at an excitation wavelength of 270 nm) and at the station 5598 (0.21 rel. units), see Figure 3.

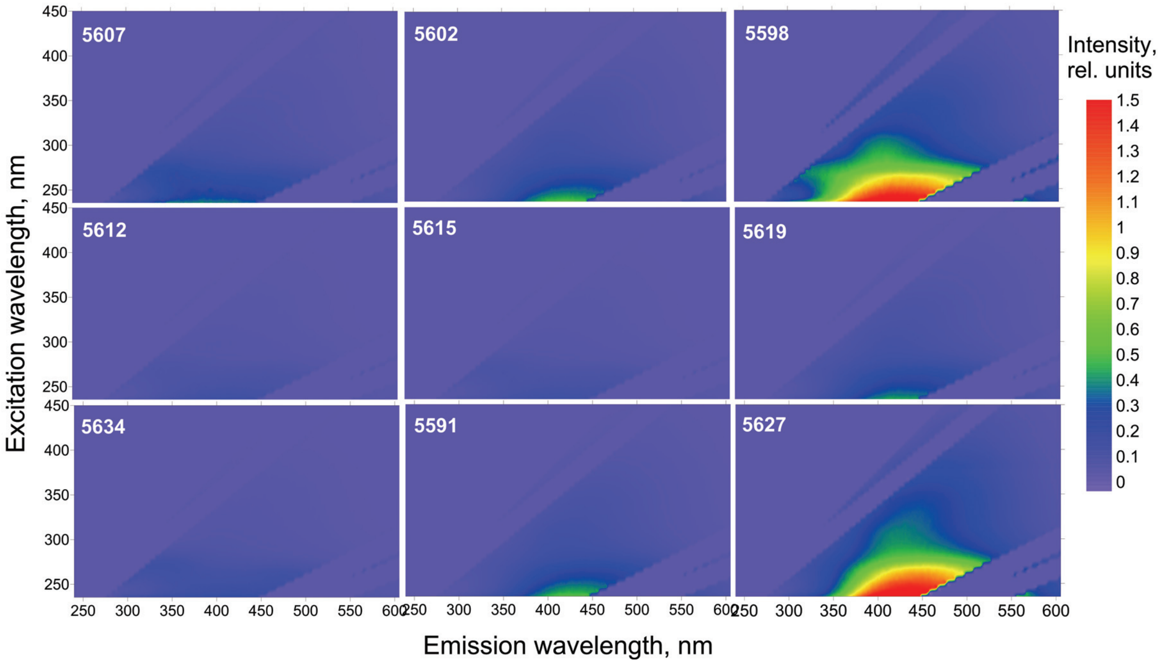

Figure 3: Excitation-emission matrices of the surface waters CDOM. Each row represent a set of sample of individual transect with salinity decreasing from left to right. Raman scatter and its second order, as well as the second order of scattered excitation radiation were removed from the spectra.

The influence of Kolyma River fresh waters was weaker. For comparison, fluorescence intensity of surface water CDOM at the southernmost station 5219, with salinity of 17 psu is comparable with that at stations 5591 (Khatanga River transect) and 5602 (Indigirka River transect), where the salinity reached 22.2 psu.

HIX and *BIX* indices for the studied samples are given in Table 1. In accordance to (13) we may conclude that a significant contribution of HS is typical for desalinated waters formed in the estuarine region of the Khatanga River, Laptev Sea.

Table 1: Characteristics of surface waters DOM according to the HIX and BIX indices (13).

Station	**Salinity, psu**	***HIX***	***BIX***	**Comments**
Indigirka – shelf				
5598	15.1	3.74	0.84	Biological or aquatic bacterial origin, strong autochthonous component
5602	22.2	4.86	0.81	Weak humic character and important recent autochthonous component
5607	30.0	1.38	1.02	Biological or aquatic bacterial origin
5607, ice	-	0.33	1.28	
Kolyma – shelf				
5619	17.0	5.11	0.73	Weak humic character and important recent autochthonous component
5615	28.1	1.53	0.94	Biological or aquatic bacterial origin, strong autochthonous component
5612	29.3	1.64	1.00	
Khatanga – shelf				
5627	3.5	9.24	0.62	Important humic character and weak recent autochthonous component
5591	22.3	6.13	0.64	
5634	30.1	1.29	0.88	Biological or aquatic bacterial origin, strong autochthonous component

HIX varies between 6.13 (salinity 22.3) and 9.24 (salinity 3.5). Desalinated waters of the East Siberian Sea with salinities above 15 psu are characterized by 1.38<*HIX*<5.11 and 0.73<*BIX*<1.28, indicating a strong autochthonous component and a weak humic one.

CONCLUSIONS

This study represents a preliminary analysis of CDOM fluorescence properties of the Laptev and East Siberian seas surface waters. Fluorescence spectra of the studied samples can be divided into two groups: the first one is characterized by an intense HS fluorescence (examples are given in Figure 2). “Blue shift” parameters of fluorescence, ($\Delta_{270\text{-}310}$; $\Delta_{355\text{-}310}$), are well-defined for such spectra and were estimated as (26 nm; 33 nm), (24 nm; 40 nm), and (25 nm; 36 nm) for the Khatanga River, Indigirka River, and Kolyma River runoff influenced regions, respectively. The second group of spectra differs in the absence of a pronounced maximum of HS fluorescence (400-500 nm) at excitation wavelength 270 nm. In this case we observed protein-like fluorescence at 330-350 nm.

The analysis of the origin and distribution of DOM within the Laptev and East Siberian seas in September 2017 has shown that desalinated waters of the Laptev Sea formed due to Khatanga River runoff has an important humic character up to salinities of 22.3 psu. In the East Siberian Sea the situation is completely different. Within this water area autochthonous protein-like substances, excited at 270-280 nm, represent an essential component of CDOM while the humic character is weak.

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