The impact of the freeze–melt cycle of land-fast ice on the distribution of dissolved organic matter in the Laptev and East Siberian seas (Siberian Arctic)

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Received: 8 December 2020 – Discussion started: 5 January 2021
Revised: 14 May 2021 – Accepted: 19 May 2021 – Published: 18 June 2021

Abstract. Permafrost degradation in the catchment of major Siberian rivers, combined with higher precipitation in a warming climate, could increase the flux of terrestrially derived dissolved organic matter (tDOM) into the Arctic Ocean (AO). Each year, ~7.9 Tg of dissolved organic carbon (DOC) is discharged into the AO via the three largest rivers that flow into the Laptev Sea (LS) and East Siberian Sea (ESS). A significant proportion of this tDOM-rich river water undergoes at least one freeze–melt cycle in the land-fast ice that forms along the coast of the Laptev and East Siberian seas in winter. To better understand how growth and melting of land-fast ice affect dissolved organic matter (DOM) dynamics in the LS and ESS, we determined DOC concentrations and the optical properties of coloured dissolved organic matter (CDOM) in sea ice, river water and seawater. The data set, covering different seasons over a 9-year period (2010–2019), was complemented by oceanographic measurements (T, S) and determination of the oxygen isotope composition of the seawater.

Although removal of tDOM cannot be ruled out, our study suggests that conservative mixing of high-tDOM river water and sea-ice meltwater with low-tDOM seawater is the major factor controlling the surface distribution of tDOM in the LS and ESS. A case study based on data from winter 2012 and spring 2014 reveals that the mixing of about 273 km$^3$ of low-tDOM land-fast-ice meltwater (containing ~0.3 Tg DOC) with more than 200 km$^3$ of high-tDOM Lena River water discharged during the spring freshet (~2.8 Tg DOC yr$^{-1}$) plays a dominant role in this respect. The mixing of the two low-salinity surface water masses is possible because the meltwater and the river water of the spring freshet flow into the Laptev Sea (LS) and East Siberian Sea (ESS). A significant proportion of this tDOM-rich river water undergoes at least one freeze–melt cycle in the land-fast ice that forms along the coast of the Laptev and East Siberian seas in winter. To better understand how growth and melting of land-fast ice affect dissolved organic matter (DOM) dynamics in the LS and ESS, we determined DOC concentrations and the optical properties of coloured dissolved organic matter (CDOM) in sea ice, river water and seawater. The data set, covering different seasons over a 9-year period (2010–2019), was complemented by oceanographic measurements (T, S) and determination of the oxygen isotope composition of the seawater.

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The study of dissolved organic matter dynamics in the AO is important not only to decipher the Arctic carbon cycle but also because CDOM regulates physical processes such as radiative forcing in the upper ocean, which has important effects on sea surface temperature, water column stratification, biological productivity and UV penetration.

1 Introduction

The mean annual air temperature in the Arctic continues to rise (Overland et al., 2019), resulting in a rapid decrease in summer sea-ice extent and volume (Stroeve and Notz, 2018) and, consequently, a longer ice-free season. Furthermore,
the terrestrial permafrost temperature is increasing (Biskaborn et al., 2019) with major implications for the Arctic carbon cycle. Due to the accelerated degradation of terrestrial permafrost, an estimated 1035 ± 150 Pg of organic carbon stored in the upper 3 m of circumpolar permafrost soils (Hugelius et al., 2014) can be either mineralised and mobilised as terrestrial dissolved organic matter (tDOM) into the hydrosphere or released as gaseous emissions into the atmosphere (Plaza et al., 2019). The release of soil carbon into the hydrosphere in combination with an increasing freshwater discharge from Arctic rivers (McClelland et al., 2004; Rawlins et al. 2010; Haine et al., 2015) might thus increase the flux of tDOM into the ocean (Frey and Smith, 2005; Guo et al., 2007; Prokushkin et al., 2011; Tank et al., 2016). Changes in the land–ocean fluxes of tDOM in the Arctic are of particular importance for the global carbon cycle since the rivers at high northern latitudes export significant quantities of tDOM to the Arctic Ocean (AO). Dissolved organic matter (DOM) is typically quantified via its carbon content (dissolved organic carbon; DOC), which contributes roughly half to the total mass of DOM. Currently, the annual riverine input of DOC into the AO is about 25–36 Tg C yr⁻¹ (Raymond et al., 2007; Anderson and Amon, 2015), with the six largest Arctic rivers discharging about 18–20 Tg C yr⁻¹ (Stedmon et al., 2011; Amon et al., 2012). The three major Siberian river systems (Ob, Yenisey and Lena) account for about 14 Tg C yr⁻¹ (Homes et al., 2012), with the Lena River alone discharging 6.8 Tg C yr⁻¹ DOC into the Siberian Laptev Sea (LS) (Juhls et al., 2020). The total riverine DOC flux to the LS is about 8.3 Tg C yr⁻¹ (Manizza et al., 2009), with the Lena drainage basin (2.61 × 10⁶ km²) accounting for about 70% of the total area of the LS watershed. The LS additionally receives freshwater from the outflow of the Kara Sea (KS), which transports river water from Ob and Yenisey through the Vilkitsky Strait into the northwestern LS (Janout et al., 2015). The combined DOC flux of the two major rivers discharging to the East Siberian Sea (ESS; Kolyma and Indigirka) is ~ 1.1 Tg DOC yr⁻¹ (Opsahl et al., 1999), which is ~ 50% of the total annual riverine DOC flux to the ESS (Manizza et al., 2009). The combined area of the drainage basin of the rivers Kolyma and Indigirka (1.01 × 10⁶ km²) accounts for ~ 75% of the total ESS watershed.

The terrigenous input (particulate and dissolved) of carbon by coastal erosion to the entire AO is estimated to be 15.4 Tg yr⁻¹ (9.2–24.2 Tg yr⁻¹ with 1 standard deviation; Terhaar et al., 2021). However, DOC concentrations measured in Guba Buor-Khaya bay east of the Lena Delta, a region known for the most rapid and extensive coastal erosion of the Siberian Arctic coastline, suggest that direct DOC input from coastal erosion must be small compared to the riverine DOC flux (Alling et al., 2010).

If the input of tDOM into the AO increases as a consequence of climate change, it is crucial to achieve a better understanding of tDOM transport dynamics and biogeochemical cycles. Previous studies in the Arctic marginal seas have reported a strong negative linear relationship between salinity and DOC, which implies that tDOM-rich river water mixes with DOM-poor marine waters from the AO without significant losses and gains along the salinity gradient (i.e. conservative mixing) (Kattner et al., 1999; Köhler et al., 2003; Amon, 2004; Amon and Meon, 2004; Shin and Tanaka, 2004; Gueguen et al., 2005; Matsuoka et al., 2012; Pugach and Pipko, 2013; Pavlov et al., 2016; Tanaka et al., 2016; Pugach et al., 2018). In contrast, a number of studies indicate significant degradation of tDOM in the Arctic Ocean (Belanger et al., 2006; Alling et al., 2010; Stedmon et al., 2011; Letscher et al., 2011; Kaiser et al., 2017a), the Fram Strait (Granskog et al., 2012) and Hudson Bay (Granskog et al., 2009; Granskog, 2012). One reason for the partly contradictory observations could be the extreme seasonality in the discharge of Arctic rivers and the associated high variability in the tDOM concentrations and composition. In the course of the peak spring discharge (spring freshet), which has the highest annual tDOM concentrations, about half of the annual tDOM is exported to the AO (Cauwet and Sidorov, 1996; Stedmon et al., 2011; Holmes et al., 2012). In summer, autumn and winter, tDOM concentrations in Arctic rivers are significantly lower (Stedmon et al., 2011; Juhls et al., 2020). Several studies have shown that tDOM discharged during the spring freshet displays a different chemical composition and a higher biological and photochemical lability compared to the summer discharge (Osburn et al., 2009; Amon et al., 2012; Mann et al., 2012; Kaiser et al., 2017b). This could lead to tDOM degradation of 20%–40% within less than 1 month during the spring freshet (Humes et al., 2008). Therefore, seasonal changes in tDOM composition and lability are another possible explanation for the observed variability in degradation rates.

Considering the high seasonal variability in input and chemical composition of tDOM and a predicted strong degradation of tDOM that is controlled by multiple processes, it appears puzzling that most studies in the LS have observed a conservative mixing of tDOM. This is especially true since the sea-ice growth–melt cycle in the Siberian shelf seas, which has a significant influence on the salinity–tDOM relationship (Anderson and Amon, 2015), should lead to much greater variability in tDOM concentrations along the salinity gradient. During sea-ice growth, DOM is expelled from ice crystals and concentrates in brines, which can then drain into the underlying seawater (Müller et al., 2013). The DOM remaining in the ice undergoes significant fractionation. The humic-like DOM fraction is most prone to rejection from the sea ice along with the brine during freezing, while the protein-like fraction is least prone to this process, which shifts the molecular composition of DOM in the ice towards a higher proportion of low molecular weight compounds (Müller et al., 2013; Granskog et al., 2015a; Retelletti-Brogio et al., 2018; Zablocka et al., 2020). On the other hand, melting of CDOM-poor drifting pack ice (Kowalczyk et al., 2017) or immobile land ice (Wegner et al., 2017) is also impor-
tant because it provides a low-salinity source that can dilute higher DOM concentrations in the surrounding seawater (Amon, 2004; Mathis et al., 2005; Granskog et al., 2015b; Logvinova et al., 2016; Tanaka et al., 2016).

At the end of winter, the LS shelf north of the land-fast ice (Fig. 1) is covered by large areas of open water (polynyas) and thin (< 50 cm) pack ice, which has almost completely retreated by the end of June (Itkin and Krumpen, 2017). The retreat of the pack ice is predominantly controlled by the prevailing atmospheric conditions in April and May (Janout et al., 2016a), whereas land-fast ice that forms in winter in the LS and ESS between 115 and 170°E retreats only during the month of July (Selyushenok et al., 2015). Bauch et al. (2013) and Janout et al. (2016b) showed that the decline in fast ice is also influenced by the input of warm river water during spring freshet. While the maximum extent of fast ice in the LS (∼130 × 10^3 km^2) shows only small annual variations (observation period 1999–2013; Selyushenok et al., 2015), the maximum area of fast ice in the East Siberian Sea (140 to 170°E) varies annually from 130 to 200 × 10^3 km^2 (2012–2021, data from https://www.meereisportal.de, last access: 15 May 2021; Spreen et al., 2008). At the end of winter, the fast ice also reaches its maximum thickness of ∼2 m (Kotch et al., 1994; Li et al., 2020). Thus, the maximum total volume of fast ice in the Laptev and East Siberian Sea is approximately between 520 and 660 km^3. Assuming an average salinity of the fast ice of 4, the land-fast ice meltwater corresponds to a maximum freshwater equivalent of up to ∼580 km^3 (reference salinity 34.8).

The presence of tDOM-poor meltwater from the land-fast ice that contains a high proportion of river water and tDOM-rich river water in the Arctic shelf seas, together with the extreme seasonality of fluvial tDOM input, make it difficult to study tDOM removal processes based on the interpretation of the relationship between tDOM concentration and salinity (Granskog, 2012; Anderson and Amon, 2015). Although degradation processes are obviously important for DOM dynamics in the Arctic Ocean, our study focuses mainly on the physical drivers controlling the distribution of tDOM in the LS and ESS. In particular, we aim to understand whether sea-ice growth and melt have a discernible influence on the distribution of tDOM in the Siberian shelf seas. We attempt to show that degradation of tDOM is probably not the determining factor for the observed tDOM concentration distributions in the LS and ESS but that instead physical mixing of meltwater from land-fast ice with river and seawater plays a key role.

This research is based on one of the most comprehensive bio-optical, DOC and hydrographic data sets from the Siberian Arctic. We report on the first multi-year study of the coloured fraction of dissolved organic matter (CDOM), which includes observations in river runoff during spring freshet (2014), marine waters from the coastal area to the shelf edge of the LS (2010–2019) and ESS (2019), and ice and water samples from the land-fast ice of the southeastern LS (2012). Sampling was carried out in different seasons of the year over a period of 9 years (2010–2019). Although it was not sampled on each expedition (Table 1), we used the stable oxygen isotope data of the water samples to calculate the river water and sea-ice meltwater (sim) fractions.

2 Materials and methods

2.1 Field sampling

Seven summer ship expeditions between 2010 and 2019 and one sea-ice-based winter expedition in 2012 were carried out to perform oceanographic and biogeochemical measurements in the LS (Table 1 and Fig. 1). During the ship-based expeditions, we operated a CTD profiler (conductivity–temperature–depth; Seabird 19+) to sample the basic hydrographic parameters. The CTD is operated on a carousel water sampler (SBE 32SC) allowing for automated water sampling at pre-selected depths. During the winter expedition (Ti12) a stand-alone CTD (Seabird 19+) was lowered through an ice hole along with Nansen water samplers. In this study we used the practical salinity scale to describe salinity (PSS-78). Ice cores (9 cm diameter) were collected in 2012 at stations on the land-fast ice between 19 March and 24 April. Six ice cores taken at three different locations (Fig. 1) in March/April 2012 were analysed (Ti12_ice, Table 1). Sub-samples were taken at 10 cm intervals to represent the different periods of ice formation, with the youngest ice in the lower section and the oldest ice from the first stages of ice formation in early winter in the uppermost sections of the ice core.

Lena River data presented here were collected as part of the Lena 2014 expedition. Samples were taken close to the Samoylov Station (72°22′N, 126°29′E; green pentagon in Fig. 1) in the central part of the Lena Delta from 21 May to 16 June 2014. The sample treatment and methods used are the same as for sea water and ice samples (see below).

2.2 Sample preparation and analytical methods

Water samples were immediately filtered through pre-combusted Whatman GF/F glass microfiber filters (4.7 cm diameter) with a nominal pore size of approx. 0.7 µm. The filtrate was filled into acid cleaned and pre-rinsed high-density polyethylene bottles, stored dark and cold for CDOM analysis, and frozen at −20 °C for DOC analysis. Filtered DOC samples from the LENA 2014 expedition were filled into a pre-combusted 20 mL glass vial, acidified with 25µL HCl (Merck, Suprapur grade, 10 M) and stored in the dark at 4 °C. The ice cores were drilled using an electromechanical ice corer (Kovacs Enterprise, USA) and subsequently placed in polyethylene bags and transported frozen to the land-based laboratory. Within a few hours after coring, the core was placed in polyethylene containers in the dark at room temperature until they were completely melted. Immediately af-
Figure 1. Map of the Laptev (LS) and East Siberian (ESS) seas and station distribution during the ship-based expeditions in summer (red dots). The border between the LS and the ESS runs along 140° E. The LS was sampled in 2010, 2011, 2013, 2014, 2018 and 2019. Only a few stations could be repeatedly sampled in multiple years. The ESS was sampled in 2019. Maps of the stations of each expedition with a detailed description of the location and date are available under the respective data sets (Table 1; Hölemann et al., 2020a–g; Kattner et al., 2010). In addition, samples of land-fast ice (fast ice) and the water column were taken from March to April 2012 (yellow stars). The extent of fast ice describes the situation on 1 May 2011. The grey line between A and B represents the oceanographic transect shown in Fig. 6. Bathymetric data were provide by IBCAO V3 (Jakobsson et al., 2012).

Table 1. Expedition data and the number of samples (#) used in this study. The data are accessible on PANGAEA.

| Campaign | Region | Year | Month | #CDOM | #DOC | Reference | δ18O | Reference |
|----------|--------|------|-------|-------|------|-----------|------|-----------|
| LD10     | LS     | 2010 | Aug   | 9     | 8    | Kattner et al. (2010) |       |           |
| NE10     | LS     | 2010 | Sept  | 234   | 0    | Hölemann et al. (2020a) | X     | Bauch et al. (2018) |
| YS11     | LS     | 2011 | Aug/Sept | 81   | 79   | Hölemann et al. (2020b) | X     | Bauch et al. (2018) |
| Ti12     | LS     | 2012 | Mar/Apr | 28   | 25   | Hölemann et al. (2020c) | X     | Bauch and Thibodeau (2020) |
| Ti12_ice | LS     | 2012 | Mar/Apr | 52   | 47   | Hölemann et al. (2020c) | X     | Bauch and Thibodeau (2020) |
| VB13     | LS     | 2013 | Sept  | 36    | 0    | Hölemann et al. (2020d) | X     | Bauch et al. (2018) |
| Lena 2014| Lena Delta | 2014 | May/June | 44  | 44   | Eulenburg et al. (2019) |       |           |
| VB14     | LS     | 2014 | Sept  | 112   | 108  | Hölemann et al. (2020e) | X     | Bauch et al. (2018) |
| AT18     | LS     | 2018 | Aug/Sept | 102 | 102  | Hölemann et al. (2020f) |       |           |
| TA19_4   | LS & ESS | 2019 | Sept/Oct | 179 | 162  | Hölemann et al. (2020g) |       |           |

After melting, the salinity of the meltwater was determined with a conductivity metre (WTW 197i) with a standard conductivity cell (WTW TetraCon 325), and samples were subjected to vacuum filtration. Also samples for the determination of dissolved inorganic nutrient concentrations, chlorophyll a, particulate matter and stable oxygen isotopes were taken from the ice cores. Only Salinity, DOC and CDOM were used in this study. In addition, under-ice water samples were collected. Sample storage and analytical procedures were identical to those described for water samples.

DOC was determined by high-temperature catalytic oxidation (HTCO) with a Shimadzu TOC-VCPN analyser. In the autosampler, 6 mL of sample volume (pre-combusted or thoroughly rinsed vials) were acidified with 0.12 mL HCl (2 M) and sparged with oxygen (100 mL min⁻¹) for 5 min to remove inorganic carbon. A 50 µL sample volume was injected directly on the catalyst (heated to 680°C). Detection of the
generated CO₂ was performed with an infrared detector. Final DOC concentrations were average values of triplicate measurements. If the standard variation or the coefficient of variation exceeded 0.1 μmol L⁻¹·C or 1 %, respectively, up to two additional analyses were performed and outliers were eliminated. Detection limit was 7 μmol L⁻¹·C with an accuracy of ±2 μmol L⁻¹·C determined with low carbon water and seawater reference material (DOC-CRM, Hansell Research Lab, University of Miami, US). Quality control was assured by measuring one Milli-Q blank and two standards after every six samples.

The optical properties of CDOM provide information on both the amount of DOM present and its chemical properties (Coble, 2007). In order to retrieve the absorption by CDOM, optical density (OD) spectra were analysed on a dual beam spectrophotometer (Specord200, Jena Analytik) within 2 months after the expedition. Spectra were measured from 200 to 750 nm using quartz cuvettes with a path length of 5 cm or 10 cm, according to the expected absorption intensity of the sample. OD of each sample was measured three times against ultrapure water. Napierian absorption per metre was calculated based on the averaged OD value using 2.303 × OD / L, where L is the lengths of the cuvette. In this study, we present the absorption coefficient (m⁻¹) at a wavelength of 350 nm: 

\[ a_{\text{CDOM}}(350) \]

The wavelength was selected to make the results comparable with previous studies in Arctic waters (Granskog et al., 2012; Gonçalves- Araújo et al., 2015; Pavlov et al., 2016). The spectral slope of the absorption spectra in the wavelength range between 275 and 295 nm \( (S_{275-295}) \) and between 300 and 600 nm \( (S_{300-600}) \) was calculated by fitting with an exponential function 

\[ a_{\text{CDOM}}(\lambda) = a_{\text{CDOM}}(\lambda_0) \times e^{-S(\lambda - \lambda_0)} \]

The usefulness of \( S_{275-295} \) and other spectral slopes at shorter wavelengths for determining the origin and diagenesis of CDOM was demonstrated in the studies by Granskog (2012) and Fichot and Benner (2012). Based on the relationship between \( S_{275-295} \) and DOC-normalised lignin yield, Fichot and Benner (2012) showed that \( S_{275-295} \) is lower than 20 μm⁻¹ when the proportion of terrestrial DOC is higher than 50 %. Steeper spectral slopes (i.e. higher \( S_{275-295} \)) are typically associated with a higher proportion of marine CDOM. Steeper \( S_{275-295} \) slopes have also been associated with photochemically induced shifts in molecular weights (Helms et al., 2008). The spectral region between 275 and 295 nm lies at the short-wavelength edge of the natural solar spectrum. Solar ultraviolet radiation shows significant degradation for CDOM in natural aquatic ecosystems. In contrast to 295 nm, almost no photons are present at 275 nm in the lower atmosphere. It is therefore assumed that solar radiation absorbed by CDOM would always lead to a greater change in \( a_{\text{CDOM}}(295) \) than in \( a_{\text{CDOM}}(275) \) and consequently to an increase in \( S_{275-295} \) so that increased slope values are a good indicator of photodegradation, while microbial degradation should have the opposite effect (Helms et al., 2008). However, in marine systems such as the LS and ESS, which are characterised by a high riverine input of terrestrial CDOM, non-terrestrial sources and non-photochemical processes only become visible once the absorption of terrestrial CDOM has been removed to a high degree (Granskog, 2012).

Stable oxygen isotopes were analysed at the Stable Isotope Laboratory of COAS at Oregon State University (Corvallis, USA), applying the CO₂–water isotope equilibration technique, and were analysed by dual inlet mass spectrometry (Thermo, DeltaPlus XL). The overall measurement precision for all \( \delta^{18} \)O analyses was ±0.04 ‰. The \( ^{18} \)O / \( ^{16} \)O ratios were calibrated with Vienna Standard Mean Ocean Water (VSMOW) and reported in the usual \( \delta \) notation (Craig, 1961). For a quantitative interpretation of the oxygen isotope data, an exact match of salinity and \( \delta^{18} \)O values is essential. Therefore, in addition to CTD measurements, bottle salinity was determined directly within the water samples taken for \( \delta^{18} \)O analysis using an AutoSal 8400A salinometer (Guildline Instruments) with a precision of ±0.003 and an accuracy greater than ±0.005. The river water and sea-ice meltwater (sim) contributions can be quantified with a mass-balance calculation, which was previously applied in the Arctic Ocean basins (Bauch et al., 2011) and shelf regions (Bauch et al., 2005). The basis for the mass-balance calculation is the assumption that each sample is a mixture of marine water \( (f_{\text{mar}}) \), river-runoff \( (f_{\text{rw}}) \) and sea-ice meltwater \( (f_{\text{sim}}) \). The following equations determine the balance:

\[ f_{\text{mar}} + f_{\text{rw}} + f_{\text{sim}} = 1 \]
\[ f_{\text{mar}} \cdot S_{\text{mar}} + f_{\text{rw}} \cdot S_{\text{rw}} + f_{\text{sim}} \cdot S_{\text{sim}} = S_{\text{meas}} \]
\[ f_{\text{mar}} \cdot O_{\text{mar}} + f_{\text{rw}} \cdot O_{\text{rw}} + f_{\text{sim}} \cdot O_{\text{sim}} = O_{\text{meas}} \]

where \( f_{\text{mar}} \), \( f_{\text{rw}} \) and \( f_{\text{sim}} \) are the fractions of marine water, river-runoff and sea-ice meltwater in a water parcel, and \( S_{\text{mar}} \), \( S_{\text{rw}} \), \( S_{\text{sim}} \), \( O_{\text{mar}} \), \( O_{\text{rw}} \) and \( O_{\text{sim}} \) are the corresponding salinities and \( \delta^{18} \) O values. \( S_{\text{meas}} \) and \( O_{\text{meas}} \) are the measured salinity and \( \delta^{18} \)O of the water samples. The analytical errors from \( \delta^{18} \)O and salinity measurements add up to approximately ±0.3 % for each of the fractions. The additional systematic error depends on the exact choice of endmember values. When endmember values are varied within the estimated uncertainties (Bauch et al., 2013), both fractions are shifted by up to ~1 % in absolute values, but relative results are qualitatively always conserved even when extreme variations in endmember values are tested (Bauch et al., 2011).

The endmembers are well known for the study area (Bauch et al., 2010, 2013). The only exception is the sea-ice endmember that is based on an assumption on the signature of the source water since sea ice and underlying water can move independently from each other. Within the direct vicinity of the Lena River, the summer surface layer is strongly influenced by summer discharge of the Lena River, so the low \( \delta^{18} \)O summer surface signature in this area is not a useful endmember for the sea ice formed during winter. Therefore, the average surface value from the winter polynya region of −7 ‰ is used in \( \delta^{18} \)O is applied as source water for sea-ice forma-
tion to all stations with a surface δ18O lower than −7 ‰. Differences in calculated sea-ice meltwater and river water fractions in the southern LS, when a constant polynya value is used instead of each station’s surface signature, are generally small (for a detailed discussion see Bauch et al., 2010), and calculated fractions remain stable relative to each other.

3 Results

3.1 CDOM-DOC relationship in the Laptev Sea and East Siberian Sea

Samples collected in the Lena River, LS, ESS, and the adjacent Nansen and Amundsen basins illustrate the range of variability in DOC concentrations and $a_{\text{CDOM}}(350)$. The highest DOC concentrations (> 1200 µmol L$^{-1}$) we observed in river water were measured during the peak of the spring freshet of the Lena River between 29 May and 7 June 2014 (see Sect. 3.2). The lowest riverine DOC concentrations (384 µmol L$^{-1}$) were recorded on 23 May 2014 before the onset of the spring freshet. The coastal waters near the Lena Delta are characterised by DOC concentrations of 185 to 853 µmol L$^{-1}$ in the surface mixed layer (0–10 m depth), with the highest values (> 500 µmol L$^{-1}$, salinity < 5) occurring near the river mouth and in the mixed layer underneath the land-fast ice east of the delta (300–520 µmol L$^{-1}$, salinity 9–20). The marine water masses of the outer shelf and in the basins with salinity above 20 show lower DOC concentrations of 50–75 µmol L$^{-1}$, with the lowest value recorded in the Atlantic Intermediate Water on the continental slope of the LS at a water depth of 300 m.

To characterise the relationship between the DOC concentration and the optical property – $a_{\text{CDOM}}(350)$ – of DOM in water and ice samples, we applied a non-linear regression analysis according to the method described by Juhls et al. (2019) and Matsuoka et al. (2017). Statistical analyses of the water samples from the LS and ESS show a strong relationship between $a_{\text{CDOM}}(350)$ and the DOC concentration ($r^2 = 0.99$, RMSE = 0.8 m$^{-1}$, $n = 527$) (Fig. 2a). In contrast, ice samples from the land-fast ice of the southeastern LS (Fig. 2a, blue diamonds) show a significantly different relationship. The $a_{\text{CDOM}}(350)$ in the ice cores with DOC concentrations > 300 µmol L$^{-1}$ is lower compared to water samples with comparable DOC concentrations. In particular, the DOC-rich (> 400 µmol L$^{-1}$) ice samples show $a_{\text{CDOM}}(350)$ values that are up to 5 times lower than in seawater with the same DOC concentration. All ice samples with DOC concentrations > 200 µmol L$^{-1}$ and $a_{\text{CDOM}}(350) < 2.5$ were taken from the upper 70 cm of a 2 m long ice core from the coastal area near one of the mouths of the Lena River. We also used the model developed by Stedmon and Markager (2001) to differentiate between marine and terrestrial organic matter (Fig. 2b). The model that suggests a dominance of tDOM in the LS and ESS is based on the relationship between the spectral slope coefficient (300–600 nm) and CDOM absorption at 375 nm. In the LS and ESS most data points show high $S_{300–600}$ values (> 17 µm$^{-1}$) that stay relatively constant as $a_{\text{CDOM}}(375)$ decreases. The results of these investigations are discussed in more detail in Sect. 4.1.

3.2 The tDOM characteristics in the Lena River during the spring freshet

The dominant feature of the hydrological cycle of the Lena is the spring freshet in May and June. We sampled this event in the central part of the Lena Delta from 21 May to 19 June 2014 (Lena 2014). The discharge data measured ~200 km upstream at Kyysyr were provided by ArcticGRO (Shiklomanov et al., 2020). In their study based on ArcticGRO discharge data, Juhls et al. (2020) give a more detailed description of the annual variability in the tDOM input of the Lena River during the spring freshet and throughout the year. We corrected the discharge data for the distance between Kyusur and Samoylov Island as described in Juhls et al. (2020) assuming a mean flow propagation speed of 88 km d$^{-1}$.

The highest $a_{\text{CDOM}}(350)$ (Fig. 3b) and DOC concentration (Fig. 3c) were measured during the peak river discharge on 31 May (Fig. 3a). During the observation period 211 km$^3$ of freshwater with a flow-weighted average $a_{\text{CDOM}}(350)$ of 26.1 m$^{-1}$ and a DOC load of 2.83 Tg entered the LS, which is one third of the annual DOC discharge of the Lena.

3.3 The tDOM in the Laptev and East Siberian seas (ESS) and in land-fast ice of the LS

Samples from the LS showed a significant negative linear relationship between salinity and $a_{\text{CDOM}}(350)$ ($r^2 = 0.90$, $n = 659$, $p < 0.01$) (Fig. 4a) and between the fraction of river (meteoric) water ($f_{\text{rw}}$) and $a_{\text{CDOM}}(350)$ ($r^2 = 0.94$, $n = 465$, $p < 0.01$) (Fig. 4b). The data points in the LS are well below the theoretical mixing line resulting from a conservative mixing between the Lena River water discharged after the spring freshet (post-freshet, “Summer” in Fig. 4), which has an average $a_{\text{CDOM}}(350)$ of 14.4 m$^{-1}$ (standard deviation 3.4 m$^{-1}$, $n = 26$; Juhls et al., 2020), and the tDOM-rich seawater (salinity > 34) of the Nansen Basin. Looking at the theoretical conservative mixing line of the flow-weighted annual river input of CDOM (“Annual” in Fig. 4) that includes the spring freshet (April 2018 to April 2019, $a_{\text{CDOM}}(370)$ of 18.7 m$^{-1}$, calculated from data published by Juhls et al., 2020) and the seawater, the discrepancy becomes even more apparent. The freshwater endmember calculated from the data in the LS on the basis of salinity has an $a_{\text{CDOM}}(350)$ of 11.7 m$^{-1}$ (interception of linear fit in Fig. 4a). The $a_{\text{CDOM}}(350)$ of the river water endmember calculated from $f_{\text{rw}}$ (interception of linear fit in Fig. 4b) is ~10 m$^{-1}$, which is about 50% lower than the annual flow-weighted average $a_{\text{CDOM}}(350)$ of the river water. Whether
Figure 2. (a) The relationship between DOC and $a_{\text{CDOM}}(350)$ for Lena River water, ice samples and seawater samples from the LS and ESS. The regression and $r^2$ was calculated only on the basis of river and seawater samples. Panel (b) shows the model developed by Stedmon and Markager (2001) to differentiate between marine and terrestrial organic matter. Data points from the LS and ESS that lie within the model boundaries of the Stedmon and Markager (2001) model (dotted red lines) are defined as marine CDOM, while the rest are terrestrial in origin.

To describe the influence of the formation and melting of sea ice on the distribution of tDOM in the LS, the stable oxygen isotope composition of the water was studied. At salinities $> 25$, most water samples, which are well below the regression line (Fig. 4a, linear fit) showed an increased fraction of sea-ice meltwater ($f_{\text{sim}}$). In contrast, many samples above the regression line showed higher proportions of brine influence ($-f_{\text{sim}}$). The addition of brines, which are expelled from the sea ice during formation, was most apparent in a winter-water sample from the northern edge of the land-fast ice taken at 10 m water depth that showed a minimum $f_{\text{sim}}$ of $-20\%$ at a salinity of 29.7 and a comparatively high $a_{\text{CDOM}}(350)$ of $\approx 4 \text{ m}^{-1}$. Shelf waters during winter also showed higher DOC concentrations (mean 254$\mu$mol L$^{-1}$, salinity from 10 to 31) compared to summer shelf waters of the same salinity (mean 199$\mu$mol L$^{-1}$).

Sampling in the ESS was carried out in August and September 2019. Across the ESS, salinities were above 20 in 2019 (Fig. 5a). Even in coastal areas near the Indigirka and Kolyma rivers surface-water salinities were above 20. Moreover, $a_{\text{CDOM}}(350)$ in the ESS (Fig. 5a, coloured dots) was significantly lower compared to LS water (Fig. 5a, black dots) at similar salinities.

In the LS, $S_{275-295}$ showed an inverse relationship with $f_{\text{fw}}$ (Fig. 4b), indicating on the one hand a fluvial source of CDOM and on the other hand a more intense photobleaching of CDOM in the water masses on the outer shelf and continental margin. When interpreting the slope data, however, it must be kept in mind that in marine systems characterised by a high input of terrestrial CDOM, non-terrestrial sources and non-photochemical processes only become visible when the absorption of terrestrial CDOM has been removed to a high degree (Granskog, 2012).

Figure 3. (a) Corrected daily Lena River discharge data. (b) $a_{\text{CDOM}}(350)$ and $S_{275-295}$, and (c) DOC concentration measured near Samoylov Island in the Lena Delta during the spring freshet in May/June 2014.

this can be explained by the dilution of low-tDOM meltwater from the land-fast ice of the southeastern LS (Fig. 5b) that contains up to 90% river water (Eicken et al., 2005) is discussed in Sect. 4.2. The group of data points with $f_{\text{fw}}$ between 40% and 60% that fall below the regression line are mostly from the surface water of the southern LS and were sampled in September 2011 (Fig. 4, YS11-data points outlined in red). The possible reason for the deviation in this sample cluster is discussed in Sect. 4.3.
Figure 4. (a) Salinity, $a_{\text{CDOM}}$(350) and the percentage of sea-ice meltwater fraction ($f_{\text{sim}}$ %) measured in the LS in summer (NE10, LD10, YS11, VB13, VB14, AT18 and TA19_4) and (b) percentage of river water ($f_{\text{rw}}$ %), $a_{\text{CDOM}}$(350) and $S_{275-295}$. The solid black line represents the linear regression fit to the data in the LS. The dashed black lines show the theoretical conservative mixing line between Lena River water after spring freshet (Summer, $a_{\text{CDOM}}$(350) of 14.4 m$^{-1}$ calculated from Juhls et al., 2020) and the marine endmember (Nansen Basin, NB, seawater), as well as the theoretical conservative mixing line of year-round flow-weighted average CDOM absorption of the Lena River (Annual, $a_{\text{CDOM}}$(350) of 18.7 m$^{-1}$ based on year-round measurements in the Lena Delta, April 2018–April 2019; Juhls et al., 2020) and the marine endmember. Red outlined dots are water samples from the surface layer (< 20 m) taken north and east of the Lena Delta in September 2011. Black dots in (a) represent samples on which stable oxygen isotope analysis was not performed (LD10).

Figure 5. (a) Salinity and $a_{\text{CDOM}}$(350) in the ESS (August and September 2019, coloured dots) and LS (black dots). The broken line shows the theoretical conservative mixing line between the Lena River water that enters the LS after the spring freshet (post-freshet) and the marine endmember (Nansen Basin seawater, NB). The colour of the dots shows the slope of the absorption spectra in the range between 275 and 295 nm ($S_{275-295}$). (b) Salinity, $a_{\text{CDOM}}$(350) and $S_{275-295}$ in land-fast ice (squares) and sub-ice water samples (diamonds) in the LS collected in (March/April 2012). The arrows indicate the direction of theoretical conservative mixing lines between the land-fast-ice meltwater and the Lena River water, as well as between the meltwater and the marine endmember. The black dots represent the samples from the LS and ESS (2010–2019).

The DOC concentration and optical properties of DOM in the land-fast ice of the southeastern LS were determined in March and April 2012. The ice core samples had a salinity of 3.6 and an $a_{\text{CDOM}}$(350) of 0.99 m$^{-1}$ (median of all cores and subsections; $n = 52$), which was approximately 10 % of the $a_{\text{CDOM}}$(350) observed in seawater with comparable salinity (Fig. 5b). Unfortunately, $\delta^{18}$O measurements of LS land-fast ice cannot be used directly as endmember for sea-ice meltwater as they represent a mixture of seawater and river water contained within the ice. The median of the DOC concentration in the ice was 96.2 µmol L$^{-1}$. The highest $a_{\text{CDOM}}$(350) values of up to 4 m$^{-1}$ were observed in the lowermost 20 cm of an ice core sampled near the northern border of the land-fast ice. The high $a_{\text{CDOM}}$(350) coincided with high chlorophyll a concentrations (Katya Abramova, personal communication, 2016). However, CDOM absorption spectra of algae-rich ice samples exhibited no ultraviolet absorption shoulders that indicate mycosporine-like amino acids from sympagic autotrophic organisms (Xie et al., 2014; Granskog et al., 2015b). Similar to the marine wa-
ters with an $a_{\text{CDOM}}(350) < 5 \text{ m}^{-1}$ (Figs. 4a and 5b), the landfast ice showed high $S_{275-295}$ values with a median slope of 20.7 $\mu$m$^{-1}$. An exception was the two chlorophyll-rich ice samples from the northern edge of the land-fast ice with slopes below 18 $\mu$m$^{-1}$, which corresponds to the $S_{275-295}$ slope of the tDOM in the winter runoff of the Lena River but which could also be caused by a higher proportion of marine DOM.

4 Discussion

4.1 Dynamics of tDOM in the freshwater-influenced LS during spring and summer

Our results show that $a_{\text{CDOM}}(350)$ correlates strongly with the DOC concentration in riverine and marine LS and ESS waters (Fig. 2a). The high correlation is clear evidence for the terrestrial origin of the DOM, which is transported with the river water to the LS and ESS (Lara et al., 1998; Dittmar and Kattner, 2003; Amon et al. 2012; Mann et al., 2016; Kaiser et al., 2017b; Juhls et al., 2019). The results of the data analysis using the model developed by Stedmon and Markager (2001) also indicate a dominance of tDOM in the LS and ESS. These results are consistent with those of Gonçalves-Araujo et al. (2015), who investigated the composition and concentration of CDOM in the southeastern LS using excitation emission matrix spectroscopy and parallel factor analysis from a data set collected in September 2013. They found that CDOM in the region of freshwater influence (ROFI) of the LS was dominated by terrestrial humic-like material. Kattner et al. (1999) were also able to show on the basis of chemical analyses of DOM that the high input of tDOM not only shapes the ROFI of the Lena but that 60% of the DOC of the entire LS and the adjacent Eurasian basin are also of terrestrial origin. One reason for the generally low DOM contribution from marine algae, which would significantly alter the dispersion in the CDOM vs. DOC dependence (Danhiex et al., 2017), could be the timing of sampling, which was mainly conducted between late August and mid-September when chlorophyll concentrations on the LS shelf are generally below 1 mg m$^{-3}$ (Janout et al., 2016a).

To describe the tDOM dynamics in the Siberian shelf seas we analysed the optical properties of DOM along the salinity gradient in the LS, the ESS and the adjacent continental slope. In water samples from the LS, we found a statistically robust negative correlation between $a_{\text{CDOM}}(350)$ and salinity ($r^2 = 0.90$, $n = 659$, $p < 0.01$) (Fig. 4a) and between $a_{\text{CDOM}}(350)$ and the fraction of river (meteoric) water ($f_{\text{rw}}$) and ($r^2 = 0.94$, $n = 465$, $p < 0.01$) (Fig. 4b). The strong linear relationship suggests that tDOM mixes conservatively with seawater during the transit of river water across the shelf. The calculated $a_{\text{CDOM}}(350)$ concentration of the river water endmember of $\approx 10 \text{ m}^{-1}$ (Fig. 5, linear fit of samples from the LS) is approximately 30% below the mean $a_{\text{CDOM}}(350)$ absorption measured in the Lena River after the spring freshet (July–September, 14.4 m$^{-1}$ with a standard deviation of 3.4 m$^{-1}$; Juhls et al., 2020) and nearly 50% below the flow-weighted annual average $a_{\text{CDOM}}(350)$ of the Lena River of 18.7 m$^{-1}$ observed in 2018/2019 that also includes the spring freshet (data from Juhls et al., 2020). Because $a_{\text{CDOM}}(350)$ in river water may show intra-seasonal fluctuations between 10 and 22 m$^{-1}$ in the post-freshet season (Juhls et al., 2020), the relatively high $a_{\text{CDOM}}(350)$ of 13.6–16 m$^{-1}$ at salinities < 6 observed in the river plume near the Lena Delta in summer 2010 (Fig. 4a) were likely caused by short-term fluctuations of $a_{\text{CDOM}}(350)$ in the river.

The dominance of riverine input of terrestrial DOM and the resulting close relationship between salinity and $a_{\text{CDOM}}(350)$ is also evident from a hydrographic transect across the LS shelf observed in September 2010 (Fig. 6; the area of the transect is indicated in Fig. 1). The oceanographic transect runs from the mouth of the Lena River in the southeastern LS (A, Fig. 6) to the Taymyr Peninsula in the northwestern LS (B, Fig. 6). While the southeastern LS is dominated by the tDOM-rich river water plume of the Lena River, the northwestern LS is mainly affected by the inflow of tDOM-poor seawater from the Nansen Basin (Janout et al., 2013).

Assuming conservative mixing, the input of more than 200 km$^3$ of tDOM-rich freshwater with a flow-weighted average $a_{\text{CDOM}}(350)$ of 26.1 m$^{-1}$ during the spring freshet in May and June should result in shelf $a_{\text{CDOM}}(350)$ values that are above the theoretical mixing line between the river water and the marine endmember (Fig. 4b). However, the $a_{\text{CDOM}}(350)$ vs. $f_{\text{rw}}$ distribution of all summer (August/September) expeditions to the LS does not indicate the presence of freshet-related river water with high $a_{\text{CDOM}}(350)$ values on the shelf (Fig. 4b). Alling et al. (2010) suggested that the absence of tDOM-rich waters from the freshet on the
LS shelf in 2008 was caused by a rapid wind-driven eastward transport into the adjacent ESS, but this is not consistent with the observation that when winds are predominantly easterly, as they were in the summer of 2008, the ROFI in the LS extends far north to the outer shelf of the LS (Janout et al., 2020). The same atmospheric forcing as in 2008 was also observed in 2011, when strong southeasterly summer winds coincided with mixed layer salinities below 16 to 300 km north of the Lena Delta (Janout et al., 2020). The northern part of the ROFI should therefore contain a significant amount of tDOM-rich freshwater from the spring freshet, but this is not evident from the data (data from YS11, Table 1).

Another explanation for the absence of freshet-related high \( a_{\text{CDOM}}(350) \) values within the ROFI could be the removal of tDOM, i.e. nonconservative mixing. This would imply that \( \sim 50\% \) of the tDOM discharged into the southeastern LS in May and June had already been removed prior to the August and September sampling period. In this context, photochemical processes, flocculation of tDOM or rapid microbial degradation could play a major role. A previous study in the Mackenzie River, Canada, showed that photodegradation of tDOM was highest after spring freshet (Osburn et al., 2009). On the other hand, Belanger et al. (2006) noted that under a closed ice cover, photochemical reactions of tDOM carried by the Mackenzie River into the Beaufort Sea do not play a significant role in the degradation of tDOM.

In the turbid nearshore waters of southeastern Hudson Bay, which have a high proportion of river water (\( f_{\text{rw}} > 25\% \)), self-shading could additionally slow photochemical reactions (photobleaching) of tDOM (Granskog, 2012). Since during the Lena spring freshet the turbid river plume mostly flows below the land-fast ice (Hölemann et al., 2005) that covers the inner shelves from October to mid-July (Barreis and Görgen, 2005; Selyuzhenok et al., 2015), photodegradation of tDOM should not play an important role in the LS either. Flocculation of DOM in the Lena River plume has been postulated as a theoretically possible removal mechanism for DOM in summer (Gonçalves-Araujo et al., 2015), which was, however, not directly observed. An investigation of the under-ice river plume during the spring freshet in 1996 (Hölemann et al., 2005) also gave no indication of flocculation processes. Furthermore, Gonçalves-Araujo et al. (2015) found that the degradation of tDOM by microbial processes plays only a minor role in the Lena Delta region. Nevertheless, if we would assume that 50% of the tDOM were removed shortly after the spring freshet, the \( a_{\text{CDOM}}(350) \) values observed in the LS should be much lower because the seawater is further diluted by CDOM-poor meltwater from the land-fast ice (Fig. 5b) that melts in the southeastern LS in June/July. This process, important to the LS and ESS, is discussed in more detail in the next two chapters.

4.2 The importance of land-fast ice meltwater for the distribution of tDOM in the LS

DOM is expelled from the ice matrix during sea-ice growth and is enriched in the brine (Giannelli et al., 2001; Müller et al., 2013). Only about 10 to 40% of the original DOM and other impurities remain in the sea ice (Petrich and Eicken, 2010). Furthermore, Müller et al. (2013) were able to show that a relatively higher proportion of DOM is incorporated into the sea ice in relation to the dissolved inorganic substances. Most of the DOM then flows off into the underlying water column along with the saline brine (Amon, 2004; Anderson and Macdonald, 2015). This explains the observed low \( a_{\text{CDOM}}(350) \) of 0.99 m\(^{-1}\) (median) and DOC concentration of 96.2 \( \mu \text{mol L}^{-1} \) (median) in the LS land-fast ice that forms from tDOM-rich surface waters sourced by the Lena River (Fig. 5b). Helms et al. (2008) showed that as a result of this process, the molecular weights of DOM in the ice and brine also decrease. Jørgensen et al. (2015) further suggest that the transformations of DOM during sea-ice formation also increase its bioavailability. We assume that the transformation processes of the DOM during ice growth, which shifts the molecular composition of DOM in the ice towards a higher proportion of low molecular weight compounds (Müller et al., 2013; Granskov et al., 2015a; Retelletti-Brogi et al., 2018; Zabolocka et al., 2020), are also responsible for the high \( S_{275-290} \) values (> 19 \( \mu \text{m}^{-1} \)) of CDOM in the ice (Fig. 5b).

The formation of the land-fast ice, which stores 30%–50% of the annual freshwater discharge of the Lena River (Eicken et al., 2005), begins in mid-November with phases of rapid development in January and February (Selyuzhenok et al., 2015) during which the release of tDOM-rich brine is highest. In the following summer, when the land-fast ice melts, the tDOM-poor meltwater mixes with the ambient seawater and thus could dilute the tDOM concentration of the surface mixed layer (Mathis et al., 2005; Logvinova et al., 2016). North of the Lena Delta, sea-ice melt begins in June (Janout et al., 2020) and progresses eastwards, while the seaward edge of the land ice slowly moves southwards (Selyuzhenok et al., 2015). In general, the ice in the southeastern LS retreats completely by the end of July. The melting of sea-ice and land-fast ice in the southeastern LS thus occurs at the same time and in the same region where the spring freshet enters the LS, leading to a mixing of the two surface water masses (Bauch et al., 2013).

To assess the influence of mixing on the tDOM concentration, we calculated the first tDOM budget for the southeastern LS. During the course of the freshet in 2014 the Lena discharged about 211 km\(^3\) of freshwater with a flow-weighted average \( a_{\text{CDOM}}(350) \) of 26.1 m\(^{-1}\) and a DOC load of 2.83 Tg. The maximum land-fast ice area in the southeastern LS is \( 134 \times 10^3 \) km\(^2\) (Selyuzhenok et al., 2015) with an average ice thickness of 2.04 m (Kotchetov et al., 1994; Barreis and Görgen, 2005). With a salinity of 3.6 (median), the land-fast
5 Sea-ice meltwater as possible cause for the $a_{\text{CDOM}}(350)$ anomaly in the LS in 2011 and the $a_{\text{CDOM}}(350)$ distribution in the ESS in 2019

Previous studies indicate that approximately 30% of the river-induced DOC is already remineralised on the shelf (Cooper et al., 2005), with the western ESS being a hotspot for organic matter degradation (Anderson et al., 2011; Anderson and Amon, 2015; Semiletov et al., 2016). Thus, increased removal of tDOM could also be the cause for the low-tDOM cluster of samples that we observed in the LS in September 2011 (red outlined dots in Fig. 4a and b). This
cluster represents water samples from the upper water column (< 20 m) north of the Lena Delta that has a \(f_{\text{sw}}\) of 40 \%-60 \% (Fig. 4b). The \(\text{a}_{\text{CDOM}}(350)\) in the low-\(\text{a}_{\text{CDOM}}(350)\) cluster was up to 50 \% lower than in samples with the same \(f_{\text{sw}}\) percentage lying on the mixing line of river water (summer discharge) and seawater. The general hydrography of the LS in September 2011 was characterised by low surface mixed layer salinities and sea surface temperatures (SSTs), which were \(\sim 2 \, ^\circ\text{C}\) higher than the long-term average (ERA5; Copernicus Climate Change Service, 2017). High SSTs caused by solar warming support the assumption that photodegradation could be the major factor leading to tDOM loss and a \(S_{275-295} > 20 \, \mu\text{m}^{-1}\) (Fig. 4b). An alternative explanation to the removal of tDOM in 2011 could be a change in the relative proportion of one of the freshwater endmembers or a change in concentration in one of the tDOM sources. In 2011, large areas of the southeastern LS were covered by melting land-fast ice until the end of July. Exceptionally strong southeasterly winds in August 2011 (Janout et al., 2020) steered the land-fast ice meltwater plume to the northwest, resulting in additional mixing of CDOM-poor meltwater into the shelves north of the Lena Delta and further dilution of the shelf water, leading to low \(\text{a}_{\text{CDOM}}(350)\).

The relationship between salinity and \(\text{a}_{\text{CDOM}}(350)\) measured in the ESS in summer 2019 was significantly different from the relationship observed in the LS. The entire ESS shelf had salinities above 20, and \(\text{a}_{\text{CDOM}}(350)\) was about 50 \% lower than in LS samples having the same salinity (Fig. 5a coloured dots and Fig. 7 red dots). During sampling in the last week of September 2019, the ESS was ice-free. However, during the first week of July 2019, the ESS was almost completely covered with land-fast ice and drifting pack ice that did not completely melt until the last week of July (data from https://www.meereisportal.de, last access: 9 February 2021; Spreen et al., 2008).

Pugach et al. (2018) found that the distribution of tDOM concentration in the ESS is mainly controlled by wind forcing. During our sampling in the ESS in 2019, winds from the east (ERA5; Copernicus Climate Change Service, 2017) pushed the inflow from the Pacific Ocean westward far onto the ESS shelf. At the same time, southeasterly winds over the LS might have blocked the Lena ROFI from extending into the western ESS (Anderson et al., 2011; Janout et al., 2020). In addition, summer 2019 was characterised by anomalously low river discharge into the LS and ESS (ArcticGRO version 2020-01-23; Shiklomanov et al., 2020). The wind forcing and low river discharge led to a tDOM and salinity distribution in the ESS in 2019 that was comparable to the distribution in 2008 and 2011, during which wind forcing was similar (Alling et al., 2010; Pugach et al., 2018). In contrast, in summers when the Lena River ROFI extends further eastward, the western ESS is characterised by lower salinities and higher tDOM concentrations (Pugach et al., 2018), with a salinity-tDOM relationship that corresponds to the one we observed in the ROFI of the LS. Alling et al. (2010) assumed that due to the long residence time of the water of the Lena River on the ESS shelf, degradation of tDOM may be more advanced, leading to generally low tDOM concentrations in the western ESS, as observed in August and September 2008. This assumption is supported by the generally high \(S_{275-295}\) values (Fig. 5a), which indicate that the CDOM in the ESS has already been strongly transformed (e.g. by photochemical processes), but as in the LS, the addition of large amounts of DOM-poor meltwater from the land-fast ice and meltwater from the pack ice, which may show even lower CDOM absorptions (Kowalczuk et al., 2017), should result in a strong dilution of the riverine tDOM. The ESS west of 170°E is characterised by an extensive land-fast ice belt that varies in extent from 130 000 to 200 000 km². The land-fast ice, which contains a freshwater equivalent of 230–360 km³, usually melts back in the first 2 weeks of July, and drifting fields of decaying ice might persist until August. We assume that the absence of the Lena ROFI in the western ESS, the generally low river runoff and the resulting higher fraction of low-tDOM sea-ice meltwater in the ESS led to the comparatively low tDOM concentrations in the western ESS observed in 2008 and 2019. This assumption contradicts Alling et al. (2010), who emphasise that the analysis of oxygen isotope data showed no evidence of meltwater input in the western ESS in September 2008. However, as the analysis of the ice distribution in 2008 (data from https://seaice.uni-bremen.de/data, last access: 9 February 2021; Spreen et al., 2008) shows, the land-fast ice still covered large areas of the southern ESS in mid-July. It is therefore more likely that the difficulty in interpreting oxygen isotope data from seasonally ice-covered shelves, which are characterised by high sea-ice export rates and thus high brine fractions in the water column (negative \(f_{\text{sim}}\) values; see Sect. 4.2), has resulted in the masking of the sea-ice meltwater signal (positive \(f_{\text{sim}}\) value).

5.1 Transport dynamics of tDOM-rich brines in the LS

We used fast ice and seawater data from the southeastern LS to estimate how much DOC might be expelled along with brine from growing land-fast ice in the LS. The observed average DOC concentration in surface waters (0–5 m) east of the Lena Delta (south of 73.4°N and east of 125.0°E) was 475 \(\mu\text{mol L}^{-1}\) (SD ± 165 \(\mu\text{mol L}^{-1}\)). Thus, the observed median DOC concentration in the land-fast ice of 96.2 \(\mu\text{mol L}^{-1}\) indicates that 379 \(\mu\text{mol L}^{-1}\) has been removed during ice growth. This resulting value was multiplied by the total volume of fast ice (273 km³; Kotchetov et al., 1994; Barreis and Görgen, 2005; Selyuzhenok et al., 2005). Assuming that the DOC is removed from the ice along with the brines, about 1.2 Tg yr⁻¹ (± 0.54 Tg) DOC would thus be expelled from the growing land-fast ice. The process of brine release is reflected in the water samples from the polynya at the northern land-fast ice edge in the southeastern LS, which show high
brine fractions with simultaneously increased $a_{\text{CDOM}(350)}$ (Ti12, winter 2012). This budget calculation, however, does not take into account that the DOM in the brines has a higher bioavailability (Jørgensen et al., 2015). Thus, the rapid removal of DOC in the brine or the remineralisation of the remaining ice-bound DOC could also play an important role.

Due to the low salinity of the surface mixed layer in the southeast LS at the beginning of the freezing season and the continuous outflow of freshwater from the Lena River in winter (Juhl et al., 2020), the loss of buoyancy, which resulted from the addition of brine to the surface mixed layer, is not high enough to completely erode the pycnocline by convective mixing processes. This leads to permanently stratified waters under the land-fast ice of the southeastern LS (Bauch et al., 2009a), as well as in the polynya north of the Lena Delta, even during phases of high ice production (Krumpen et al., 2011). The strong stratification results in the trapping of tDOM-rich brines in the upper water column followed by advection, together with the winter river discharge (Macdonald et al., 1995). How fast the brines are advected across the shelf depends on the ocean currents in winter. Eicken et al. (2005) described under-ice spreading velocities of 1–2.7 cm s$^{-1}$. Moored velocity records from below the land-fast ice (1998–1999, Hölemann unpub. data) showed a residual northeastward flow of $\sim 2$ cm s$^{-1}$. These velocities are on the same order of magnitude as those measured north of the Lena Delta in winter (Bauch et al., 2010; Janout et al., 2013). Further north the geostrophic velocity fields show eastward velocities above 5 cm s$^{-1}$ with northward directions on the northeastern LS shelf in March/April (Kwok and Morrison, 2011). At the continental margin residual eastward velocities can reach more than 20 cm s$^{-1}$ (Janout et al., 2015). The tDOM-rich brine formed in the southeast LS in December could thus be transported over several hundred kilometres in a northeasterly direction until the end of June, when the land-fast ice melts. This is in accordance with Bauch et al. (2009b) who showed that the residence time of the brines on the shelf could be as short as 1 year. A significant proportion of the surface waters (0–20 m) of the LS and western ESS leaves the Siberian shelf north of the New Siberian Islands (Morison and Kwok, 2012) and supplies the Transpolar Drift Stream with tDOM-rich water masses (Charette et al., 2020), while denser bottom waters flow north of the New Siberian Island further to the east and leave the shelf in the western ESS (Anderson et al., 2017). The transport of tDOM in the water masses at the upper halocline is confirmed by investigations in the East Greenland Current where a higher CDOM absorption occurring between 30 and 120 m water depth at salinities between 32 and 33 is explained by a high fraction of brine and river water from the Siberian shelves (Granskog et al., 2012).

During the northward transport of the brine-enriched water masses across the shelf, an increase in density occurs due to the further influx of brines from ice formation in leads and coastal polynyas of the western LS (Janout et al., 2017). Erosion of the density stratification at the end of winter and mixing with denser water masses from the western shelf of the LS could dilute the tDOM-rich brines from the southeastern LS but at the same time increase the density and bring them to greater water depths where they then flow into the Arctic halocline. The seasonal evolution of the density stratification in the LS is described in more detail in Janout et al. (2020). The water depth at which the brine is transported across the LS shelf and into the Arctic halocline depends mainly on the density structure of the water column in winter, which in turn depends on the position of the ROFI in the previous summer (Bauch et al., 2012). An eastward-directed transport south of the New Siberian Islands towards the ESS at a depth greater than $\sim 20$ m is inhibited by the shallow water depths of the Dmitry Laptev (10 m) and Sannikov straits (18 m).

6 Conclusions

The eastern LS and western ESS together represent a region where much of the freshwater-influenced waters of the Siberian shelves discharge into the transpolar drift current and the Arctic halocline, which carries the shelf waters towards Greenland and the Nordic seas (Morison et al., 2012; Timmermans and Marshall, 2020). This region is thus a key region for a better understanding of the Arctic marine carbon cycle. Analysis of the extensive data set in this study, spanning several years and different seasons, illustrates that the distribution of tDOM in the LS and ESS is mainly determined by the physical mixing of river water, sea-ice meltwater and seawater. Our study highlights that the formation and melting of land-fast ice in the Laptev and East Siberian seas significantly shapes the concentration distribution of tDOM in the area of the Siberian shelf seas. In this context, the observed concentration distribution on the shelves indicates a conservative mixing behaviour of tDOM introduced by the river rather than a removal or an additional DOM supply from other sources. The reason for this could be the short residence time of the river water on the Siberian shelves, as well as a reduced photochemical degradation of the tDOM due to the ice cover of the southern shelves lasting until July. The extremely high CDOM absorption and suspended matter concentrations within the ROFI (Juhl et al., 2019; Heim et al., 2014), which lead to a self-shadowing effect, may also reduce photodegradation. The results of the study also illustrate that the growth of fast ice and the associated formation of CDOM-rich brines have an important role in the transport pathways of tDOM across the Siberian shelves and the AO.

The duration of the land-fast-ice season in the LS is reduced by 2.8 d per year (observational period 1999 to 2013; Seyushenok et al., 2015), while in the second decade of the 21st century the onset of the spring freshet of the Lena River happens about 6 d earlier than at the beginning of the observational period in 1940 (Shiklomanov et al., 2020). Further changes of the ice regime and the timing of spring freshet...
will certainly have an impact on the dynamics of tDOM in the AO. In addition, the decline of Arctic sea ice and the associated longer ice-free season will lead to changes in wind forcing in the shelf systems of the Arctic and to an increased input of solar radiation into the water column. This will significantly change freshwater transport pathways, the heat content of the water column, and stratification in the LS and ESS. The heat content in turn influences the formation of new ice and thus also the production of DOM-rich brines. Because density stratification also controls where and at which depth the DOM-rich brine leaves the shelf, changes in stratification also impact the future transport pathways of tDOM in the AO. Studying these processes is important not only to decipher the Arctic carbon cycle but also because it regulates physical processes such as radiative forcing in the upper ocean, which has important effects on, for example, sea surface temperature, water column stratification and UV penetration (Pegau, 2002; Hill, 2008; Granskog et al., 2015b; Gnanadeskian et al., 2019; Soppa et al., 2019).

Our special thanks go to Heidemarie Kassens who headed all summer and winter expeditions and made sure that the scientific programme could be carried out as planned even under the most difficult conditions. We greatly acknowledge Leonid A. Timokhov, Heidemarie Kassens and Vladimir V. Ivanov for coordinating the German–Russian Laptev Sea System project.

**Financial support.** This research has been supported by the Bundesministerium für Bildung und Forschung (grant nos. 03G0833 and 03F0776). Bennet Juhrs was supported by Geo. X, the Research Network for Geosciences in Berlin and Potsdam (grant no. SO_087_GeoX).

The article processing charges for this open-access publication were covered by the Alfred Wegener Institute, Helmholtz Centre for Polar and Marine Research (AWI).

**Review statement.** This paper was edited by Anja Engel and reviewed by Piotr Kowalczuk and one anonymous referee.

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