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DOM and its optical characteristics in the Laptev and East Siberian seas: Spatial distribution and inter-annual variability (2003-2011)

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Abstract. The East Siberian Arctic Shelf (ESAS) is the broadest and shallowest continental shelf in the World Ocean. It is characterized by both the highest rate of coastal erosion and a large volume of riverine input of terrigenous dissolved organic matter (DOM). DOM plays a significant role in marine aquatic ecosystems. The colored (chromophoric) fraction of DOM (CDOM) directly affects the quantity and spectral quality of available light, thereby impacting both primary production and UV exposure in aquatic ecosystems.

A multi-year study of DOM optical parameters and the spectral characteristics of the DOM chromophoric fraction were carried out in the vast ESAS in the summer-fall seasons. The spectral characteristics of CDOM were applied to identify different biogeochemical provinces in the surveyed area.

The analysis of CDOM spectral characteristics showed that the major part of the Laptev and East Siberian Sea shelf (making up the ESAS) is influenced by terrigenous DOM with high aromaticity, stemming from riverine discharge. The atmospheric circulation regime is the dominant factor controlling CDOM spatial distribution on the ESAS. A western and an eastern regime of ESAS, separated around 165-170° E, were identified with distinctly different DOM optical properties.

Strong correlation between DOC and CDOM concentrations in surface shelf waters influenced by terrigenous discharge indicates feasibility of estimating DOC content from the CDOM assessed *in situ* using a WETStar fluorometer. The direct estimation of optical characteristics of DOM in ESAS waters provided by this study will also be useful for validation and calibration of remote sensing data.

1 Introduction

Current climate change is particularly evident and amplified in the high latitudes of the Northern Hemisphere. The system change is characterized by an increase in the average annual temperature and atmospheric circulation intensity, a reduction in sea ice coverage and thickness, and in accelerated degradation of permafrost, as well as in an increase in coastal erosion and river flows (IPCC, 2013; AMAP, 2012). Unlike other oceans, the Arctic Ocean is completely surrounded by permafrost. The Arctic region contains an abundance of organic carbon (OC) buried inland and within the sedimentary basin of the Arctic Ocean ('Arctic carbon hyper pool', Gramberg et al., 1983), which might become a part of the current marine biogeochemical cycle due to thawing of on-land and sub-sea permafrost, an increased coastal and bottom erosion, accelerated river discharge, and soil-based carbon losses (e.g., Semiletov et al., 2000; Savelieva et al., 2000; Stein and Macdonald, 2004; Shakhova et al., 2009; Vonk and Gustafsson, 2013; Vonk et al., 2012, 2014). The recent studies accomplished within the framework of the International Siberian Shelf Study project (e.g., Semiletov and Gustafsson, 2009; Semiletov et al., 2011; Tesi et al., 2014, 2016; Bröder et al., 2016 a,b; Charkin et al., 2011; Dudarev et al., 2015; Karlsson et al., 2011) demonstrate that coastal erosion is the main source of particulate organic carbon (POC) to the East Siberian Arctic Shelf (ESAS), the broadest and shallowest shelf in the World Ocean. At the same time, river discharge gives input to shelf waters of terrestrial carbon in the form of dissolved organic carbon (DOC) and waters enriched by carbon dioxide (CO_2) (Alling et al., 2010; Anderson et al., 2009; Semiletov et al., 2011, 2012; Amon et al., 2012).

Annually, the Arctic rivers transport 25-36 Tg of DOC to the Arctic Ocean, which is ~10 % of the global riverine DOC discharge (Raymond et al., 2007). The Siberian rivers have the highest DOC concentration among the major rivers worldwide, with concentrations typically ranging between 500-900 μM DOC (Gordeev et al., 1996; Shiklomanov et al., 2006; McClelland et al., 2012; Amon et al., 2012). Furthermore, Arctic and subarctic regions contain approximately 50 % of the global terrestrial OC in their frozen soils (Tarnocai et al., 2009; Hugelius et al., 2011). Warming and intensification of the hydrologic cycle lead to increased rate of water and dissolved organic matter (DOM) discharge from the Siberian rivers.

The present study synthesizes recent observations on the remote ESAS with the focus on exploring the extent and dynamics of riverine DOC, using colored or chromophoric DOM (CDOM) as a proxy. In recent years an interest in CDOM and its characterization has increased substantially due to: 1) rapid development of satellite monitoring methods elaborated to study various processes in seas and oceans, including the coastal water areas (Coble, 2007; Bondur et al., 2006; Vantrepotte et al., 2012), detect their pollutions, as well as to estimate the potential of offshore areas for the presence of hydrocarbons based on satellite data (Bondur, 2011); 2) remote sensing of ocean color related to organic carbon cycle (Blough and Del Vecchio, 2002); 3) possible interference of chlorophyll as an indicator of primary productivity with remote sensing measurements (Heim et al., 2014); 4) tracing of river discharge of organic carbon to the ocean and carbon cycle in coastal waters (Amon and Meon, 2004; Belzile et al., 2006; Guéguen et al., 2005, 2007; Matsuoka et al., 2012; Pugach and Pipko, 2013; Mann et al., 2016).

Quantitative descriptions of the dynamics and variability of CDOM optical properties are often required, particularly in the coastal waters, in order to accurately predict light penetration and primary production (Matsuoka et al., 2007). It should be noted that reliable estimation of optical characteristics of coastal waters is crucial for validation and calibration of remote sensing data processing results (Vantrepotte et al., 2012; Bondur et al., 2006).

According to Coble (2007), up to 70 % of DOM in shelf waters is represented by its chromophoric fraction, which is critical in a number of biochemical and photochemical processes and which defines the optical properties of natural waters, thus affecting the depth of the photic layer (Granskog et al., 2007; Hill, 2008). High CDOM values are typical for the eastern Laptev Sea; in the western East Siberian Sea (ESS) they result from excessive discharge of the Lena River which is characterized by the high CDOM concentrations. Most likely, the color resulting from the presence of CDOM in this water reflects the color resulting from the presence of chlorophyll when seen from space (Heim et al., 2014). This may explain the recently proposed increase in the net primary production rates reported for these ESAS areas based on satellite data interpretation (Arrigo and van Dijken, 2011).

Empirical relationships between the optical properties of CDOM and DOC have already been the subject of investigation in different seas of the Arctic Ocean in various seasons (Ferrari et al., 1996; Stedmon et al., 2000, 2011; Guéguen et al., 2005; Belzile et al., 2006; Kowalczuk et al., 2010; Pugach and Pipko, 2013). The purpose of this paper is to study the inter-annual dynamics and optical characteristics of DOM in shelf waters of the Eastern Arctic seas on the basis of multi-year summertime (August –September) expedition data (2003-2005, 2008, 2011).

2 Study area

This study is focused on the Laptev and East Siberian seas, where the influence of the river discharge and biogeochemical signal of the permafrost degradation are the most prominent (Guo et al., 2004; Rachold et al., 2004; Pipko et al., 2005; Pugach and Pipko, 2013; Semiletov, 1999; Alling et al., 2010; Nicolsky and Shakhova, 2010; Sánchez-Garcia et al., 2011; Semiletov et al., 2005, 2011; Shakhova et al., 2015; Vonk et al., 2012, 2014). The shelf area of these seas covers 40% of the Arctic shelf and 20% of the entire Arctic Ocean area (Stein and Macdonald, 2004). Annually, 767 km^3 of fresh water flows into the Laptev Sea with discharges of the Lena, Khatanga, Anabar, Olenek, and Yana rivers, which amounts to over 30 % of the total river discharge into all Arctic seas in Russia. The Lena River accounts for more than 70 % of the total discharge to the Laptev Sea (Semiletov et al., 2000; Cooper et al., 2008). Over 85 % of its discharge flows into the sea through channels of the eastern Lena delta. Therefore, the hydrological and biogeochemical regime of the Laptev Sea, and its southeast part in particular, is mainly controlled by discharge fluctuations of the Lena River which is the largest river in the Eastern Siberia (Nikiforov and Shpaikher, 1980; Pipko et al., 2010; Semiletov et al., 2012 Bröder et al., 2016a). Moreover, it has been found that in the past the Lena River played a dominant role in sediment discharge, flushing out soil OM from its vast watershed (Tesi et al., 2016); a significant fraction of “fresh” terrestrial OM would be oxidized to DOM (Vonk et al., 2013).

The ESS is one of the least-studied seas; this lack of attention is mainly attributed to severe ice-bound conditions. The Kolyma and Indigirka are the main rivers for which the ESS serves a receiving basin; however their total average annual discharge does not exceed 180 km^3. Hence, considering cyclonic transfer of waters in the Arctic Seas (Nikiforov and Shpaiher, 1980), the main freshening effect is due to the Lena River. Depending on hydrometeorological conditions, the plume of the Lena River reaches 165° E (typical for anticyclonic circulation), and even as far as Long Strait at 180° E (typical for cyclonic circulation) (Semiletov et al., 2005).

In this paper, we employ a coupled analysis of literature sources and our data obtained in the present multi-year study to carry out a comprehensive study of the optical characteristics of ESAS waters, to identify different shelf areas using their spectral parameters, to calculate their average values, and to identify the physical drivers of these processes. We compare lab-based spectrophotometric and in situ fluorometric CDOM techniques. We also consider the possibility of using optical characteristics, not only to obtain quantitative DOC data, but also to understand DOM genesis in the shelf waters of the Arctic seas.

3 Materials and methods

3.1 Field work

This paper presents data from research expeditions held during the summer-fall season of 2003 and 2004 (HV Ivan Kireev), 2005 (MV Auga), 2008 (HV Yakob Smirnitsky), and 2011 (RV Academician M.A. Lavrentyev) on ice-free Laptev and East Siberian seas (Fig. 1).

The study was carried out using a hydrological conductivity-temperature-depth (CTD) SBE 19plus SEACAT Profiler probe (www.seabird.com) with CDOM sensor (WETStar CDOM Fluorometer). This fostered in situ synchronous high-precision measurements of vertical temperature distribution, conductivity and CDOM.

In 2003-2005, 2008, and 2011 the measurements were carried out at 399 oceanological stations and along the ship’s track using a seawater intake system. Water was pumped from 4 m depth at 30 L min^{-1} through stainless steel and silicon tubes into an on-deck 300 L barrel, and then through a distribution network, from which samples were collected. Table 1 shows detailed information on cruises, including dates, number of stations and parameters measured.

3.2 Methods for determination of dissolved organic carbon

In 2003-2004, DOC concentration was measured in an International Arctic Research Center laboratory at the University of Alaska (Fairbanks, Alaska, USA), in 2008 on board RV Yakob Smirnitsky, and in 2011 in the hydrochemistry laboratory of the Pacific Oceanological Institute, Far Eastern Branch of the Russian Academy of Sciences (POI FEBRAS). All samples were analyzed using the Shimadzu TOC-V$_{CPH}$ system (Alling et al., 2010; Semiletov et al., 2005, 2013). The 1-3 L seawater samples were vacuum-filtered onboard with 25 mm diameter pre-combusted filters within an all-glass filtration system. The samples were stored in 60 mL Nalgene high-density polyethylene (HDPE) bottles. DOC was analyzed via high-temperature catalytic oxidation (Shimadzu TOC-V_{CPH}). Inorganic carbon was removed by acidifying the samples to pH 2 with 2 M HCl and sparging for 8 min prior to analysis. All procedures for calibration and data analysis followed Sharp et al. (1995). Certified Reference Materials (CRMs, from the University of Miami) of low carbon content (1-2 μM C) and deep-sea reference water (41-44 μM C) were run prior to each analysis batch (Alling et al., 2010).

3.3 Methods for determination of colored dissolved organic matter

3.3.1 In situ measurements of CDOM fluorescence

The WETStar DOM fluorometer is a commercially available tool allowing DOM fluorescence (DOM-FL) to be measured in situ without prior filtration of water (Belzile et al., 2006). The WETStar uses two UV LEDs centered at ~ 370 nm and modulated at 1 kHz to provide the excitation. The emitted blue fluorescence is synchronously detected at 1 kHz by a silicon photodiode. The detector, positioned at 90° to the axis of the LED mounts, measures the emitted light from the ~ 0.25 cm^3 sample volume defined by the intersection of excitation light with the detector field of view, within a quartz flow tube of 7 mm internal diameter. A UV-violet blocking filter (cut off at 400 nm) and a 460 ± 60 nm interference filter were used to discriminate against the scattered UV excitation light. To analyze discrete water samples, DOM-FL was measured by introducing an unfiltered water sample into the flow tube of the WETStar fluorometer while closing the bottom end of the tube. The voltage output from the fluorometer was read using a digital voltmeter. Replicated measurements always remained within ± 0.01 V. The raw voltage from the fluorometer was converted to quinine sulfate units (QSU) (Belzile et al., 2006).

3.3.2 CDOM optical properties

Spectroscopic analysis of CDOM samples was performed using a UNICO 2804 spectrophotometer with a 1 cm quartz cuvette over the spectral range from 200 to 600 nm at 1 nm intervals. Milli-Q (Millipore) water was used as the reference for all samples. Water samples for CDOM underwent filtration through acid-washed Whatman glass fiber filters (GF/F, nominal pore size 47 mm).

The obtained ranges were approximated via the least squares adjustment according to the following formula:

$$a(\lambda) = a(\lambda_0)\, exp\, \{-S\,(\lambda - \lambda_0)\}, \qquad (1)$$

where a(λ), $a(\lambda_0)$ represent the absorption coefficients at wavelength λ and reference wavelength $\lambda_0 = 254$ nm, and S is a spectral slope defining spectral dependence of the absorption coefficient resulting from CDOM presence (Blough and Del Vecchio, 2002). The absorption coefficient was calculated as follows:

$$a(\lambda) = 2.303A(\lambda)/L, \qquad (2)$$

where A (λ) is optical density at wavelength λ, and L is the cell pathlength in meters.

Generally, several characteristics are used in order to define CDOM spectral properties; optical density and/or absorption coefficient of a particular wavelength (A_λ or a_λ), spectral slope (S), and spectral slope ratio (S_R) in various ranges. Recently, another complex parameter has also been used, i.e. molar or specific UV absorbance (a^*_λ or SUVA), which represents the relationship of UV absorbance to dissolved OC concentration in the studied sample. The last parameter is not often applied in whole water analysis, mainly due to limited high-precision data on DOC content.

Percent aromaticity for samples obtained in this study was calculated using the equation given in Weishaar et al. (2003):

$$C_{Ar} = 6.52 * SUVA + 3.63, \quad (3)$$

where C_{Ar} is percentage of aromatic carbon of the total carbon.

This equation is applicable for a wide range of aquatic environment(seas, bogs, lakes) since the authors used humic substances that have different chemical characteristics and demonstrated a strong correlation ($R^2 = 0.97$) between the specific UV absorbance and aromatic carbon content.

The spectral slope, S, indicates the rate at which the CDOM absorption coefficient decreases with wavelength increase; it has been used to distinguish different sources of CDOM and CDOM modification by chemical and biological processes (Carder et al., 1989). The value of S increases with the decrease of the CDOM absorption coefficient, aromatic content, and molecular weight. Therefore, it is also widely accepted that the spectral slope S can be used as a proxy for CDOM composition (Kowalczuk et al., 2003). However, its usefulness is limited by the fact that S depends on the wavelength interval over which it is calculated (Carder et al., 1989; Stedmon et al., 2000). According to historical data (Carder et al., 1989; Weishaar et al., 2003; Helms et al., 2008; Fichot and Benner, 2011; Pavlov et al., 2015) a wavelength interval of 275-295 nm was chosen for detailed spectral analysis because it demonstrates the biggest variability of optical parameters under mixing conditions of water with contrasting optical characteristics. S_R was calculated as the ratio of $S_{275-295}$ to $S_{350-400}$ as described by Helms et al. (2008).

3.4 Statistical treatment and graphical representation of the data

Data were tested statistically using an empirical distribution function test in the Statistics 7.0 software package. Descriptive statistics were calculated for the 95 % confidence interval of the mean (P = 0.95, alpha = 0.05). Most of the plots and maps in this study were created with the Ocean Data View software (Schlitzer, 2011).

4 Results and discussion

4.1 Spatial variability of spectral characteristics of colored dissolved organic matter

The study of the spatial variability of CDOM spectral characteristics (a_λ, S, S_R and a^*_λ) in shelf waters of the Eastern Arctic seas was conducted on the basis of data obtained during summer-fall season (August-September) of 2004, 2005, and 2011 in the East Siberian and eastern Laptev seas (Fig. 1). The 2004 survey was chosen for detailed analysis of specific UV absorbance spatial variability along a wavelength of 254 nm (a_{254}) in the surface water of the ESAS.

In 2004, the distribution of a_{254} in surface waters demonstrated considerable spatial variability, from 45 m^{-1} in waters of the Laptev Sea to 1.15 m^{-1} eastwards of the ESS (Fig. 2a). The a_{254} decreases with an increase in salinity (Fig. 2b) (with increasing distance from the direct influence of river discharge). The strong negative correlation of these parameters (R^2 = –0.87) confirms the assumption that terrestrial discharge is the major source of CDOM on the East Siberian Shelf.

Figure 3 shows spectral dependences and calculated values of $S_{275-295}$ for surface waters of three stations located in typical shelf zones: station 25 is under direct Lena River influence (the Laptev Sea), station 60 is located in the ESS (moderate zone of river and ocean waters mixing), and station 97 in Long Strait.

The lowest $S_{275-295}$ = 16.4 μm^{-1} was found near the river delta in the Laptev Sea; this value characterizes the surface waters of the eastern Arctic seas which are dominated by allochtonous DOM during the late summer season. This value is comparable to values found in other rivers studied in the Pacific sector of the Arctic. For example, $S_{275-295}$ reaches 12 μm^{-1} in the Yukon River during the peak flood periods when the concentrations of DOM and its colored fraction are the greatest (Spencer et al., 2009). $S_{275-295}$ increases up to 18.9 μm^{-1} in the western ESS where river influence decreases. $S_{275-295}$ further increases to 21 μm^{-1} in the Long Strait where primary production is high (Walsh et al., 1989) and the main portion of DOM is produced in situ.

S_R was calculated for three typical areas of the ESAS that are characterized by different intensities of terrigenous influence. This ratio is used to indicate the source and molecular weight of CDOM (Helms et al., 2008). The lowest values were obtained in the southeastern Laptev Sea (0.94) and were close to the values recorded in the Yukon and Yenisei rivers (~0.79, Spencer et al., 2009). The difference in S_R values can be attributed to different seasons; i.e., this study was carried out at the end of arctic summer, in September, while Spencer and his group made their calculations for early summer conditions characterized by flood season when products of land plant origin with high molecular weight predominate in DOM. The maximum S_R (3.85) was found in the area influenced by the highly productive Pacific-origin waters in Long Strait where the optical properties are determined by phytoplankton-derived autochthonous CDOM with low molecular weight. Therefore, S_R is a sensitive parameter that can be used to identify the CDOM origin (terrigenous vs marine) in different parts of the ESAS, and in other arctic seas as well.

Figure 4 demonstrates the spatial distribution of aromatic carbon in ESAS surface water. The corresponding calculations showed that the content of aromatic carbon within DOC remains almost constant in the region of substantial river impact up to ~ 165° E (Fig. 4). In the eastern part a gradual decrease in aromaticity percentage was observed indicating contribution of the Pacific genesis waters with DOM of allochtonous origin, of predominantly aliphatic character with much lesser absorption capabilities.

The spectral characteristics of CDOM and salinity in different ESAS areas (obtained during the 2004, 2005, and 2011 surveys) were used to separate the ESAS into western and eastern biogeochemical provinces (Table 2).

Analysis of CDOM spectral characteristics has proved that the major coastal regions of the Laptev and East Siberian seas are influenced by the inflow of terrigenous DOM, which is represented by highly aromatic CDOM.

4.2 Inter-annual colored dissolved organic matter spatial variability

Comparative analysis of 2003-2005, 2008, and 2011 data showed that, in general, spatial CDOM variability in ESAS surface waters depends upon distance from the river water source: the maximum CDOM content was recorded near river mouths, and the minimum in regions remote from direct river discharge. However, CDOM concentrations and the spatial distribution of waters with high CDOM content on the ESAS differed significantly in different years (Fig. 5). The 15 QSU isoline in Figure 5 can be used to compare the distribution of river water in different years.

The strong negative correlation between CDOM and salinity (Fig. 5) indicates that rivers are the main source of CDOM to the ESAS. Thus, it can be assumed that CDOM spatial variability in coastal ESAS waters predominantly depends on the total annual river discharge.

Comparison of the discharge of the main rivers flowing into the Laptev and East Siberian seas (the Lena and Kolyma rivers), which was based on Tiksi Hydromet data and the http://rims.unh.edu website, demonstrated that the maximum total discharge of the Lena and Kolyma rivers during the study period was recorded in 2008 (829 km^3) and the minimum in 2003 (543 km^3). However, the maximum distribution of ESAS waters with high CDOM concentrations was observed in 2004 (Fig. 5) and the minimum was observed in 2011 (Fig. 5). This indicates a complex and multifactorial correlation between river discharge and distribution of CDOM-enriched waters on the ESAS.

Dominant atmospheric processes and differences in ice-coverage area, along with other factors, determine inter-annual CDOM distribution variability on the ESAS. The National Centers for Environmental Prediction (NCEP) sea level pressure (SLP) data were employed to describe the atmospheric circulation over the Arctic Ocean (www.esrl.noaa.gov). The SLP fields, averaged over the summer season (July – September) for each year, are shown in Figure 6. During the 2003 summer season cyclonic atmospheric circulation dominated over the central Arctic Ocean. SLP down to 1005 mbar extended into the Laptev and the East Siberian seas (Fig. 6a). The development of a deep atmospheric depression caused onshore winds on the western periphery of the cyclone and transferred freshened shelf waters to the east (Pipko et al., 2008; Savel'eva et al., 2008). Waters with high CDOM concentrations spread out to 165° E although river discharge was at a minimum in 2003 (Fig. 5). The September sea-ice extent was at a maximum from 2003 to 2011 in the Arctic Ocean ($6.1 \cdot 10^6$ km^2, http://nsidc.org/data/seaice_index/), but Dmitry Laptev Strait was clear of ice in early August; thus, intensive water exchange occurred between the Laptev and East Siberian seas under a prevailing west wind.

In 2004 the summer low pressure north of the ESS was weaker while an anticyclone formed above the Canadian Arctic Archipelago (Fig. 6b). High river discharge, ice conditions, and strong offshore winds determined the maximum distribution of river waters in the ice-free ESS (Fig. 5).

Predominance of cyclonic atmospheric circulation over the western Laptev Sea and anticyclonic circulation over the Beaufort Sea created significant SLP gradients and, thus, strong winds in 2005 (average wind speed of up to ~ 11.2 m sec^{-1}, Fig. 6c). Strong north and west winds prior to the expedition hampered the spread of river waters north of the river delta (Fig. 6c) and also intensified the processes of thermoabrasion (Günther et al., 2013), and the release of eroded carbon into the water. This is the year when the maximum absolute CDOM values (over 100 QSU, the average was 25 QSU during the study period) was recorded in Buor-Khaya Bay surface water.

In the warm season of 2008, the atmospheric pressure field was conditioned by the dominant anticyclone over the Beaufort Sea and weak cyclone over Siberia, which caused southeast winds over the ESAS (Fig. 6d). Thus, although the river discharge was great (the Lena River maximum occurred during the study period), freshened waters were located in the southeastern Laptev Sea and the western ESS and did not penetrate into the eastern part of the sea. It should be noted that the ice extent was less in September 2008 compared with the previous study periods. The whole shelf was ice-free that year and the ice boundary moved north of 80° N in some areas (http://www.aari.nw.ru/).

An area of high SLP over the Arctic Basin and low SLP above the continent occurred in the summer season (June-August) of 2011 (Fig. 6d). The averaged meridian wind speed was 1.5 m s^{-1} and the averaged area wind speed was 3.5 m s^{-1} (http://www.cdc.noaa.gov), which determined weak offshore east and southeast winds of 4 m s^{-1}. September sea-ice extent in the Arctic Ocean was smaller in 2011 than in 2008 (4.6 and 4.7 * 10^6 km^2, respectively), but the ESAS ice edge was markedly closer to the median extent for 1981-2010 in 2011 (http://nsidc.org/data/seaice_index/). During the summer season, the ESS ice edge did not reach 73° N and meltwater was transported to the Laptev Sea under the influence of east and southeast winds. The situation radically changed in September, when a low SLP area dominated over the Arctic Basin (Fig. 6f). The wind changed towards the north and northwest and became stronger. Low river discharge, weak winds in preceding summer months, and onshore winds during the study period provided for a weak spreading of river water. Eventually, the lowest absolute CDOM and the minimum distribution area for CDOM-enriched waters were recorded in September 2011 (Fig. 5).

Therefore, expedition data analysis showed that the prevailing type of atmospheric circulation and the position of action centers relative to each other were the dominant factors controlling ESAS surface CDOM spatial distribution, although inter-annual variabilities of river discharge and ice extent were also significant. The greatest distribution of ESAS waters with high CDOM content was recorded when intensive development of a cyclone occurred above the central region of the Arctic Ocean basin.

4.3 Rapid assessment of dissolved organic carbon based on optical characteristics of dissolved organic matter

Methods to predict DOC concentrations from absorbance characteristics were pursued in the early 1970s (Banoub, 1973; Lewis and Tyburczy, 1974) and should have enabled a quick and inexpensive alternative to direct analytical methods. However, a prerequisite for successfully predicting DOC concentration is that the non-absorbing DOC is at a constant or low level (Ferrari and Dowell, 1998). The processes responsible for DOC and CDOM distribution in the open ocean are typically independent and the two pools usually demonstrate a negative rather than a positive correlation (Coble, 2007). The situation is different in shelf areas where terrestrial discharge is strong and circulation of river and sea water controls the distribution of both DOC and CDOM. DOC and CDOM concentrations were measured simultaneously in the surface shelf waters of the Laptev and East Siberian seas during the 2004 and 2008 surveys to find possible correlations between the two parameters.

In 2004, along with the study of filtered sea water sample absorption coefficients, DOM-FL was measured in situ using a WETStar fluorometer. Strong positive correlation ($R^2 = 0.93$) was observed between a_{254} measured in the filtered samples and DOM-FL of the unfiltered samples measured simultaneously at 38 ESAS surface water stations (Fig. 7). This confirms previous results (Belzile et al., 2006) showing that the presence of suspended matter in water samples has little impact on DOM-FL even in regions of intensive terrigenous discharge. Artifacts resulting from filtration or sample storage can therefore be avoided in a full range of samples when DOM-FL measurements are made using the WETStar fluorometer.

Figure 8 demonstrates the linear dependence of DOC/DOM-FL for 2004 and 2008, which is characterized by a high correlation ($R^2 = 0.99$ and 0.98, respectively) that makes it possible to calculate DOC concentrations from DOM-FL using the equations given in Figure 8.

This high linear correlation was used to calculate DOC values with a high spatial resolution based on direct fluorescence measurements, which allows various artifacts induced by filtering and storing samples to be avoided and, thus, adds to the limited available data on DOC, which can hardly be measured in laboratory conditions.

Figure 9 shows DOC spatial distribution measured in the laboratory for isolated points of the ESS surface layer in September 2004 (Fig 9a) and DOC distribution calculated from DOM-FL (Fig. 9b). It can be seen that the measured DOC vs calculated CDOM/DOC values demonstrate similar distribution patterns.

Therefore, this rapid assessment of DOC concentrations on the ESAS using WETStar fluorometer is an effective tool for obtaining information on DOC distribution in summer seasons. This approach is reliable in areas that are greatly influenced by river discharge, for which the 24.5 psu isohaline is a conventional distribution border (Nikiforov and Shpaikher, 1980). In addition, the 5 psu isohaline was defined as the lowest conventional salinity level when all the major marginal filters have already been passed (Lisitsyn, 1994).

5 Conclusions

A multi-year study of DOM optical parameters and the spectral characteristics of the DOM chromophoric fraction were carried out on the vast ESAS (from the Lena River delta in the Laptev Sea to Long Strait in the ESS) in summer-fall seasons. The spectral characteristics of CDOM were applied to identify two clearly distinct biogeochemical provinces in the surveyed area.

The analysis of CDOM spectral characteristics has proved that the major part of the Laptev and ESS shelf is influenced by terrigenous DOM with high aromaticity, transported by riverine discharge. It has also been shown that the type of atmospheric circulation is the dominant factor controlling CDOM spatial distribution on the ESAS.

Strong correlation between DOC and CDOM concentrations in surface shelf waters that are influenced by terrigenous discharge makes it possible to calculate DOC content from CDOM assessed in situ using the WETStar fluorometer. Moreover, the reliable estimation of optical characteristics of coastal waters is crucial for validation and calibration of remote sensing data processing results.

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Table 1. Dates, number of stations, samples collected, and parameters measured during cruises.

Dates of cruises	Region	Number of stations	Parameters measured
HV "Ivan Kireev", 7 - 21 Sept. 2003	East Siberian Sea	41	CTD, CDOM
HV "Ivan Kireev", 31 Aug. - 15 Sept. 2004	Southeastern Laptev Sea, East Siberian Sea	92	CTD, CDOM, a_{CDOM} (λ), DOC
MV "Auga" 14 – 25 Sept. 2005	Southeastern Laptev Sea, southwestern East Siberian Sea	64	CTD, CDOM, a_{CDOM} (λ)
HV "Yakob Smirnitskiy", 8 Aug. – 18 Sept. 2008	Eastern Laptev Sea, East Siberian Sea	74	CTD, CDOM, DOC
RV "Academician M.A. Lavrentyev", 15 Sept. – 4 Oct. 2011	Eastern Laptev Sea, East Siberian Sea	89	CTD, CDOM, DOC, a_{CDOM} (λ)

Table 2. Spectral characteristics of CDOM and salinity in two biogeochemical provinces of the ESAS (obtained during the 2004, 2005, and 2011 surveys).

Parameter	**Absorption coefficient (a_{254}), m^{-1}**						$S_{275\text{-}295}$, μm						**Specific UV absorbance,** L/(mgC$_*$m)						**Salinity**					
Region	AVG	Md	STD	Min	Max	N	AVG	Md	STD	Min	Max	N	AVG	Md	STD	Min	Max	N	AVG	Md	STD	Min	Max	N
Western province	**22.4**	19.7	11.9	2.9	65.4	75	**17.1**	17.6	3.9	3.7	23.3	74	**2.2**	2.0	0.7	1.2	3.5	20	**16.3**	17.0	5.0	3.3	30.3	75
Eastern province	**1.7**	1.5	0.5	1.1	2.2	15	**26.1**	23.8	4.9	23.3	33.5	15	**0.7**	0.6	0.2	0.5	1.0	6	**28.7**	29.1	3.8	24.7	32.1	15

AVG – average value, Md – median value, STD – standard deviation, N – number of measurements.

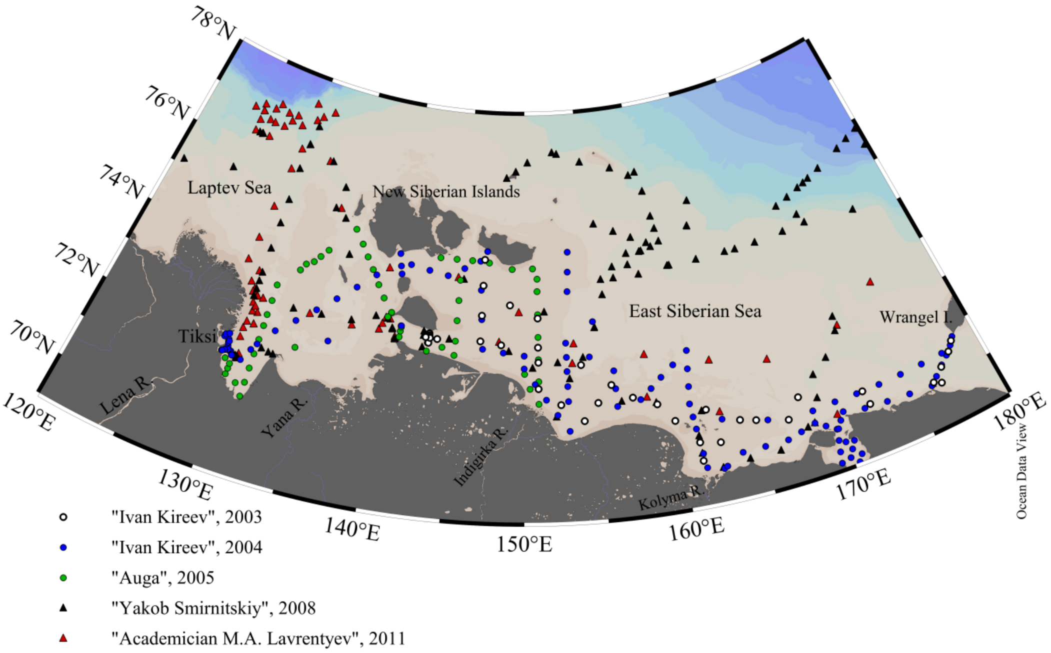

Figure 1. Study area: Location of oceanographic stations accomplished in August-October 2003-2005, 2008, and 2011.

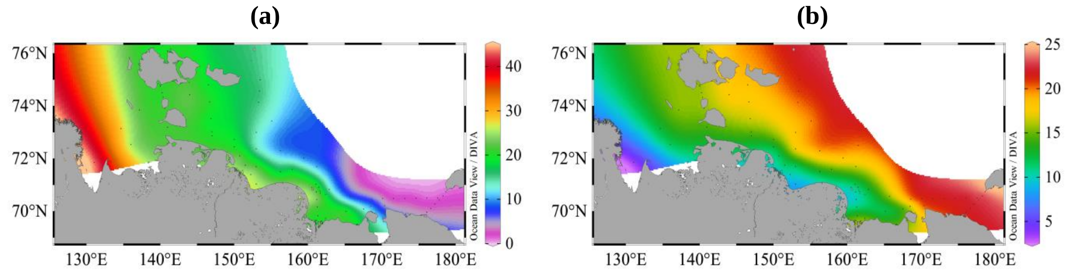

Figure 2. Spatial distribution of (**a**) DOM absorption coefficient at the 254 nm wavelength (a_{254}, m^{-1}) and (**b**) of salinity (S) in the ESAS surface waters, September 2004.

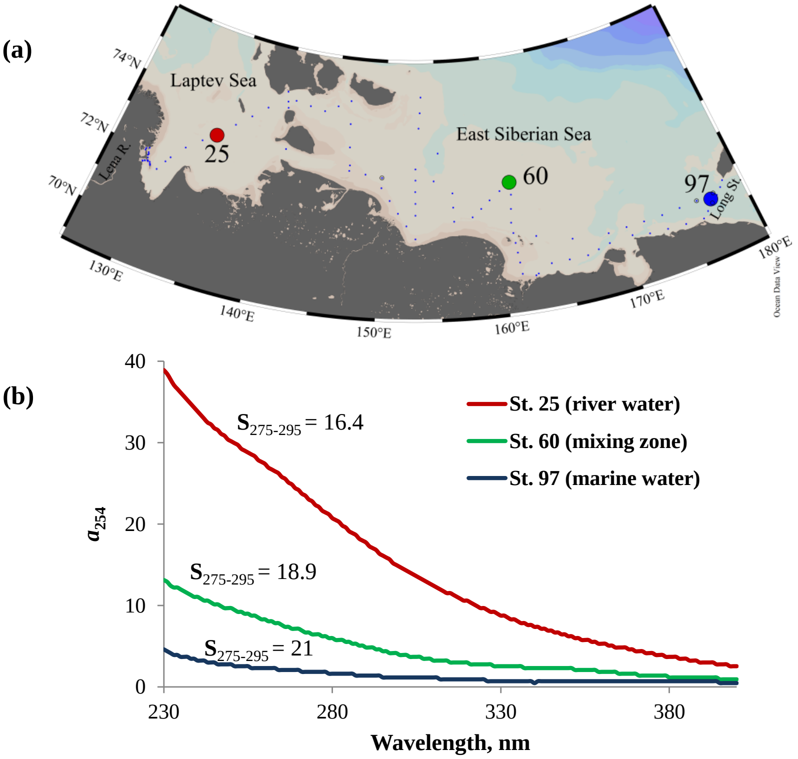

Figure 3. Location of stations on the East Siberian Shelf (**a**), and surface CDOM absorption coefficient spectra a_{254} (**b**) for station (St.) 25, 60, and 97, September 2004.

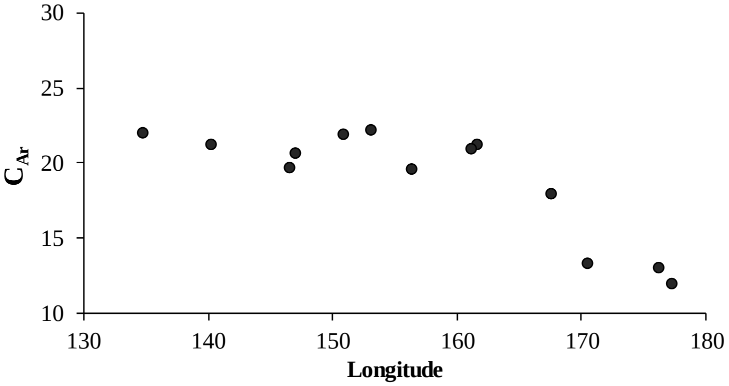

Figure 4. Distribution of aromatic carbon (C_{Ar}, %) in the ESAS surface waters, September 2004.

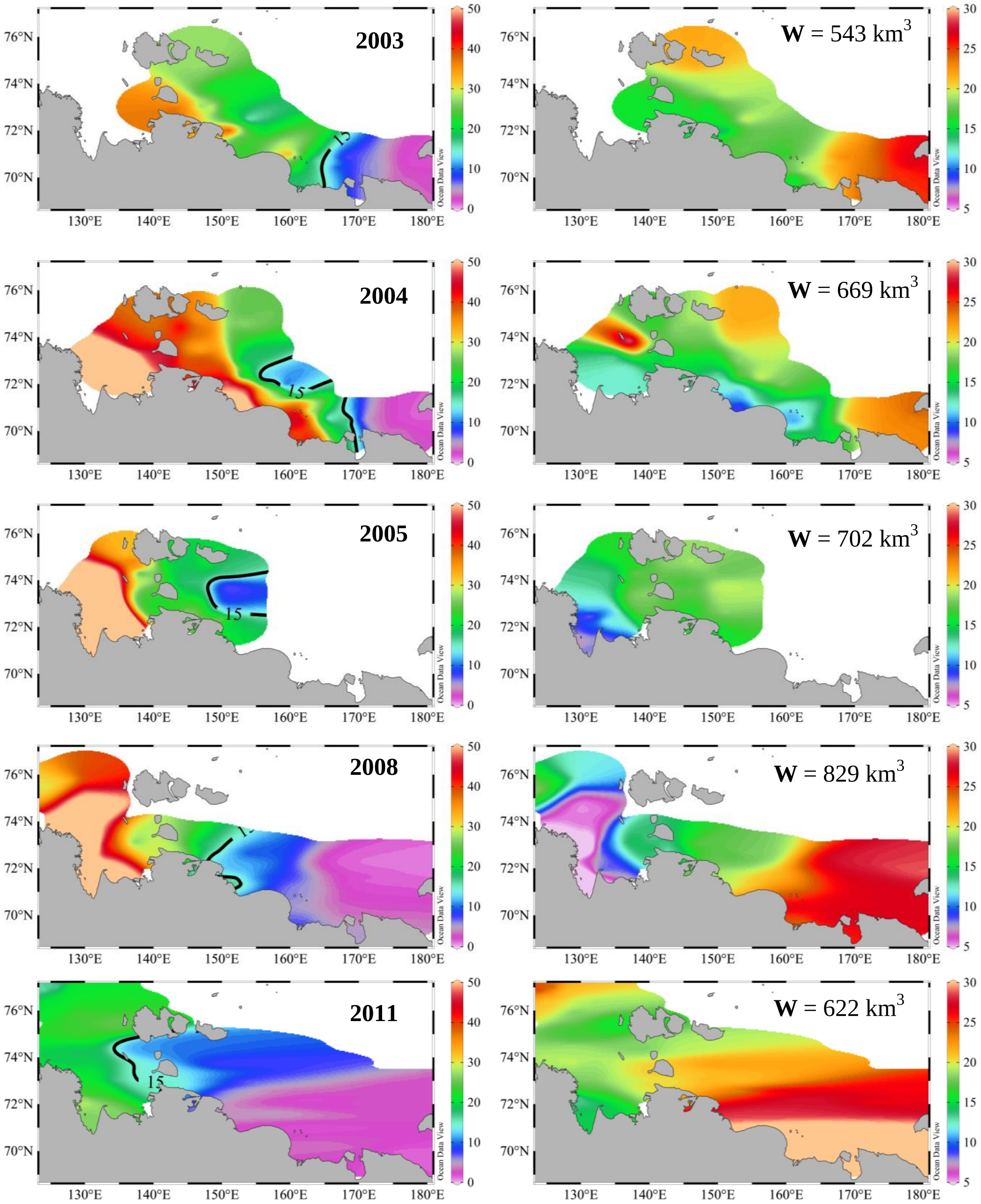

Figure 5. Distributions of surface CDOM (left) and Salinity (right) in September 2003, 2004, 2005, 2008, and 2011; **W** - annual total river discharge.

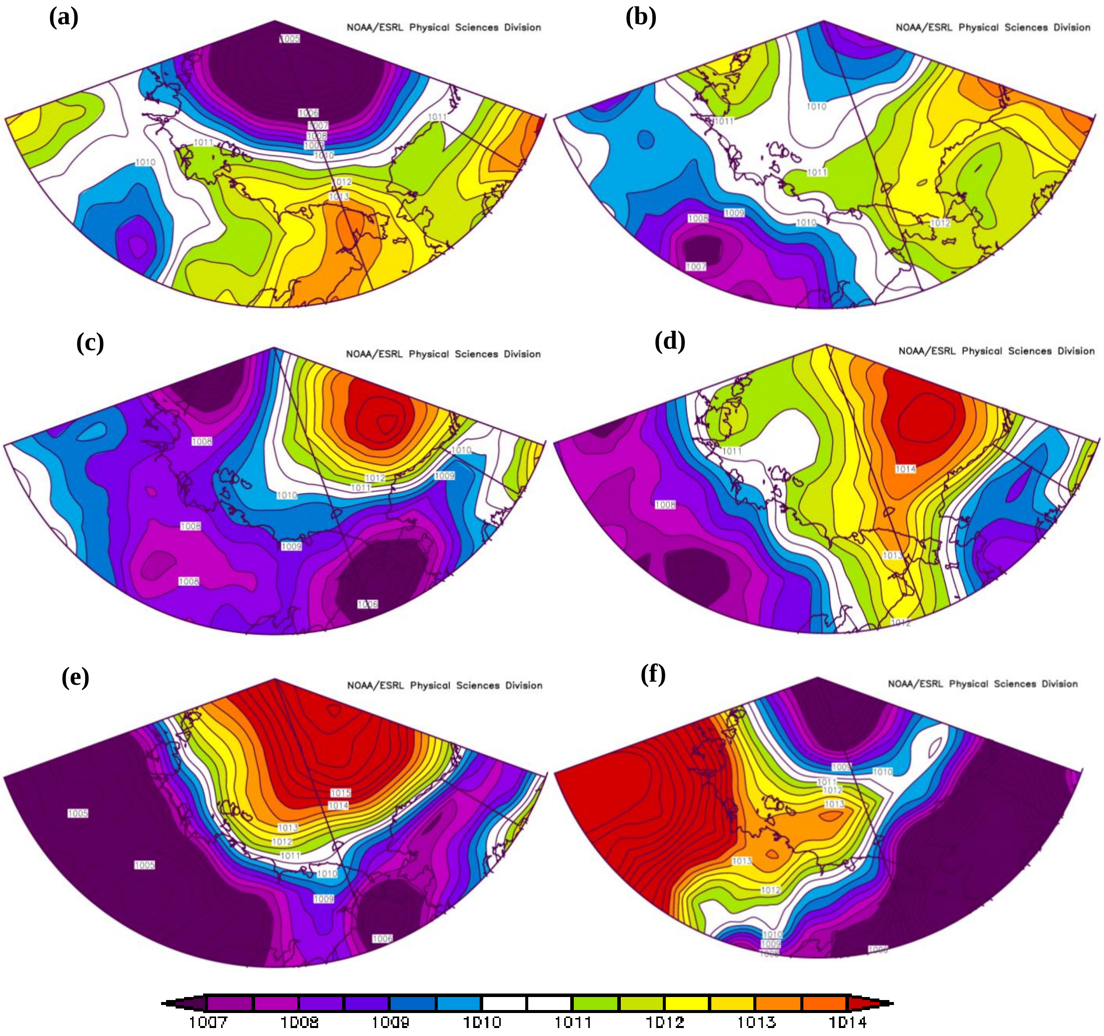

Figure 6. Sea level pressure fields (mbar), averaged over the summer season (July–September) in 2003 (**a**), 2004 (**b**), 2005 (**c**), 2008 (**d**), 2011 (**e**), and September 2011 (**f**), from NCEP data.

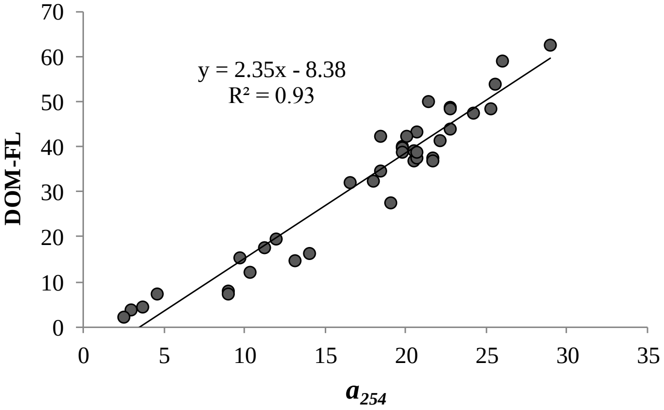

Figure 7. DOM-FL (QSU) measured using the WETStar fluorometer versus DOM absorption coefficient (a_{254}, m^{-1}) in ESAS surface water, September 2004.

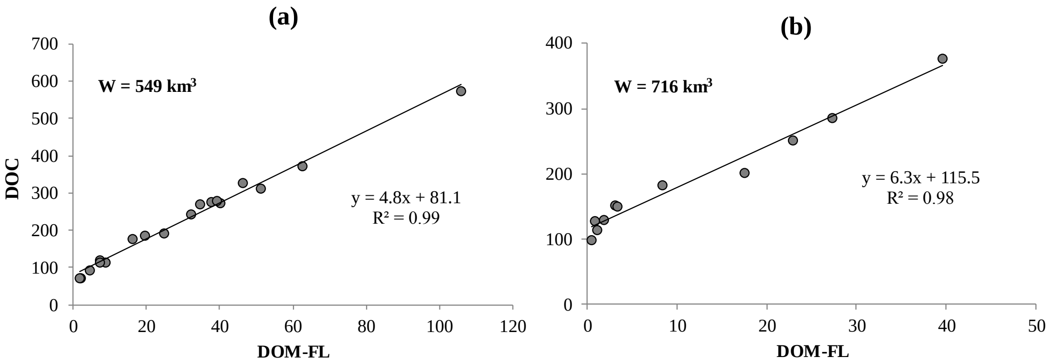

Figure 8. DOC concentration (µmol l^{-1}) versus DOM fluorescence measured using the WETStar fluorometer (DOM-FL, QSU) in the ESAS surface water, September 2004 (**a**) and 2008 (**b**); **W** - annual Lena River discharge.

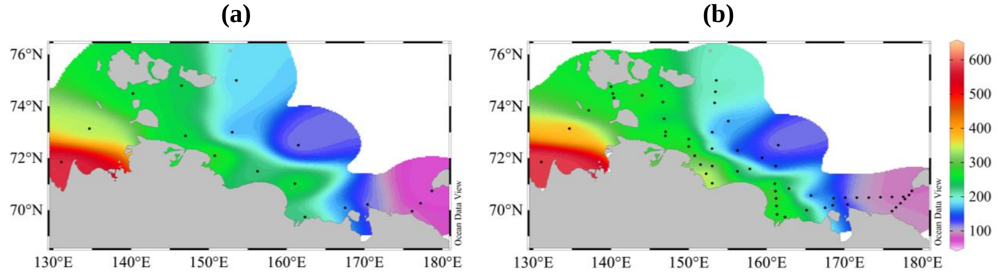

Figure 9. DOC distribution (µmol l^{-1}) in the ESAS surface waters in September 2004: **(a)** laboratory measurements, **(b)** data from DOM-FL.