Nonconservative behavior of dissolved organic carbon across the Laptev and East Siberian seas

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[1] Climate change is expected to have a strong effect on the Eastern Siberian Arctic Shelf (ESAS) region, which includes 40% of the Arctic shelves and comprises the Laptev and East Siberian seas. The largest organic carbon pool, the dissolved organic carbon (DOC), may change significantly due to changes in both riverine inputs and transformation rates; however, the present DOC inventories and transformation patterns are poorly understood. Using samples from the International Siberian Shelf Study 2008, this study examines for the first time DOC removal in Arctic shelf waters with residence times that range from months to years. Removals of up to 10%–20% were found in the Lena River estuary, consistent with earlier studies in this area, where surface waters were shown to have a residence time of approximately 2 months. In contrast, the DOC concentrations showed a strong nonconservative pattern in areas with freshwater residence times of several years. The average losses of DOC were estimated to be 30%–50% during mixing along the shelf, corresponding to a first-order removal rate constant of 0.3 yr^{-1}. These data provide the first observational evidence for losses of DOC in the Arctic shelf seas, and the calculated DOC deficit reflects DOC losses that are higher than recent model estimates for the region. Overall, a large proportion of riverine DOC is removed from the surface waters across the Arctic shelves. Such significant losses must be included in models of the carbon cycle for the Arctic Ocean, especially since the breakdown of terrestrial DOC to CO_2 in Arctic shelf seas may constitute a positive feedback mechanism for Arctic climate warming. These data also provide a baseline for considering the effects of future changes in carbon fluxes, as the vast northern carbon-rich permafrost areas draining into the Arctic are affected by global warming.

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1. Introduction

[2] The Eurasian Arctic shelf is the world's largest continental shelf. It receives extensive runoff of terrestrial organic carbon from the many rivers draining the Siberian Arctic landscape. The Arctic tundra and taiga drainage basins hold 30%–50% of the global soil carbon, much within shallow permafrost [*Gorham*, 1991; *Tarnocai et al.*, 2009]. Since this region is subjected to larger climate warming than elsewhere, and dramatic changes in the release of soil carbon are expected to occur, better understanding of the dynamical fate of the terrestrial carbon exported to the Eurasian-Arctic shelf seas is essential.

[3] A distinctive feature of the Arctic Ocean is its shallow low-salinity shelves, which are particularly extensive on the Eurasian side. The East Siberian Arctic Shelf (ESAS), i.e., the Laptev and East Siberian seas, alone constitutes 20% of the total area of the Arctic Ocean, with a mean depth of only

50 m [*Stein and Macdonald*, 2004; *Jakobsson et al.*, 2008]. These Arctic shelf seas play a key role in land-sea interaction processes and in the transport and transformations of terrestrially exported organic matter.

[4] Each year, Arctic rivers transport 25–36 Tg of dissolved organic carbon (DOC) to the Arctic Ocean, which is ~10% of the global riverine DOC discharge [*Schlünz and Schneider*, 2000; *Raymond et al.*, 2007]. The Siberian rivers have among the highest DOC concentrations of the world's main rivers, with concentrations typically between 500 and 900 μM DOC [*Gordeev et al.*, 1996; *Stein and Macdonald*, 2004; *Cooper et al.*, 2008]. Eastern Siberia and the adjacent seas are predicted to experience the highest increase in temperature on Earth as climate changes [*Zwiers*, 2002], and now observations indicate that the region is warming even faster than predicted [*Richter-Menge et al.*, 2006]. Hydrological runoff has also increased substantially in the region [*Savelieva et al.*, 2000; *Peterson et al.*, 2002, 2006]. It has been suggested that these changes will lead to increased DOC export to the Arctic Ocean due to increased river runoff, the thawing of permafrost, the increased exposure of old sequestered carbon to the hydrological cycle, and increased productivity in the terrestrial system [*Gorham*, 1991; *Frey and Smith*, 2005]. However, some studies point to a decrease in DOC export with increased temperature, due to a transition from surface-water-dominated systems to more groundwater-dominated systems [*Striegl et al.*, 2005], depending upon the features of individual catchments. In either case, it is likely that terrestrial carbon discharges to the Laptev and East Siberian seas will significantly change in the future [*Frey and McClelland*, 2009; *McGuire et al.*, 2009].

[5] The fate of terrestrial DOC in the marine environment is still a matter of debate. Some have argued that riverine DOC in high-latitude areas is refractory and behaves conservatively in the estuaries and shelves of the Arctic Ocean based upon shelf DOC-salinity relationships, with little influence on biological cycles and the net ocean-atmosphere exchange of CO_2 [*Anderson*, 2002; *Dittmar and Kattner*, 2003; *Köhler et al.*, 2003; *Amon*, 2004; *McGuire et al.*, 2009]. Also, short-term microbial incubation experiments have shown little or no degradation of Arctic estuarine DOC [*Amon and Meon*, 2004], and high concentrations of lignin and other refractory DOC components provide indirect indications that the material is highly recalcitrant [*Amon and Benner*, 2003; *Köhler et al.*, 2003; *Lobbes et al.*, 2000]. In contrast, others have argued that riverine DOC in high-latitude areas has a relatively large labile fraction and is broken down by microbial respiration or photochemical oxidation, either within the water column or in the sediments after burial [*del Giorgio et al.*, 1997; *Cooper et al.*, 2005; *Holmes et al.*, 2008; *van Dongen et al.*, 2008]. Observations of substantial CO_2 emanations to the atmosphere above coastal regions in the sub-Arctic [*Algesten et al.*, 2006] and in the ESAS [*Pipko et al.*, 2002; *Semiletov et al.*, 2007; *Anderson et al.*, 2009] further support the view of substantial degradation of DOC (the main form of terrestrial OC delivered by rivers). Also, it was recently found that DOC in Arctic spring flood waters has a large labile fraction, as opposed to DOC in more commonly sampled late summer base flow [*Holmes et al.*, 2008]. In the Arctic, DOC-salinity mixing relationships from the deep ocean suggest that freshwater end-member concentrations are much lower than the actual mean DOC concentrations in the Arctic rivers, which require losses of DOC at lower salinities [*Cooper et al.*, 2005]. However, this assumption has never been supported by actual DOC measurements from the Arctic shelves. Given the magnitude of Siberian Arctic DOC export and the uncertain extent to which it is degraded to greenhouse gases, intensified studies to better quantify and understand this large carbon pool and processes acting on it are urgently needed.

[6] In the present study, the behavior of riverine DOC on the ESAS is addressed. Previous ESAS DOC data are sparse and unevenly distributed, and there are no synoptical studies of the riverine DOC distribution of the whole area. In the present study, the distribution and inventories of DOC for the whole region are obtained, and the processes of mixing, transformation, degradation, removal by settling, and export to the deeper ocean that determine the observed DOC distribution patterns are evaluated. The data set and conclusions presented here provide a comprehensive baseline for studies of future changes in carbon release to the Arctic Ocean.

2. Methods

2.1. Study Area

[7] The ESAS covered in detail here (Figure 1) comprises 40% of the Arctic shelf area and 20% of the Arctic Ocean area [*Stein and Macdonald*, 2004]. The Laptev Sea, between ~110°E (Severnaya Zemlya) and 140°E (New Siberian Islands), covers ~500 × 10^3 km^2 and has an average water depth of 50 m [*Jakobsson et al.*, 2004]. This sea receives high freshwater discharge (~745 km^3 yr^{-1}), largely from the Lena River (566 km^3 yr^{-1}) [*Cooper et al.*, 2008]. The East Siberian Sea (average depth, 58 m), is the largest, most ice-bound and least explored Arctic marginal sea [*Stein and Macdonald*, 2004]. It covers 987 × 10^3 km^2 from 140°E to 180°E. Two major rivers enter directly into the East Siberian Sea, the Indigirka (152°E) and Kolyma (162°E) rivers.

[8] The coastal currents across the Laptev and East Siberian seas predominantly flow eastward [e.g., *Steele and Ermold*, 2004]. At ~160°E, these low-saline coastal shelf waters meet Pacific inflow waters entering the East Siberian Sea [*Anderson et al.*, 1998; *Jakobsson et al.*, 2004; *Semiletov et al.*, 2005]. The eastward currents also transport a major proportion of the freshwater discharge from the Lena River through the Dmitry Laptev Strait [*Semiletov et al.*, 2005]. The spring flood, which occurs from the end of May to the beginning of July, constitutes 60%–90% of the riverine freshwater discharge [*Raymond et al.*, 2007].

2.2. Sampling

[9] A comprehensive set of samples was obtained from the H/V *Yacob Smirnitskyi* during August and September as part of the International Siberian Shelf Study 2008 (ISSS-08). The samples cover a wide range of salinities, from Lena River waters to high-salinity Arctic Ocean waters. Good

Figure 1. Cruise track, stations sampled for DOC during the ISSS-08, 14 August to 26 September 2008. Red markers, seawater intake stations (only surface samples); white markers, CTD stations, normally four depths; gray markers, samples taken with R/V *TB-0012* (August 2008).

spatial coverage was also obtained from the Lena river delta and plume and across the East Siberian Sea up to the shelf-break and eastward to the Herald Canyon (Chukchi Sea), where Pacific waters enter the shelf (Figure 1). Seawater samples for analysis of particulate organic carbon (POC), dissolved organic carbon (DOC), total organic carbon (TOC), and optical parameters were collected both from Niskin bottles on a rosette attached to a Seabird® CTD and from a continuously flushed seawater intake (SWI) system during transit. 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, where samples were collected. Niskin bottle samples for DOC were drawn into polycarbonate bottles from four different depths; the surface layer (2–4 m), halocline (4–10 m), middle bottom layer, and bottom. Prior to filling, samples bottles were rinsed three times with sample water.

[10] Near the outer estuary of the Pechora River (Figure 1), test samples were collected from both the Niskin bottles (at 4 m depth) and the SWI system. There were no detectable differences in TOC concentrations between the two sampling systems (SWI (n = 3): 202 ± 13.7 μM TOC, Niskin bottle (n = 3): 195 ± 13.1 μM TOC). Furthermore, on 20 occasions during the cruise, samples were collected in triplicate and analyzed in different runs to constrain the total variance.

2.3. TOC and DOC Analysis

[11] The bulk organic carbon components were separated into POC (>0.7 μm GF/F filters; Whatman, Inc.), DOC (GF/F filtrate) and TOC (unfiltered). The 1–3 L seawater samples were vacuum-filtered onboard with 25 mm diameter precombusted filters within an all-glass filtration system. The samples were kept in 60 mL Nalgene HDPE bottles and measured directly onboard. The DOC and TOC analyses were done by high-temperature catalytic oxidation (Shimadzu TOC-VCPH). Inorganic carbon was removed by acidifying the samples to pH 2 by 2 M HCl and sparging for 8 min prior to analysis of the total carbon content (NPOC method). All procedures for calibration and data analysis followed *Sharp et al.* [1995]. Consensus Reference Materials (CRM, from 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. Our results throughout the expedition for the deep-sea reference water were 42.3 ± 3.4 μM (n = 15). Additionally, an internal control sample from the Yenisey estuary (DOC 494 ± 23 μM) was run in duplicate after every 10 samples to monitor drift or interruptions during the run. New calibrations were made when the results of the CRM or the internal control samples differed from known concentrations by more than ~5%. Each sample was run in five replicate injections. The overall precision of the measurements was generally better than 5% (85% of data set). For samples with < 80 μM DOC, from the outer shelf and deep waters, the precision was ~8%.

2.4. Optical Measurements of Humic Substances

[12] Samples for optical analysis were collected without filtration in precombusted (12 h at 450°C) amber glass bottles, immediately stored under cold and dark conditions, and then analyzed onboard. Humic substance (HS) concentrations were determined in triplicate with fluorescence spectrometry (Hitachi F-7000) using the excitation/emission wavelength pair 350/450 nm, with slit widths of 2.5 nm (excitation) and 10 nm (emission), which have been shown

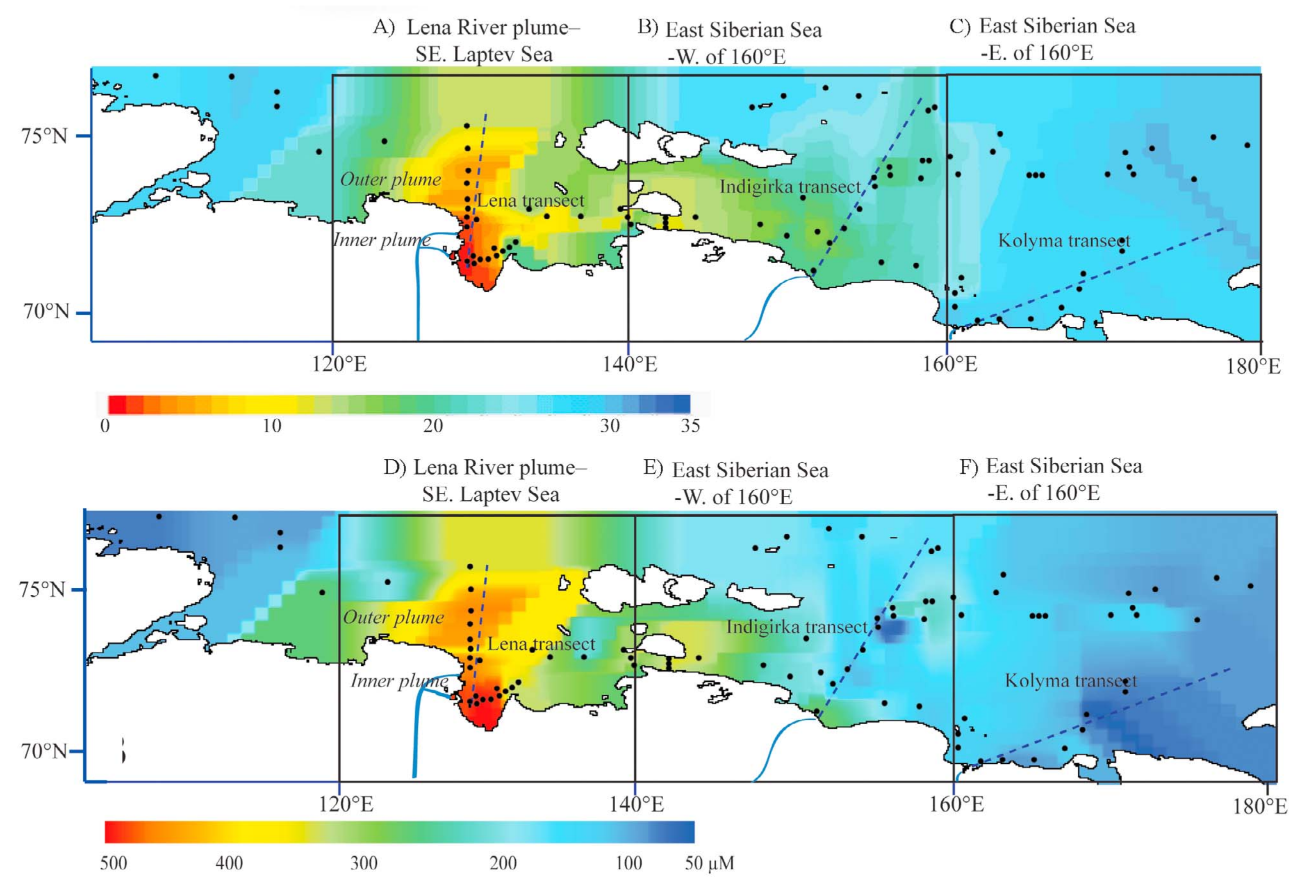

Figure 2. (a–c) Surface salinity and (d–f) DOC (μM) in the Laptev and East Siberian Sea during the ISSS-08 cruise within each region discussed separately in the text. Note that the sense of the DOC scale is opposite that of the salinity scale, so that blue represents high salinity in Figures 2a–2c and low DOC concentrations in Figures 2d–2f.

to be appropriate for the chromophoric moieties of HS in coastal waters strongly influenced by terrestrial runoff [*Skoog et al.*, 1996; *Gustafsson et al.*, 2001]. The instrument was calibrated using quinine sulfate, and the fluorescence intensities obtained for the water samples are thus reported as quinine sulfate equivalents (μg QSE L^{-1}).

2.5. Interpolations and Estimations of Inventories

[13] The Data Assimilation System (DAS) program [*Sokolov et al.*, 1997] (http://nest.su.se/das/) was used to contour concentration distributions and calculate total inventories and mean values for different water bodies. All bathymetry data used are from the International Bathymetric Chart of the Arctic Ocean (IBACO) [see *Jakobsson et al.*, 2008]. The outer border of the ESAS is taken to be where the depth is 200 m. The program averages all observations found within a cell of selected dimensions (here 10 km^2, 5 m depth), and linearly interpolates values for empty cells. Extrapolations were limited to 50 km for this study, and concentrations were kept constant beyond this. Inventory estimates changed less than 5% if distances of accepted inter/extrapolations, and the cell sizes were changed by an order of magnitude.

3. Results and Discussion

3.1. Local Circulation Patterns and Freshwater Distribution

[14] During summertime, there is a significant component of freshwater from Siberian river inflows into the coastal ESAS, extending to approximately 160°E, the long-term average position of the Pacific frontal zone [*Semiletov et al.*, 2005]. Generally, the coastal currents transport a large part of the Lena River water eastward into the East Siberian Sea (Figures 2a–2c), leaving the Vilkitsky Strait and the Laptev Sea west of 117°E with little influence from the Lena River. Pronounced plumes were not seen from either the Indigirka or the Kolyma, the two largest rivers entering the East Siberian Sea [*Cooper et al.*, 2008]. Based upon the salinity distribution, three distinct regions were identified and were the focus of detailed sampling in late summer 2008:

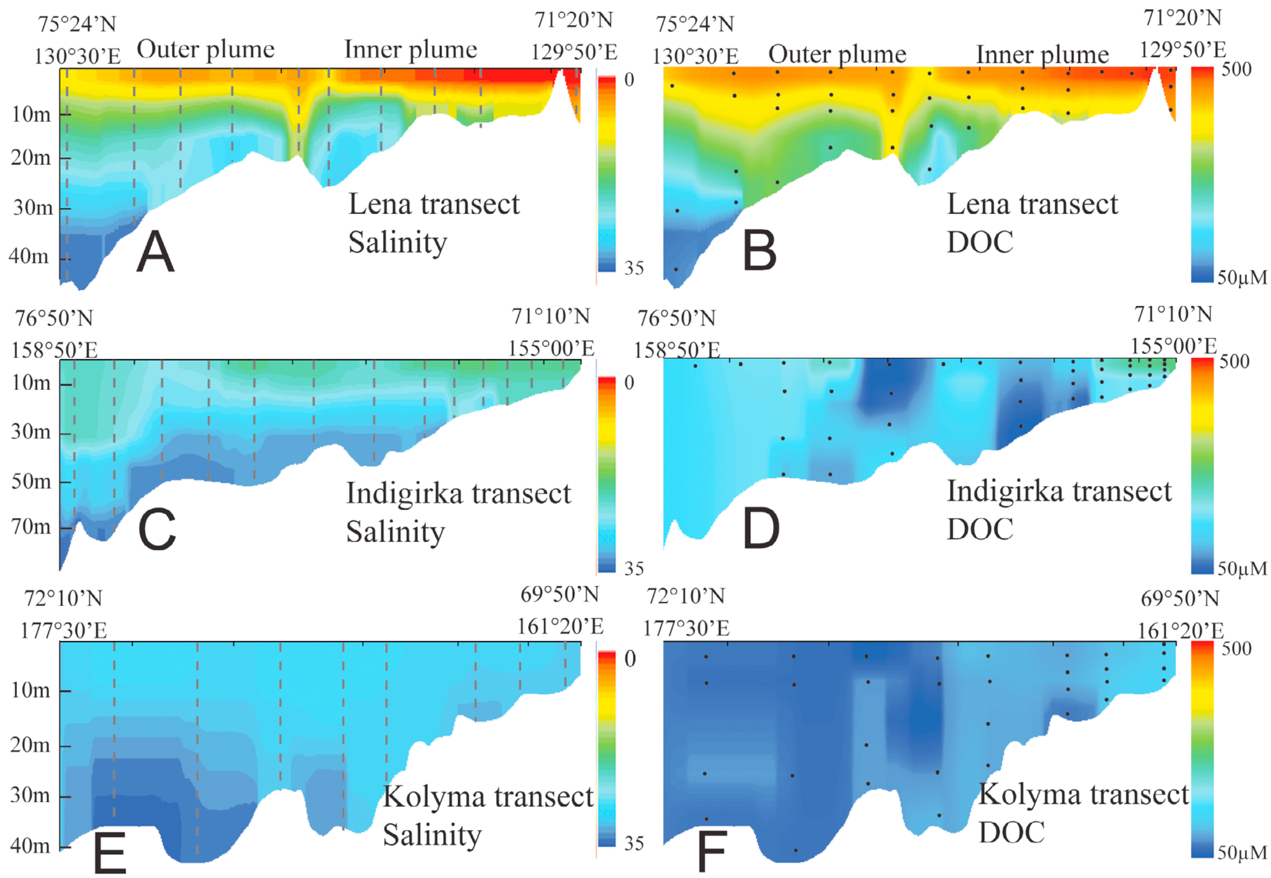

Figure 3. Salinity and DOC concentrations in depth profiles from the (a and b) Lena River plume, (c and d) Indigirka River Mouth, and (e and f) Kolyma River Mouth. Note different scales for depth between panels. Transects are shown in Figure 2.

[15] 1. The pronounced Lena River plume in the Laptev Sea (see section 3.4), which exhibits very low salinities in the surface waters (<1–15, Figure 2a) and a strong halocline, at ~8 m depth (Figure 3).

[16] 2. The western part (140°E to 160°E) of the East Siberian Sea (see section 3.5.1), which has a surface layer that is clearly influenced by Lena River discharge and has salinities of 12–25 (Figure 2). The halocline is less pronounced than in the Laptev Sea and situated at 15 m depth (Figure 3). The residence time in the surface layer of this area may be several years (see section 3.5.1) and so provides the opportunity for studying processes affecting the DOC over longer time.

[17] 3. The eastern part (160°E to 180°) of the East Siberian Sea (see section 3.5.2), which is highly influenced by Pacific inflow water. The salinity in this region is much higher (>28 in the surface layer) than in the western part of the East Siberian Sea (Figure 2c).

[18] The surface waters of the Arctic Ocean are affected each year by sea ice melting, ice formation and export. This effect can be estimated from the measured δ^{18}O signatures of each water sample [*Östlund and Hut*, 1984; P. S. Andersson et al., Distribution of δ^{18}O in water from the Laptev and East Siberian seas, manuscript in preparation, 2010] (see Text S1).[1] Salinity variations in the samples of the present study dominantly reflect mixing between river water and marine water (P. S. Andersson et al., manuscript in preparation, 2010). It is important to note that there are no DOC concentrations that have been lowered by the addition of melted sea ice. On the contrary, there has been some export of sea ice, which has increased DOC concentrations somewhat in the remaining water. The correction for this is only significant for the samples from the Laptev Sea below the halocline. Most samples show just minor influence (<10%) of the formation and export of sea ice. As discussed in Text S1, both DOC and salinity have been corrected for sea ice using δ^{18}O in samples above a salinity of 8 (for salinity versus DOC relationship during ice formation, see *Amon* [2004]). For samples with lower salinities in the Lena plume, the uncertainty of the value of the Lena River component, which can vary seasonally [*Cooper et al.*, 2008], is very large, and δ^{18}O measurements cannot be used to examine the effects of ice processes. For salinities >8, the corrections are negligible (<10%), and so additional samples in

[1] Auxiliary materials are available with the HTML. doi:10.1029/2010GB003834.

Table 1. The Mean Concentrations and Inventories of DOC in the Laptev Sea and East Siberian Sea Obtained During ISSS-08 and Compared With Earlier Measurements and With Annual River Discharge of DOC

	This Study					Other Studies	
	Depth (m)	Mean Salinity (PSU)	Volume Basin (km^3)	Mean Concentration (μM DOC)	Inventory (g DOC)	Concentrations (μM DOC)	River DOC Discharge[a] (gC yr^{-1})
Laptev Sea							Lena: 5.9×10^{12}
Surface layer (n = 50)	0–10	20	4240	258 ± 13	1.3×10^{13}	300–600 (n = 36)[b]	
Bottom layer (n = 27)	10–200	29	12625	133 ± 7	2.0×10^{13}	200 (n = 29)[b]	
Total (n = 77)	0–200	27	16900	165 ± 8	3.3×10^{13}		
East Siberian Sea							Indigirka: 0.47×10^{12}
Surface layer (n = 74)	0–15/20	-	16600	-	2.2×10^{13}		Kolyma: 0.81×10^{12}
Bottom layer (n = 65)	20–200	-	31900	-	5.0×10^{13}		
Total (n = 139)	0–200	31	48500	101 ± 6	6.0×10^{13}	50–350[c] (only range reported)	
W of 160°E							
Surface layer (n = 35)	0–15	22	4710	170 ± 9	9.6×10^{12}		
Bottom layer (n = 27)	20–200	26	4040	146 ± 7	6.5×10^{12}		
Total (n = 62)	0–200	24	8750	158 ± 8	1.7×10^{13}		
E of 160°E							
Surface layer (n = 39)	0–20	28	10010	93 ± 5	1.3×10^{13}		
Bottom layer (n = 38)	20–200	33	29900	87 ± 4	3.1×10^{13}		
Total (n = 77)	0–200	31	39900	88 ± 4	4.3×10^{13}		
ESAS (Laptev and East Siberian Sea)		-		-			Lena, Indigirka and Kolyma: 7.1×10^{12}
Surface layers	0–10/15/20	-	19000	-	3.5×10^{13}		
Bottom layers	10/15/20–200		46500		5.8×10^{13}		
Total (n = 216)	0–200	29	65500	119 ± 6	9.4×10^{13}		

[a] *Cooper et al.* [2008] and *Gordeev et al.* [1996] (riverine DOC discharge to East Siberian Sea is estimated from the Indigirka River, Kolyma River, as well as Lena River discharge, see section 3.5.1).
[b] *Cauwet and Sidorov* [1996].
[c] *Olsson and Anderson* [1997].

this salinity range for which there are no δ^{18}O measurements have also been used.

3.2. Large-Scale DOC Inventories and Residence Times on the Eastern Siberian Arctic Shelf

[19] The DOC concentrations in the surface waters of the ESAS ranged from 500 μM in the Lena River mouth, down to 50–80 μM at the outermost stations in the East Siberian Sea and Russian part of the Chukchi Sea (Figures 2d–2f). The correlation of DOC with salinity (Figures 2a–2c) suggests that rivers are the major source of DOC. The mean DOC concentrations and calculated DOC inventories in the different regions of the ESAS are presented in Table 1. The total DOC discharged annually to the East Siberian Sea includes the Indigirka and Kolyma loads, as well as that of the Lena River, since a major but not well-constrained part of Lena River discharge is transported eastward into the East Siberian Sea [*Ekwurzel et al.*, 2001; *Semiletov et al.*, 2005]. The range of concentrations found in this study are comparable to those reported for the southeast Laptev Sea by *Cauwet and Sidorov* [1996] and for the East Siberian Sea by *Olsson and Anderson* [1997] (see Table 1). The study of *Cauwet and Sidorov* [1996] provides a valuable data set compiled from 3 years of sampling in the Lena estuary, although it contains insufficient quasi-synoptic data to obtain a well-constrained inventory at any time. The highest values of up to between 500 and 550 μM found in the Ob and Yenisey river mouths [*Köhler et al.*, 2003; *Amon and Benner*, 2003; *Hessen et al.*, 2010] are similar to those found in the present study for the Lena River mouth.

[20] The mean concentration of DOC for the whole ESAS is estimated to be 119 μM (n = 216), corresponding to a total inventory of 9.4×10^{13} gC (Table 1). This is the first estimate of the total DOC inventory of the ESAS. It is an order of magnitude smaller than the total DOC in the surface layer of the interior Central Arctic basins, and similar to the total annual export of organic carbon from the Arctic Ocean to the Atlantic Ocean [*Anderson et al.*, 1998]. This DOC inventory is 13 times greater than the annual riverine DOC load of 7.1×10^{12} gC from the Lena, Indigirka and Kolyma rivers [*Gordeev et al.*, 1996; *Cooper et al.*, 2008].

[21] It is useful to compare this data to the residence time of freshwater on the shelves and calculate the DOC removal rate. The most widely quoted value for the shelf freshwater residence time is by *Schlosser et al.* [1994] of 3.5 ± 1.5 years. However, this is based upon tritium and tritium-helium ages measured in the central Nansen Basin and so cannot be easily related to the East Siberian Sea. Other tritium ages for the Laptev and Kara seas have been used to suggest residence times of ~5 years for these areas [*Östlund and Hut*, 1984; *Östlund*, 1994], which is consistent with the water balance of the Kara Sea [*Hanzlick and Aagaard*, 1980]. However, no data are available for the East Siberian Sea.

[22] The data obtained here can be used to calculate the residence times of freshwater and DOC, as well as the

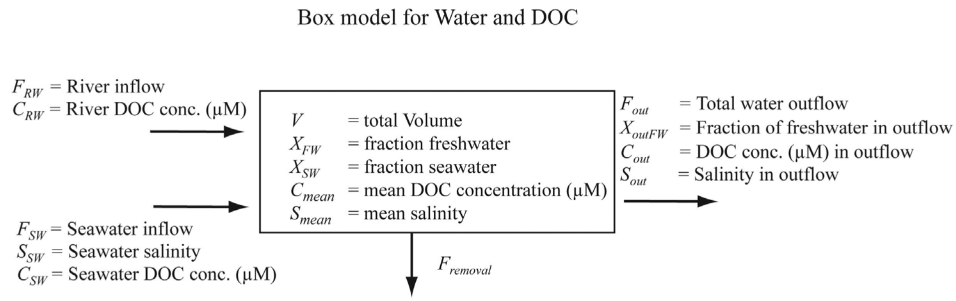

Figure 4. A general box model, used to obtain first-order removal rate constants for DOC, along with residence times for water and DOC, for the Eastern Siberian Arctic Shelf (ESAS), as well as separately for the East Siberian Sea west of 160°E. The model incorporates inflow of riverine freshwater and DOC as well as the inflow of seawater and DOC from outside the box and the export of water, freshwater, and DOC from the box. The waters on the ESAS are not well mixed, and these calculations therefore distinguish between outflow water properties and mean water properties.

removal rate of DOC, using a straightforward box model. This is shown in Figure 4, where the fluxes and reservoirs are defined. Residence times and removal rates are related through a number of simple relationships and can be calculated largely from salinities and concentrations. The residence time of freshwater can be obtained from (as derived in Text S1):

$$\tau_{FW} = \frac{V}{F_{RW}} \frac{(S_{sw} - S_{mean})}{S_{sw}} \quad (1)$$

where the residence time of freshwater, τ_{FW}, is a function of the mean salinity of the shelf waters (S_{mean}), and that of seawater flowing in (S_{sw}). In the ESAS, S_{mean} = 29. If the salinity of waters flowing into the ESAS from the west (S_{sw}) were entirely composed of Atlantic water with a salinity of 35, then a freshwater residence time of 12 years is obtained. However, the inflowing waters have much lower salinities than 35, due to river inputs to waters flowing from the Kara Sea and the Pacific. This is difficult to constrain from the present data. If it is assumed that τ_{FW} is as low as 3.5 years [*Schlosser et al.*, 1994], then this requires an average value for S_{sw} of 30.2. However, we have salinities that exceed 32 in both Laptev and East Siberian Sea, so that the salinities of inflowing waters in some areas must be considerably higher. Therefore, the resulting residence time is somewhat higher than the value of *Schlosser et al.* [1994], but is not well constrained in the total ESAS, though better constrained in the western East Siberian Sea (see section 3.5).

[23] Because of uncertainty in the freshwater budget for the whole area, the overall residence time for DOC cannot be constrained. However, this can be determined for more restricted regions (see sections 3.4 and 3.5.1).

3.3. Processes Controlling the Distribution of Organic Matter

[24] For all the measured samples taken during the ISSS-08 cruise, there is an overall linear relationship between DOC concentration and salinity (Figure 5a) and between HS

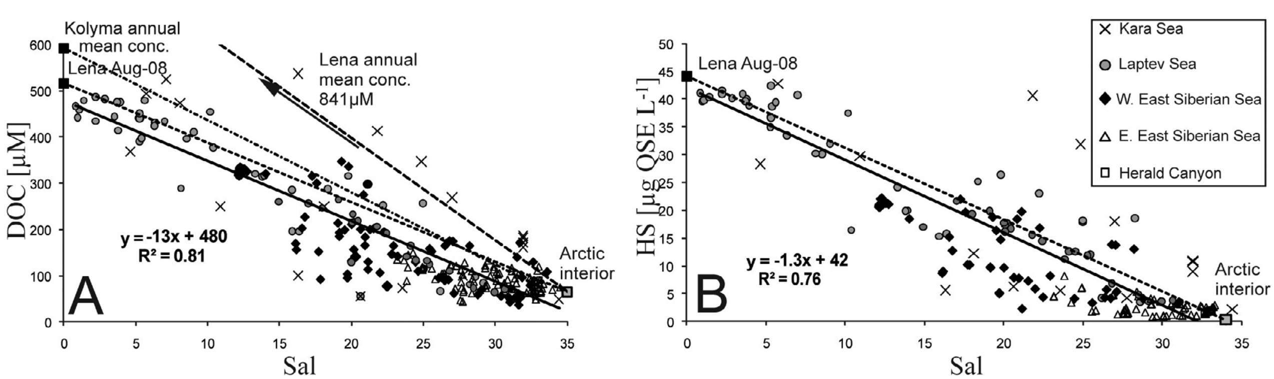

Figure 5. All samples from ISSS-08, showing (a) DOC concentrations and (b) humic substance (HS) concentrations plotted against salinity. There are overall correlations, shown by solid lines, between DOC (R^2 = 0.77; Mean Absolute Percentage Error (MAPE) = 42%) and salinity (R^2 = 0.72, MAPE = 130%). Conservative mixing of Arctic interior water with Lena River waters, as well as with Kolyma River water, is also shown with dotted lines.

and salinity (Figure 5b), with significant scatter between salinity 7 and 30. The DOC-Sal correlation is in general agreement with previously published data for the Eurasian Arctic shelf seas [e.g., *Dittmar and Kattner*, 2003]. The DOC and HS concentrations, as well as salinities, for a range of inputs to the shelf are shown in Figures 5a–5b. These include the annual flow-weighted mean concentration for the Lena River, with DOC concentrations from *Raymond et al.* [2007], the Lena River concentrations as represented by August 2008 samples from the three lower delta channels (this study), the Kolyma annual flow-weighted mean DOC concentration [*Cooper et al.*, 2008], and the Arctic interior concentrations, as represented by the Fram Strait for DOC [*Opsahl et al.*, 1999] and by the Amundsen and Nansen basins for HS [*Sobek and Gustafsson*, 2004]. By comparing theoretical conservative mixing lines between the river inputs and the Arctic interior waters with observed concentrations, it is clear that a significant part of the observed scatter in both DOC and HS concentrations may be caused by the annual variations in the freshwater contributions to the ESAS from the major rivers. However, a detailed assessment of the three different areas of the ESAS (see section 3.1) reveals that there are strong indications of additional sources of DOC to the water column, as well as of processes that remove both DOC and HS.

[25] The additional sources of DOC include primary production in the estuarine waters, as well as additions from coastal erosion and sediments; these processes would increase the DOC concentrations compared to that expected from conservative mixing. While primary production would mainly add non-HS DOC, coastal erosion adds HS-containing terrestrial carbon [*Dutta et al.*, 2006]. The organic matter in the sediments of some of the shelf areas studied here have been shown to have a very high terrestrial component [*Boucsein and Stein*, 2000], up to 100% in the Dmitry Laptev Strait, which is strongly impacted by coastal erosion [*Semiletov et al.*, 2005].

[26] The possible removal mechanisms would include microbial activity that has been found to degrade nonhumic DOC preferentially over HS [*Lobbes et al.*, 2000; *Amon and Benner*, 2003]. In contrast, photochemical degradation would preferentially degrade HS due to its chromophoric nature, and this has been suggested as an important process removing refractory terrestrial DOC in the oceans [*Kieber et al.*, 1989; *Opsahl and Benner*, 1998]. This process has been shown to be an important removal process in temperate estuaries [*Benner and Opsahl*, 2001] and found to be significant in the upper part of the surface waters of the Kara Sea [*Amon and Meon*, 2004]. There is some evidence that the commonly seen processes of flocculation and sedimentation of DOC in estuaries [*Mantoura and Woodward*, 1983; *Gustafsson et al.*, 2000] removes HS to a greater extent than DOC [*Sholkovitz et al.*, 1978].

[27] In the sections 3.4–3.5, the relationships between DOC, HS, and salinity will be used to determine the extent of losses and additions of DOC in each area and outline the processes behind the observed deviations from conservative mixing. Across the ESAS, the river end-member concentrations will differ, and the appropriate compositions will be considered for each region.

3.4. The Laptev Sea–Lena River Plume and Short-Term Mixing Patterns

[28] The Lena River DOC plume extends northeast in the Laptev Sea (Figures 2a–2c). There are two distinct subplumes in the northward direction, separated at 73°22′N, 129°60′E (Figures 2 and 3). This is north of the mouths of both the Trofimovskaya and Bykowskaya channels (75% and 15% of annual Lena discharge, respectively [*Dudarev et al.*, 2006]), and so does not appear to be due to different discharge sources. The mean surface DOC concentration in the inner and outer subplumes is 420 and 400 μM, respectively. The mean DOC concentration is lower below the plume halocline (260 μM). These values are in good agreement with earlier reports of 65 measurements in the southeast Laptev [*Cauwet and Sidorov*, 1996]. The mean DOC concentration for the entire Laptev Sea is 165 μM (n = 77), and 260 μM for surface waters (Table 1). Earlier measurements for the shelf slope north of the Lena River mouth are between 50 and 200 μM DOC [*Kattner et al.*, 1999; *Fransson et al.*, 2001], and a broad linear relation with salinity [*Kattner et al.*, 1999] is consistent with mixing with freshwater with 531 μM DOC, close to that measured in our study in August 2008 (505 μM).

[29] In general, the Laptev surface DOC concentrations can be explained by conservative mixing between Lena River water, as measured in August 2008 (Figure 6a, n = 3, from each of the three biggest delta channels), and Arctic deep water [*Opsahl et al.*, 1999]. The estuarine samples from below the halocline were the only samples in the study that clearly showed a significant increase in DOC due to brine formation. The δ^{18}O corrected DOC concentrations showed losses of DOC compared to any mixing line, even if the bottom waters also have the late summer Lena water as a river end-member.

[30] Bour-Khaya Bay, the site of the inner Lena plume, is also one of the sites known for the most rapid and extensive coastal erosion of the ESAS shorelines [*Rachold et al.*, 2004; L. Sanchez-Garcia et al., submitted to *Global Geochemical Cycles*, 2010]. DOC added by this source should be seen as higher DOC concentrations than expected from conservative mixing with Lena water. No such positive deviations are seen in the data, and so the export of coastal erosion DOC to the waters of the ESAS must be small compared to the riverine flux of DOC. The fate of these large amounts of erosion-derived DOC is still unknown and needs further investigation.

[31] Like the DOC, the HS concentrations in the surface plume also fall close to the line for conservative mixing (Figure 6b) between Lena River water (44 μg QSE L^{-1}, August 2008, n = 3) and the interior Arctic Ocean water (0.3 μg QSE L^{-1}) [*Sobek and Gustafsson*, 2004]. Further, the δ^{18}O-corrected HS measurements of the estuarine samples from below the halocline coincide very well with conservative mixing of Lena August waters and Arctic interior waters.

[32] The nutrient concentrations also show very different levels in the inner versus the outer plumes. The NO_3^{2-} and PO_4^{3-} [from *Anderson et al.*, 2009] concentrations (Figures 7a–7b) are strongly depleted in the outer plume,

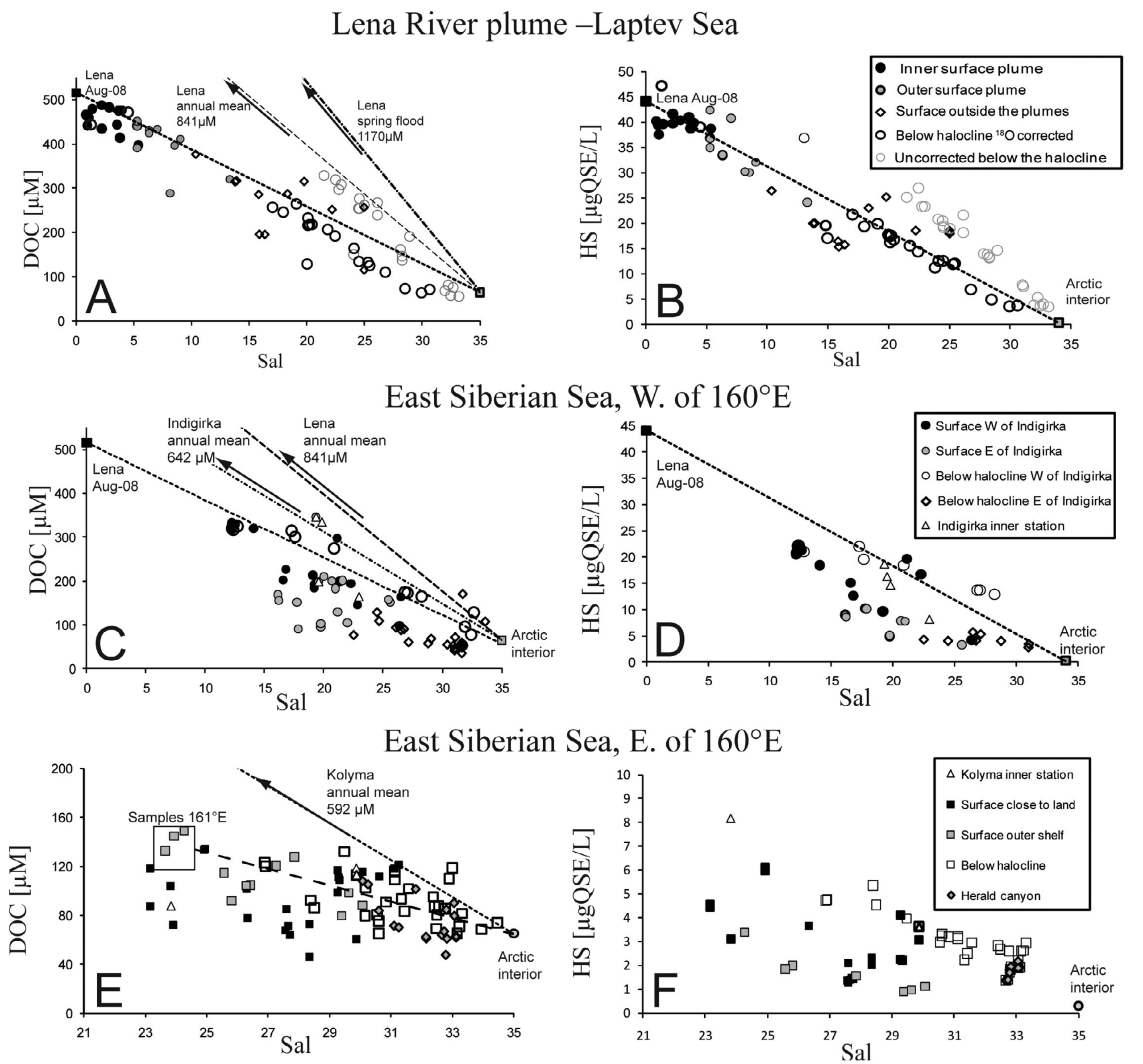

Figure 6. Property-salinity plots for the three different regions: (a–b) Lena River plume in the Laptev Sea, showing that the DOC and humic substance (HS) concentrations in the surface plume, as well as the underlying water below the halocline, fall close to the line for conservative mixing between Lena River water (as measured August 2008) and Arctic deep water. Conservative mixing of Arctic deep water with annual mean Lena River water, as well as with Lena River spring flood water, is also shown in Figure 6a. (c–d) The East Siberian Sea west of 160°E. Conservative mixing of Arctic deep water with annual mean Lena River water, as well as with Indigirka River water, is also shown in Figure 6c. (e–f) East Siberian Sea east of 160°E and Herald Canyon. Note scale difference from Figures 6a–6d. Conservative mixing between Arctic deep water with Kolyma annual mean water, as well as inflowing water from the west, is also shown in Figure 6d. For all of the East Siberian Sea (Figures 6c and 6e), the sample DOC concentrations generally fall below the lines for conservative mixing between any river water composition and Arctic deep water, indicating substantial losses of terrestrial DOC.

and the Si concentrations (Figure 7c) in the outer plume are half of those in the inner plume. The Si concentration is lower than what a conservative mixing would give, and indicate that a diatom bloom has occurred in these waters. Such a bloom would then also have caused the depletion of NO_3^{2-} and PO_4^{3-}. While primary production in the outer plume would have added DOC to the water, this addition must be small compared to the mass of terrestrial DOC

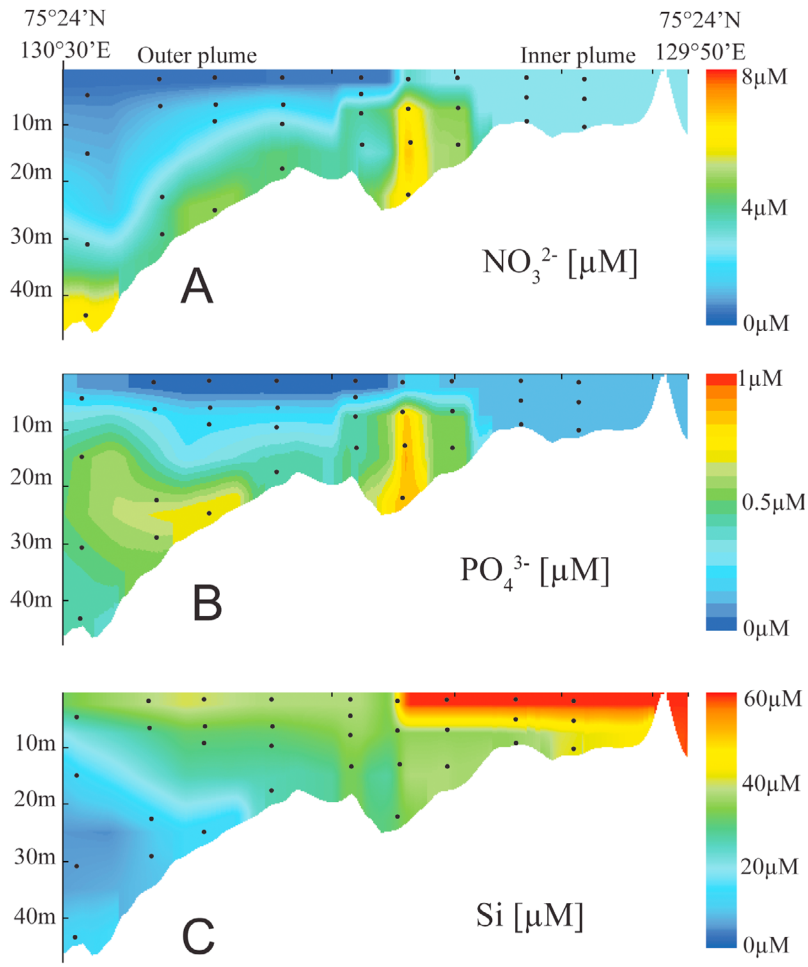

Figure 7. Nutrient depth profiles for the Lena transect (see Figure 2). The nutrient concentrations show very different levels in the two plumes. (a and b) The NO_3^{2-} and PO_4^{3-} concentrations are strongly depleted in the outer plume, and (c) the Si concentrations in the outer plume compared to the inner plume are half of those in the inner plume. The depletion in the waters of the outer plume must have been caused partly by phytoplankton blooms.

present in the plume water, as the data in Figure 6a do not show signs of addition of DOC.

[33] An important implication of the distributions of DOC and HS in the Lena-Laptev Sea plume is that the age of both the inner and the outer plumes is approximately 2 months, since both appear to contain Lena freshwater with low DOC concentrations like those seen in August 2008, rather than the high concentrations seen in spring flood water discharged earlier in May and June (Figures 6a–6b). The residence time of waters beneath the halocline also appear to have this rather young river water as a component, especially for the HS, which has concentrations that correlate well with mixing of Lena August waters and Arctic interior waters. In the samples from the Laptev Sea, removal of up to ~10% of the DOC can be accommodated within the scatter of the data, which reflects a substantial rate of removal as these waters are relatively young. This is also evident in the HS data for the low-salinity samples, but at high salinity, the removal of DOC seems to be more pronounced. This indicates that degradation of non-HS DOC occurs in these waters. However, while August Lena river water is certainly the freshwater component at the lowest salinities near the river mouth, the June (spring flood) river waters are likely present further out in the estuary, which implies losses even greater than 10% (Figure 6a).

3.5. East Siberian Sea

3.5.1. West of 160°E: Distant Lena River Plume and Long-Term Mixing Patterns

[34] The Lena river discharge is the main source of freshwater to the western East Siberian Sea, as discussed in section 3.1, and imprints low salinities and high DOC concentrations in waters above the halocline (Figure 2). The mean concentration of DOC in the western East Siberian Sea surface layer (0–15 m, Figures 3c–3d) was 170 μM (n = 35, Table 1). Particularly high DOC concentrations were found in the Dmitry Laptev Strait (defined as part of East Siberian Sea) where Lena River water flows

eastward, consistent with the Lena being a main source of terrestrial DOC to the area. However, coastal erosion in the strait may also be a local contributor to this signal [*Rachold et al.*, 2004], as shown for POC by Sanchez-Garcia et al. (submitted). Further east, the Indigirka River enters the East Siberian Sea at 152°E. However, neither the surface distribution of DOC (Figures 2d–2f), nor the relationships between HS, DOC, and salinity for the western East Siberian Sea (Figures 6c–6d), show any signs that the Indigirka River is a substantial source of DOC or HS, except at the station closest to the Indigirka River mouth. Thus, the terrestrial DOC pool in the East Siberian seawaters west of 160°E appears to be dominated by the DOC discharged by the Lena. A distinctive feature in the property-salinity plots for the western East Siberian Sea is that the DOC and HS concentrations generally fall below the lines for conservative mixing between any measured river water end-member (Lena and Indigirka annual means, and Lena August 2008) and the Arctic deep water (Figures 6c–6d), indicating that substantial losses of terrestrial DOC, including HS, occur over the timescale of freshwater transportation to the area.

[35] Interestingly, the HS versus salinity plot indicates that the losses of HS are higher in the surface waters than in the bottom waters (Figure 6d); this is less pronounced for the DOC concentrations (Figure 6c). As there is no value available for the annual mean concentration of HS in the Lena River, losses of HS are hard to estimate quantitatively. However, it is most likely that the HS concentrations in the spring flood water is high, as the spring flood flushes the humic-rich surface layers in the catchment of Arctic rivers [*Neff et al.*, 2006]. The greater removal of HS compared to nonhumic DOC in surface waters could reflect photochemical degradation of HS. This process, though, is restricted in this region by the low incident angle of the limited sunlight and the turbidity of coastal Siberian shelf waters, and it is not clear how great its impact is on the total flux of carbon. It is also possible that this reflects preferential aggregation and settling of the HS component of DOC, as observed in the Baltic Sea [*Gustafsson et al.*, 2004]. Another possibility is additions to surface waters of nonhumic DOC from primary production, which would increase the proportion of marine-derived DOC. This is supported by the observation that nutrients were strongly depleted in the surface waters in the East Siberian Sea west of 160°E, due to removal by primary production [*Anderson et al.*, 2009]. There may also be interactions between the processes of particle settling, photodegradation, and microbial degradation that may promote losses of DOC.

[36] The western East Siberian Sea is of particular interest because, by the time Lena river DOC has reached this region, it has been exposed to aging and any settling/degradation mechanisms for substantially longer times than in the southeast Laptev Sea, while having remained within relatively low salinities and at high DOC concentrations. In contrast to the generally conservative mixing pattern seen in the Laptev Sea (Figures 6a–6b), it appears that the East Siberian Sea is a site for major removal of terrestrially derived DOC (Figure 6c).

[37] The appropriate selection of end-member for this distant Lena river water is the annual mean Lena river water (Figure 6c). Net losses of DOC were calculated from the deviation of each measured concentration from the conservative mixing line, and then a volume-weighted mean value was determined using the DAS program. The net losses of DOC is ~50% for DOC from both below and above the halocline, with a clear pattern of higher losses further east in the area. Since additional sources of DOC to the area (e.g., coastal erosion and primary production) are not taken into account, the actual degradation of terrestrial DOC may be even higher.

[38] A relevant question here is the residence time of riverine freshwater and DOC in the western East Siberian Sea (see Text S1 for all calculations). The freshwater is supplied by the Indigirka River, along with much of the Lena River discharge, which flows eastward into the region [*Semiletov et al.*, 2005]. In the western East Siberian Sea, S_{mean} is 24, and by letting S_{sw} vary between the reasonable numbers 32–34 for the western East Siberian Sea, this yields a freshwater residence time of 3.5 ± 1.5 years (equation (1)). The residence time for DOC is

$$\tau_{DOC} = \frac{V\ C_{mean}}{F_{RW}\left[C_{RW} + C_{sw}\frac{S_{out}}{S_{SW}-S_{out}}\right]} \qquad (2)$$

where the concentrations of DOC in river water, inflowing seawater, and the reservoir are C_{RW}, C_{sw}, and C_{mean}. The first-order DOC removal rate constant λ can be related to this, as well as concentrations, by

$$\lambda = \frac{1}{\tau_{DOC}} - \frac{C_{out}}{\tau_{water}}\frac{1}{C_{mean}} = \frac{F_{RW}\left[(C_{RW} - C_{out}) + S_{out}\frac{(C_{SW} - C_{out})}{(S_{SW} - S_{out})}\right]}{VC_{mean}} \qquad (3)$$

The ratio $\frac{(C_{SW}-C_{out})}{(S_{SW}-S_{out})}$ is obtained from values for the waters flowing out of the box and must lie on the mixing lines shown in Figure 6c, or below those lines where removal of DOC occurs. This ratio is equivalent to the slope of the line for such mixing relationships in a DOC versus salinity plot, and so can be constrained from the plot. Note that this ratio is reasonably well-constrained by the full set of data, rather than just detailed considerations of the composition of the seawater end-member. Estimates of the slope from Figure 6c for samples with salinities of 29–35 give an approximate value of −4.5.

[39] The estimated residence time for DOC in this area is 2.5 ± 1.7 years. The annual net DOC loss flux from western East Siberian Sea, based on the estimated 50% deficit of the DOC inventory, and a water residence time of 3.5 years is ~5.1 × 10^{12} gC yr^{-1}. This corresponds to a first-order removal rate constant of ~0.3 yr^{-1} and is the first removal rate constant that is directly derived from observational data for the Arctic shelves.

[40] These losses of DOC can be compared to the observed oversaturation of pCO_2 for the same area.

Anderson et al. [2009] estimated an annual atmospheric outgassing of CO_2 from the ESAS of 10×10^{12} gC yr^{-1} and interpreted this to come from degradation of terrestrial OC (POC and/or DOC). The agreement of the magnitude of the DOC deficit, directly estimated in the current study, and that inferred from this pCO_2 oversaturation for the total ESAS, further confirms the degree of DOC loss from shelf waters. This is also consistent with the removal rate constant of 0.3 yr^{-1} obtained by *van Dongen et al.* [2008] for a subarctic estuary in the northernmost Baltic Sea using a simple box model.

[41] The DOC mass balance results from this study may also be compared to recent modeling results for the whole Arctic Ocean, which also suggest nonconservative DOC behavior. Using arguments based on a three-dimensional circulation model of the Arctic Ocean and monthly Arctic river discharges of DOC, *Manizza et al.* [2009] showed that the apparently linear DOC-salinity relationship presented by *Amon and Benner* [2003] for the eastern Arctic could be reproduced by assuming decay of riverine DOC by a first-order rate constant of 0.1 yr^{-1}. The linear DOC-salinity correlation from *Amon and Benner* [2003] is only composed of low-salinity (1–13) samples from the Ob and Yenisey estuaries in the western Siberian shelf and of high-salinity (29–35) interior Arctic Ocean samples. Our results from the Lena River plume–Laptev Sea yield a similar DOC-salinity relationship to that obtained from the Ob and Yenisey estuary in September. However, our data from the western East Siberian Sea, with a freshwater component that is also from the Lena but with a higher age than the Lena-Laptev samples, show more clearly that DOC does not behave conservatively. The concentrations are well below those predicted by the linear DOC-salinity mixing line of *Amon and Benner* [2003] and used by *Manizza et al.* [2009], and a higher removal rate constant than 0.1 yr^{-1} derived by *Manizza et al.* [2009] is necessary to explain the DOC patterns in the East Siberian Sea. At the same time, the higher removal rate of 0.3 yr^{-1} calculated here would not reproduce the concentrations found in the Arctic Interior, as shown by *Manizza et al.* [2009]. Hence, there must be different rate constants for DOC degradation in estuaries, coastal/shelf areas, and the Arctic interior.

3.5.2. East of 160°E: Mixing Processes With the Pacific Inflow on the Outer Shelf

[42] The area east of 160°E is influenced by inflow of Pacific Ocean waters and freshwater from the Kolyma River, as well as by mixing with the western low-salinity coastal waters at the frontal zone 160°E (see Figures 2a–2c). In the Herald Canyon area, the East Siberian seawaters mix with the Pacific waters. The concentrations of DOC in this area range between 50 and 150 μM (n = 77), with a mean concentration of 93 μM in the surface waters (n = 39), 87 μM below the halocline (n = 38), and 88 μM for the total water mass (Table 1). All of the DOC and HS concentrations are shown in Figures 6e–6f, along with the Kolyma flow-weighted annual mean concentration of DOC [*Cooper et al.*, 2008]. The DOC concentrations generally fall below the lines for conservative mixing between waters from the Kolyma River and the Arctic interior (Figure 6d), indicating that substantial losses of terrestrial DOC have occurred also in the eastern part of the East Siberian Sea.

[43] The surface waters of the outer East Siberian Sea shelf have both very low HS concentrations and DOC concentrations that are similar to marine values [i.e., *Opsahl et al.*, 1999], suggesting that only a small fraction of the DOC in these samples is of terrestrial origin, even though the salinities are as low as 24. Samples tend to show higher HS concentrations in the bottom waters than in the surface waters relative to salinity, a pattern not seen in the DOC concentrations. This indicates higher losses of HS than DOC in the surface waters, but the opposite in the bottom waters.

[44] In contrast to the other areas, in the eastern East Siberian Sea, primary production is significant relative to degradation processes, resulting in the drawdown of pCO_2 below that of atmospheric equilibrium [*Pipko et al.*, 2002; *Semiletov et al.*, 2007; *Anderson et al.*, 2009]. However, while such primary production alone might increase the DOC concentrations in the surface waters and dominate the DOC budget, overall there have been net losses of DOC due to degradation and removal to sediments (Figure 6e).

[45] A volume-weighted mean value for net DOC loss of 35% was calculated from the deviation of each measured concentration from the conservative mixing line between Kolyma annual mean water and Arctic Ocean water, using the DAS program. The losses of HS seem to be much higher, as the surface concentrations of HS are close to the Arctic interior concentration [*Sobek and Gustafsson*, 2004]; the apparent difference in loss rates between DOC and HS could be either explained by very different relative depletions, or by addition of primary production DOC. However, the fresh water end-member concentration for this area is highly uncertain: A considerable part of the freshwater must be transported from the western part of the East Siberian Sea, since the Kolyma River discharge alone cannot account for all the freshwater in the region. This is evident by comparing the total freshwater budget in the region of ~4560 km^3 to the annual Kolyma discharge of 114 km^3; without another freshwater input, the residence time is several decades, which is unreasonably long. This inflow is difficult to quantify, since the flow conditions have not been constant. For example, the Pacific frontal zone position has sometimes been further east than observed this year [*Semiletov et al.*, 2005]. The freshwater component coming from the west has already suffered losses of DOC, as seen in section 3.5.1. However, if these waters are represented by the westernmost samples (Figure 6e), then other surface water samples from further east still generally exhibit losses of ~10%–20% compared to mixing between these waters and an Arctic interior end-member. Unfortunately, the rate at which this water mixes across the frontal zone is difficult to constrain. Overall, the residence time for both freshwater and DOC in this area cannot be readily calculated from the available data, and a reasonable estimate of yearly net DOC losses is therefore impossible to make from this data set. However, the similarity to the removal seen in the western East Siberian Sea indicates that large-scale removal of terrestrial DOC is a general phenomenon throughout the Arctic Shelf seas, and is resolvable in water masses with at least yearlong ages.

4. Conclusions

[46] Results of the ISSS-08 campaign clearly demonstrates that DOC behaves nonconservatively over the extensive Eastern Siberian Arctic Shelf (ESAS) that represents 40% of the total Arctic shelf and covers almost 20% of the Arctic Ocean. The net DOC deficit for the East Siberian Sea was one third to one half of the inventory predicted from conservative mixing. A key to identifying this deficit was the sampling over extensive areas, including the East Siberian Sea, where the residence time for the freshwater component was >1 year. However, a 10%–20% net removal of DOC also could be accommodated for the younger water masses of the Laptev Sea. The actual degradation rate of riverine DOC is probably even higher, as there are additional DOC sources such as coastal erosion and marine phytoplankton production that are counterbalancing removal.

[47] A large number of previous studies of DOC in the Arctic Ocean have argued that DOC behaves conservatively over the shelves [e.g., *Dittmar and Kattner*, 2003; *Amon*, 2004; *Köhler et al.*, 2003; *Amon and Benner*, 2003; *McGuire et al.*, 2009]. These studies had more limited geographical coverage and were focused to the inner part of the plumes generated from the Ob, Yenisey and Lena, encompassing surface waters with shorter residence times where any losses were not as evident.

[48] There have been a number of limitations on understanding DOC in the Arctic. Sampling in the Arctic Ocean has been largely restricted to the late summer months, due to ice cover and weather conditions. Also, the Russian Arctic river discharges have until recently not been well monitored on an annual basis. Behavior of DOC over the shelves has therefore been evaluated by comparing to river concentrations extrapolated from concentrations measured in the estuaries in late summer. However, recent efforts have delivered good year-round measurements of river DOC concentrations [*McClelland et al.*, 2008; *Holmes et al.*, 2008]. It has been shown that the spring flood water, delivering 60%–90% of the annual DOC load to the Arctic Ocean, has a much higher percentage of labile DOC [*Holmes et al.*, 2008]. The fate of this labile DOC is not captured in studies restricted to estuaries in the late summer. While the ISSS-08 cruise took place in late summer, it fortunately covered areas with longer water residence times, thereby sampling freshwater components representative of discharge throughout the year. Based on estimates of the freshwater and DOC residence times in the western East Siberian Sea, a first-order DOC removal rate constant of ~0.3 yr^{-1} was calculated here. Such a value may apply to much of the shelf, although in the Laptev Sea the residence times for freshwater are too short to obtain a well-constrained removal rate, and further east in the East Siberian Sea it is difficult to calculate the freshwater residence time because freshwater inputs are poorly constrained. Nonetheless, this value is a factor of 3 higher than that inferred in a recent modeling study [*Manizza et al.*, 2009]. That study used a single degradation rate for the entire Arctic; the data presented here can provide a basis for a more complex approach, incorporating a higher removal rate constant for the shelves than for the Arctic interior. However, even though this data set covers a large area, still no seasonal measurements of DOC in the ESAS are available, and additional studies are required to further constrain DOC degradation throughout the year.

[49] Interestingly, our study shows that removal of HS, which generally is regarded as being composed of rather refractive components, is pronounced in the East Siberian Sea. The HS appears to be removed to a higher extent than DOC, which is probably due to HS-specific removal processes such as flocculation-sedimentation and photodegradation, along with a shift from domination of the DOC pool by terrestrial material to a higher fraction of marine-produced DOC further out on the shelf. As humic substances are common in permafrost organic matter [*Dutta et al.*, 2006], this study emphasizes the concerns about consequences of increased DOC delivery caused by thawing permafrost and the degradation of old peat organic carbon in the Arctic Ocean. The rates of such degradation may also change significantly as changes in ice cover in the region affect photodegradation.

[50] The extent of DOC degradation on the shelf found here substantiates the nonconservative behavior of DOC inferred in a recent modeling study [*Manizza et al.*, 2009] and in a study on the export of terrestrial DOC to the Atlantic [*Hansell et al.*, 2004]. Also, this removal of DOC can account for a significant fraction of the levels of pCO_2 oversaturation also found for this area during ISSS-08, due to degradation of OC [*Anderson et al.*, 2009]. Therefore, the present study implies that Arctic riverine DOC is a potential large source of CO_2 to the atmosphere. Overall, there is a growing set of studies that challenge the paradigm [*Anderson et al.*, 1998; *Stein and Macdonald*, 2004] of conservative DOC mixing in the Arctic Ocean, and the complexities of carbon loss on the shelves must be considered in determining the present and future fluxes of carbon into the Arctic interior and in future modeling of the Arctic carbon cycle.

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