Dissolved organic nitrogen dynamics in the Arctic Ocean

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1. Introduction

Dissolved organic nitrogen (DON) is an important source of reactive nitrogen in the surface ocean, and the dominant pool of fixed N when inorganic nutrients are depleted. Marine DON ultimately results from primary production in the surface ocean, subsequently providing N as substrate for heterotrophic growth (Azam and Hodson, 1977; Azam and Cho, 1987) via direct uptake of smaller molecules providing N as substrate for heterotrophic growth (Azam and Hodson, 1987). However, recent studies show that terrigenous material exported via river runoff to the Arctic Ocean is partially labile and that there is a significant sink for the terrigenous dissolved organic carbon (tDOC) pool within the Arctic marine environment (Hansell et al., 2004; Alling et al., 2010; Letscher et al., 2011).

The Arctic Ocean provides a unique system in which to study the dynamics of DON. Inflow shelves [e.g., Barents and Chukchi Seas; (Carmack and Wassmann, 2006)] are highly influenced by Atlantic and Pacific Ocean inflow of nutrient-rich waters and can be highly productive seasonally [e.g., during sea-ice retreat; (Hansell et al., 1993; Salskaug, 2004; Bates et al., 2005)], while there are large inputs of terrigenous organic material from the many rivers that drain into the interior shelves [e.g., Siberian shelves and Beaufort Sea shelf; (Carmack and Wassmann, 2006; Raymond et al., 2007; Seitzinger and Harrison, 2008; Holmes et al., 2012)]. As Arctic permafrost thaws due to a warming climate, river export of DON is expected to increase by another half in western Siberia by year 2100 (Frey et al., 2007), with similar increases expected for Alaskan rivers (Frey and McClelland, 2009). Terrigenous material comprises a significant fraction (20–30%) of the surface DON pool in the Siberian shelf seas (Kattner et al., 1999; Dittmar, 2004), but this terrigenous DON (tDON) was reported to be largely refractory and resistant to degradation based on near conservative mixing gradients (Dittmar et al., 2001). However, recent studies show that terrigenous material exported via river runoff to the Arctic Ocean is partially labile and that there is a significant sink for the terrigenous dissolved organic carbon (tDOC) pool within the Arctic marine environment (Hansell et al., 2004; Alling et al., 2010; Letscher et al., 2011).

Terrestrially derived DON that survives degradation can be exported from the Arctic shelves to the Polar Surface Layer (PSL), the relatively fresh upper 30 m of a vertically stratified water column formed from inputs of river runoff and sea-ice melt in the Arctic basins (e.g., Canada and Eurasian Basins). Elevated concentrations of DON ([DON]) reported in Arctic waters (8–65 μM N) (Cauwet and Sidorov, 1996; Gordeev et al., 1996; Lara et al., 1998; Lobbes et al., 2000; Dittmar and Kattner, 2003; Köhler et al., 2003; Guo and Macdonald, 2006; Holmes et al., 2012), compared with lower concentrations of ~3–8 μM N found in Arctic marine waters (Davis and Benner, 2005; Mathis et al., 2009), provide sufficiently resolved spatio-temporal gradients required to overcome the analytical limitations of DON measurement, thereby allowing elucidation...
of geochemical transformations and processes that influence the Arctic DON pool.

In addition to fluvial inputs, marine waters entering the Arctic Ocean via the North Atlantic in the east and Bering Strait in the west carry large loads of nitrate (−4–25 μM N) (Hansell et al., 1993; Olsen et al., 2003), in turn supporting high rates of phytoplankton production in the Barents (Sakshaug, 2004) and Chukchi Seas (Springer and McRoy, 1993; Hill and Cota, 2005; Walsh et al., 2005; Bates et al., 2005), respectively. The annual generation of large amounts of organic matter in these highly productive shelf ecosystems (Walsh, 1995; Macdonald et al., 2010) suggests the likelihood of observing significant marine DON production.

In this study, we combine observations of [DON], nitrogenous nutrients, and tracers of freshwater taken within the summer-seasone PSL of the Arctic Ocean during the last decade. Surface distributions of [DON] from four cruises determine those shelf processes important for controlling DON dynamics. These ocean observations of [DON] are compared to modeled [DON] in the six largest Arctic rivers (Holmes et al., 2012) and the fate of tDON in the marine environment is investigated.

2. Regional hydrography

2.1. Eastern Arctic

The eastern Arctic system (here defined as waters north of the Arctic Circle in the eastern hemisphere 0–180° E) receives marine water with a mean salinity of ~34.9 from the Atlantic Ocean (Fig. 1). Surface flow is generally cyclonic; to the east over the Barents Sea shelf, passing into the Kara Sea (Macdonald et al., 2004) and subsequent transport into the Laptev and East Siberian Seas where they receive another ~581 km3 yr−1 from the Lena River (Holmes et al., 2012). The direction of flow within the Laptev and East Siberian Seas is strongly influenced by the prevailing summertime winds that in turn are controlled by the phase of the Arctic Oscillation (AO) (Ekwurzel et al., 2001; Guay et al., 2001; Anderson et al., 2004). During a negative AO phase, weakened subpolar westerlies due to a stronger Beaufort High allow for a northerly flow in the Laptev Sea, with shelf discharge joining the Transpolar Drift (TPD) near the Lomonosov Ridge. In contrast, a positive AO phase is characterized by a weaker Beaufort High, which intensifies the subpolar westerlies, driving a strong easterly flow from the Kara and Laptev Seas into the East Siberian Sea. There, the fluvial component mixes with runoff from the Kolyma River [111 km3 yr−1; (Holmes et al., 2012)] before detachment from the shelf to join the TPD near the Mendeleyev Ridge. This circulation in the eastern Arctic system allows for a 2–5 years residence for river runoff over the Eurasian shelves (Schlosser et al., 1994; Ekwurzel et al., 2001; Karcher and Oberhuber, 2002) before export to the interior Arctic Ocean. The combined input of Atlantic Ocean waters across the Barents Sea and freshwater from Siberian rivers is approximately balanced by shelf-basin transport into the Eurasian Basin and eventual export out of the Arctic with the Transpolar Drift through Fram Strait.

2.2. Western Arctic

The western Arctic system (here defined as those waters in the western hemisphere 0–180° W, north of Bering and Fram Straits) receives Pacific Ocean water with a mean salinity of ~33 via Bering Strait (Coachman et al., 1975). These waters contain elevated levels of nitrate (up to 25 μM), which support high seasonal levels of phytoplankton primary production in the Chukchi Sea during sea-ice retreat (Sambrotto et al., 1984; Hansell et al., 1993; Mathis et al., 2009). In addition, the Bering Strait inflow is influenced by the Yukon River (Woodgate and Aagaard, 2005), delivering 208 km3 yr−1 of freshwater to the eastern Bering Sea shelf (Holmes et al., 2012). Waters overlying the Chukchi Sea shelf flow north and east, with a portion entering the anticyclonic circulation of the Beaufort Gyre over the Canadian Basin. The PSL of the Beaufort Gyre is further modified by input from the Mackenzie River [298 km3 yr−1; (Holmes et al., 2012)]. At 12–15 years, the residence time for the fluvial component in the PSL is much longer in the western than the eastern Arctic due to retention within the Beaufort Gyre circulation (Kadko and Muench, 2005). Western Arctic waters are exported to the North Atlantic through both the Canadian Archipelago and Fram Strait (Jones et al., 1998).

3. Methods

3.1. Field collected data sets

Observations of dissolved nitrogen species [TDN] (total dissolved nitrogen), [NO3− + NO2−], [NH4+], stable oxygen isotopes, and salinity within the PSL were collected from numerous CTD/hydrocast stations on four cruises in the Arctic over the last decade (Fig. 1). During the western Shelf-Basin Interactions (SBI) project (Grebmeier and Harvey, 2005), samples were collected in spring (5 May–15 June 2002; 80–100% sea-ice cover) and summer (16 July–26 Aug 2002; 0–20% sea-ice cover) cruises with hydrocast stations located in the outer shelf region of the Chukchi Sea shelf and in deep waters of the adjacent Beaufort Gyre. The timing of the two cruises allows direct comparison of biogeochemical conditions during sea-ice cover and subsequent sea-ice retreat in the same year. Cruise ARKXXIII/3 occupied stations over the

Fig. 1. Station locations for cruises ARKXXIII/3 (black dots), SBI (red dots), and RUSALCA (purple dots) in reference to general surface circulation (black arrows) and rivers of the Arctic Ocean. The eastern Arctic system (0°–180° E) is characterized by cyclonic circulation over the Eurasian shelf seas with return flow in the Transpolar Drift (TPD) towards Fram Strait. The anticyclonic circulation of the Beaufort Gyre (BG) dominates the western Arctic system (180° W–0°). Geographic features are marked as follows: Atl = Atlantic Ocean, FS = Fram Strait, BarS = Barents Sea, KS = Kara Sea, EB = Eurasian Basin, LS = Laptev Sea, LR = Lomonosov Ridge, MR = Mendeleyev Ridge, MB = Makarov Basin, ESS = East Siberian Sea, CS = Chukchi Sea, BS = Bering Strait, BerS = Bering Sea, BS = Beaufort Sea, CA = Canadian Archipelago, and CB = Canadian Basin.
deep Arctic basins from 12 August to 17 October 2008 and spanned waters of the western and eastern Arctic systems from the Canada Basin west to the Eurasian Basin. The RUSALCA 2009 cruise occupied the southern and western Chukchi Sea as well as the adjacent East Siberian Sea during 1 September to 30 September 2009. Data reported here were collected at depths <10 m, well within the ~30 m deep PSL.

The marine data reported here are also compared to dissolved nitrogen species in the six largest Arctic rivers sampled during the 2003–2006 PARTNERS (Pan-Arctic River Transport of Nutrients, Organic Matter, and Suspended Sediments) program (http://arcticgreatrivers.org/), and recently modeled by Holmes et al. (2012). Annual flow-weighted mean values were calculated for [DON], [NO$_3^-$ + NO$_2^-$], [NH$_4^+$], and [TDN] in each river using the modeled annual loads of each N species and annual river discharge from Holmes et al. (2012).

3.2. Nitrogen species

3.2.1. Sampling

Marine samples were filtered for the removal of particulate organic matter (POM) using precombusted Whatman GF/F filters (nominal pore size, 0.7 μm) held in acid-cleaned polycarbonate filter holders. Filter holders were connected inline with the seawater source (clean seawater intake during ARKXXIII/3 and CTD-Niskin bottle during RUSALCA-09 and SBI) using acid-cleaned, DOC-free silicon tubing. Seawater was collected into preconditioned 60 mL HDPE bottles and immediately frozen upright at −20 °C. New filters were loaded prior to each sample filtration. Riverine samples were similarly filtered for the removal of POM (pore size, 0.45–1.0 μm) into HDPE bottles and frozen before analysis (Cooper et al., 2008; Holmes et al., 2012). In order to best characterize the constituent flux that reached the ocean, river sampling occurred as close to the mouths of rivers as feasible (Holmes et al., 2012).

3.2.2. TDN

Analyses of total dissolved nitrogen were performed by high-temperature combustion using a Shimadzu Total Nitrogen analyzer coupled to a Shimadzu TOC-VCSH system (Dickson et al., 2007). The oxidation product of nitric oxide (NO) is quantified by reaction with ozone and detection of the resulting chemiluminescence. Standardization for TDN was achieved using potassium nitrate. Deep seawater and low carbon reference waters as provided by the Hansell CRM Program (Hansell, 2005) were measured every sixth analysis to assess the day-to-day and instrument-to-instrument variability. The precision for TDN analyses is ~0.5 μM or a CV of 5–10%.

3.2.3. NO$_3^-$ + NO$_2^-$

For cruises ARKXXIII/3 and RUSALCA-09, the sum of [NO$_3^-$ + NO$_2^-$] in filtered (0.7 μm) samples was measured by reduction to NO using a solution containing heated, acidic V(III), followed by chemiluminescent detection of NO (Braman and Hendrix, 1989). Standardization was achieved using potassium nitrate. Samples were measured using a configuration yielding a limit of detection of 0.05 μM with a precision of ±0.1 μM. Nitrate + nitrite data from the SBI 2002 cruises were taken from the SBI data archive at http://www.eol.ucar.edu/projects/sbi/.

3.2.4. NH$_4^+$

For the RUSALCA-09 cruise, ammonium was measured on frozen-archived samples using a fluorescence technique with orthophthalaldehyde (OPA) (Holmes et al., 1999). Filtered (0.7 μm) samples are allowed to react for 2 h at room temperature with an OPA-containing solution, with subsequent measurement of fluorescence at an excitation/emission of 350 nm/410–600 nm. Standardization was achieved using ammonium chloride. The limit of detection was 0.025 μM with a precision of ±0.01 μM. For the SBI 2002 cruises, ammonium values, measured by the Berthelot reaction (Patton and Crouch, 1977), were retrieved from the SBI data archive. No measurements of ammonium were made for cruise ARKXXIII/3; however, surface [NH$_4^+$] at deep ocean stations during SBI 2002 was observed to be relatively low (<0.025 μM).

3.2.5. DON

[DON] was calculated by subtracting the sum of dissolved inorganic nitrogen ([DIN]=[NO$_3^-$ + NO$_2^-$] + [NH$_4^+$]) from the measured [TDN]; [DON]=[TDN]−[DIN]. Ammonium was not measured during ARKXXIII/3, but the very low ammonium values in the off-shelf PSL (see the Results section) add only a small error to the DON estimate. Propagation of error yields a precision on DON determinations of ±0.5 μM.

Table 1

<table>
<thead>
<tr>
<th>River</th>
<th>DON</th>
<th>NO$_3^-$</th>
<th>NH$_4^+$</th>
<th>TDN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ob</td>
<td>18.4±1.0</td>
<td>9.5±0.5</td>
<td>4.9±0.26</td>
<td>31.1±1.7</td>
</tr>
<tr>
<td>Yenisey</td>
<td>12.5±0.7</td>
<td>5.5±0.3</td>
<td>0.2±0.01</td>
<td>18.3±1.0</td>
</tr>
<tr>
<td>Lena</td>
<td>16.6±0.9</td>
<td>3.0±0.2</td>
<td>1.1±0.06</td>
<td>20.1±1.1</td>
</tr>
<tr>
<td>Kolyma</td>
<td>10.9±0.6</td>
<td>3.2±0.2</td>
<td>1.3±0.07</td>
<td>16.1±0.9</td>
</tr>
<tr>
<td>Mackenzie</td>
<td>7.4±0.4</td>
<td>5.8±0.3</td>
<td>0.7±0.04</td>
<td>14.4±0.8</td>
</tr>
<tr>
<td>Yukon</td>
<td>16.1±0.9</td>
<td>8.2±0.5</td>
<td>0.7±0.04</td>
<td>23.0±1.2</td>
</tr>
</tbody>
</table>
δ Mean Ocean Water (VSMOW) and expressed using the conventional notation. Samples were analyzed in duplicate with a precision of ±0.08 ‰. Oxygen isotope data for the SBI 2002 cruises were taken from the SBI data archive; precision was reported to be ±0.04 ‰. Isotopic compositions were not measured during cruise RUSALCA-09.

### 3.3. Stable oxygen isotopes and salinity

#### 3.3.1. δ18O

For cruise ARKXXXIII/3, samples for stable oxygen isotope measurements (δ18O) were collected unfiltered into 10 ml glass vials and immediately capped and sealed. Analyses were performed by mass spectrometry at the Stable Isotope Laboratory at RSMAS, University of Miami, using a modified method of Epstein and Mayeda (1953) detailed elsewhere (Swart, 2000). Counts were calibrated using Vienna Standard Mean Ocean Water (VSMOW) and expressed using the conventional δ18O ‰ notation. Samples were analyzed in duplicate with a precision of ±0.08 ‰. Oxygen isotope data for the SBI 2002 cruises were taken from the SBI data archive; precision was reported to be ± 0.04 ‰. Oxygen isotopes were not measured during cruise RUSALCA-09.

#### 3.3.2. Salinity

Salinity was measured by conductivity using the ship’s salinometer mounted at the seawater intake (cruise ARKXXXIII/3, RUSALCA-09) or a Guildline Autosal 8400A salinometer (SBI 2002 cruises).

### 3.4. Calculations of river and sea-ice melt fractions in the polar surface layer

Oxygen isotope and salinity data were used to calculate the fractions of river water (RW), sea-ice melt (SIM), and marine water (SW) present in samples collected from the PSL [e.g., (Cooper et al., 2005; Bates, 2006; Mathis et al., 2007; Letscher et al., 2011)]. Each end-member was assigned a characteristic δ18O and salinity based on values reported in the literature. The water source fractions (RW, SIM, and SW) were calculated from the mass balance solutions to these equations:

\[ \delta^{18}O = \left( \frac{\text{RW} \times \delta^{18}O_{\text{RW}}}{\text{RW} S_{\text{RW}}} \right) + \left( \frac{\text{SIM} \times \delta^{18}O_{\text{SIM}}}{\text{SIM} S_{\text{SIM}}} \right) + \left( \frac{\text{SW} \times \delta^{18}O_{\text{SW}}}{\text{SW} S_{\text{SW}}} \right) \]

\[ S = \left( \frac{\text{RW} S_{\text{RW}}}{\text{RW} \times \delta^{18}O_{\text{RW}}} \right) + \left( \frac{\text{SIM} S_{\text{SIM}}}{\text{SIM} \times \delta^{18}O_{\text{SIM}}} \right) + \left( \frac{\text{SW} S_{\text{SW}}}{\text{SW} \times \delta^{18}O_{\text{SW}}} \right) \]

\[ 1 = \text{RW} + \text{SIM} + \text{SW}. \]

Stations were separated by hemisphere, with those from the eastern hemisphere (west of 180°E) assigned eastern Arctic end-member values and those from the western hemisphere (east of 180°E) assigned western Arctic end-members. Eastern Arctic end-member values were: RW δ18O = −18.6 ‰, RW S = 0; SIM δ18O = −1.9 ‰ (Eicken et al., 2002), SIM S = 4.5 (Mathis et al., 2007); and Atlantic SW δ18O = +0.3 ‰ (Bauch et al., 1995), Atlantic S = 34.9. Western Arctic end-members were assigned: RW δ18O = −19.6 ‰, RW S = 0; SIM δ18O = −1.9 ‰, SIM S = 4.5; and Pacific SW δ18O = +0.3 ‰, Pacific S = 33 (Coachman et al., 1975). Riverine end-members were assigned using the flow weighted δ18O values from Cooper et al. (2008) for the Mackenzie and Yukon Rivers (western Arctic RW) and the Ob, Yenisey, Lena, and Kolyma Rivers (eastern Arctic RW).

### 4. Results

#### 4.1. Delivery of nitrogen species by Arctic rivers

The six major Arctic rivers exhibit the largest fluxes of dissolved nitrogen (DON, NO3−, NH4+, and TDN) in the early summer months following the spring freshet. Typically, the months of May–June coincide with both the highest seasonal concentration of each nitrogen species and the highest river volume flux (Holmes et al., 2012). Fluxes of DON and NH4+ during the winter months (November to April) are an order of magnitude lower than their summer peak while NO3− has a generally lower but more varied wintertime flux (Holmes et al., 2012). These six Arctic rivers deliver each year a total of 32 Gmol N as DON, 13 Gmol N as NO3−, and 3 Gmol N as NH4+. For a total TDN flux of 48 Gmol N (Holmes et al., 2012; Tank et al., 2012).

Modeled annual loads of each N species and annual river discharge from Holmes et al. (2012) were used to calculate annual flow weighted mean concentrations in the Arctic rivers. The flow weighted means ranged from 7.4 to 18.4 μM for [DON], from 3.0 to 9.5 μM for [NO3−], from 0.2 to 4.9 μM for [NH4+], and from 14.4 to 31.1 μM for [TDN] (Table 1). A mean end-member [DON] in eastern Arctic rivers was calculated from the mass balance solutions to these equations:

\[ [\text{DON}]_{\text{fl}} = \frac{[\text{DON}]_{\text{RW}} \times \text{RW} S_{\text{RW}}}{[\text{DON}]_{\text{RW}}} + \frac{[\text{DON}]_{\text{SIM}} \times \text{SIM} S_{\text{SIM}}}{[\text{DON}]_{\text{SIM}}} + \frac{[\text{DON}]_{\text{SW}} \times \text{SW} S_{\text{SW}}}{[\text{DON}]_{\text{SW}}}. \]

\[ [\text{N}_{\text{fl}}] = [\text{DON}]_{\text{fl}} + [\text{NO3}^{-}] + [\text{NH4}^{+}]. \]

#### 4.2. Summertime salinity distributions, river runoff and sea-ice melt contributions to the Arctic Ocean PSL

#### 4.2.1. Surface salinity

Salinities at Bering Strait and in the southern Chukchi Sea were −31 to −32 (Fig. 2a), reduced from the characteristic salinity of 33 for Pacific Ocean inflow waters due primarily to the presence of river runoff. Farther downstream at the outer Chukchi Sea shelf, salinities were reduced further to −26 to −28 by both sea-ice melt and river...
Low salinities (~22–24) were also found in the waters of the Beaufort Gyre. Salinities were generally higher in the eastern Arctic, with a salinity front observed over the outer shelf just east of 180° E separating the higher salinity (~29–30) eastern Arctic from the lower salinity (~27) western Arctic. Salinities over the Eurasian Basin (Fig. 1) were ~32–33, characteristic of the Atlantic inflow waters. Elsewhere in the eastern Arctic, isolated regions of low salinity were observed over the Makarov Basin and the eastern sector of the East Siberian Sea, decreasing to values of 26–27.

4.2.2. RW
River water, with its contribution having been determined using oxygen isotopes, was ubiquitous within the summertime PSL, with contributions ranging from 5 to 25% (Fig. 2b). Highest river water contributions (~20–25%) were observed in the eastern Arctic coinciding with the regions of reduced salinity over the Makarov Basin and East Siberian Sea. Contributions were more varied over both the Eurasian Basin and the outer Siberian shelf, ranging from 6 to 12%. Highest fractions in the western Arctic were found within the southern Beaufort Gyre, reaching 18–19%. Lower river water contributions were found on the Chukchi Sea shelf, decreasing from ~15% on the northern outer shelf to ~5% in the southern Chukchi Sea.

4.2.3. SIM
A composite map of sea-ice melt fractions from data collected in the summers of 2002 and 2008 is shown in Fig. 2c. The stations were located in open (ice free) water, post sea-ice retreat, with the exception of all stations north of 80° N in the eastern Arctic, which were located in pack ice. In general, contributions from sea-ice melt were higher in the western Arctic compared to the eastern Arctic, ranging from 10 to 18% over the Beaufort Gyre to 4–9% over the outer Siberian shelf. Highest sea-ice melt fractions (>30%) were observed off the north coast of Alaska; these stations had been sampled ~2 weeks after sea-ice breakup and retreat. Sea-ice melt contributions were negligible over the deep basins of the eastern Arctic (Eurasian, Makarov) owing to the continued presence of sea-ice at these stations throughout the summer season.

4.3. Dissolved nitrogen in the Arctic Ocean PSL

4.3.1. DON
The summertime distribution of [DON] within the Arctic Ocean PSL is shown in Fig. 3a. Highest concentrations (6–8 μM) were observed in the southern Chukchi Sea, immediately north of Bering Strait. Concentrations elsewhere in the western Arctic were lower, generally ~5 μM over the outer shelves decreasing to <4 μM within the Beaufort Gyre. In the eastern Arctic, [DON] of ~5 μM was observed over the outer East Siberian shelf and within the Eurasian Basin. Higher concentrations (6–7 μM) were found in the Makarov Basin and the eastern sector of the East Siberian Sea. [DON] in the surface Arctic Ocean is lower than reported by Wheeler et al. (1997), perhaps reflecting interannual variability or differences in analytical techniques. There were contrasting relationships between [DON] and salinity (Figs. 2a and 3a) between the two Arctic systems. In the eastern Arctic, the highest [DON] correlated with the low salinity waters of the Makarov Basin and East Siberian Sea. By contrast, lower salinity water within the Beaufort Gyre had the lowest [DON], while the highest [DON] in

![Fig. 4. DON-salinity plots for the (a) late summer season eastern Arctic system, (b) spring season western Arctic system (SBI 2002 data only), and (c) summer season western Arctic system. Fraction of RW is represented by the color data points. Stations lacking δ18O data, for which estimates of RW cannot be made, are shown with black data points. Calculated Model II regression for the eastern Arctic (dashed line in (a)): DON = −0.154 × salinity + 9.1; R² = 0.18, n = 98; standard error of intercept = ±1.0 μM.](image-url)
4.3.3. NH$_4^+$

Waters present in Bering Strait. In addition, nitrate reached 26 μM from rivers (Ob, Yenisey, Lena, and Kolyma) is 15.2±0.8 years on the Eurasian shelves before its transport offshore to the region (Mathis et al., 2005; Letscher et al., 2011). Eastern Arctic river water has a multi-year residence time of 6.1±1.3 years, indicating a net loss of 3.5±2 yr$^{-1}$ over the Siberian Arctic shelves. If the annual apparent loss of DON provides a conceptual first-order decay constant for tDON, as estimated using a $^{228}$Ra/$^{226}$Ra aging technique (Hansell et al., 2004).

4.3.2. NO$_3^-$

Summertime nitrate concentrations within the PSL were generally low (<0.5 μM) (Fig. 3b), while values reached 15 μM in the Pacific waters present in Bering Strait. In addition, nitrate reached 2–3 μM over the Eurasian shelves sampled in October 2008.

4.3.3. NH$_4^+$

Ammonium concentrations within the PSL were low (<0.05 μM) over the outer East Siberian and Chukchi Sea shelves (Fig. 3c), indicative of the availability of nitrate from sea ice melt (Codispoti et al., 1987) and Yenisey) as contributing riverine waters to the shelf where elevated [NH$_4^+$] has been observed previously (Codispoti et al., 2005).

5. Discussion

Property-salinity plots have been used extensively in the Arctic to discern hydrographic controls on chemical distributions, as for example, evaluation of the dissolved organic carbon (DOC) pool (Kattner et al., 1999; Köhler et al., 2003; Hansell et al., 2004; Cooper et al., 2005; Mathis et al., 2005; Letscher et al., 2011). Here we employ DON-salinity plots along with estimates of river water fractions present in the Arctic PSL to investigate the behavior of DON across shelf-to-basin mixing gradients.

5.1. Non-conservative behavior of tDON over the eastern Arctic shelves

A plot of [DON] versus salinity for stations occupying the eastern Arctic is shown in Fig. 4a. Mixing between two end-members is evident: DON-enriched river water at low salinities and lower DON marine water at high salinity. The impact of a third potential end member in Arctic summer from sea ice melt is both reduced in this region (Fig. 2c) and likely to be negligible for reasons of its [DON] (detailed below in Section 5.5). Regression analysis reveals an apparent [DON] within the river water fraction of 9.1 ± 1.0 μM N (Model II regression, ± standard error of intercept), taken from the y-intercept (salinity = 0) in Fig. 4a. This apparent river end-member [DON] can be compared to estimates of the [DON] in the Siberian rivers draining to the region from (Holt et al., 2005). The calculated annual mean flow weighted [DON] within the four Siberian rivers (Ob, Yenisey, Lena, and Kolyma) is 15.2 ± 0.8 μM N. The [DON] found within the river water fraction from the regression observed over the Makarov and Eurasian Basins is reduced relative to that measured in the regional riverine sources, indicating a net loss of 6.1 ± 1.3 μM tDON over the Siberian Arctic shelves. If the annual flow weighted [DON] for the more local eastern Siberian Lena and Kolyma Rivers is employed instead (15.7 ± 0.9 μM N), the net loss of tDON is 6.6 ± 1.3 μM.

Coupling of shelf residence times for the river water fraction with the apparent loss of DON provides a first-order decay constant for tDON, as described previously for the Arctic tDOC pool in this region (Alling et al., 2010; Letscher et al., 2011). Eastern Arctic river water has a multi-year residence on the Eurasian shelves before its transport offshore to the join the TPD (Schlosser et al., 1994; Guay et al., 2004). Using a He$^{33}$H technique, Schlosser et al. (1994) and Ekwurzel et al. (2001) estimated the Eurasian river water shelf residence at 3.5 ± 1.5 years and 2–5 years, respectively. System modeling by Karcher and Oberhuber (2002) found a similar result of 2–3 years. In addition, measurements of $^{228}$Ra ($\lambda_{1/2}$ = 5.7 yr), a tracer of shelf water provenance, did not show significant decay across the shelf break into the TPD (Letscher et al., 2011). Here we assign an eastern Arctic river water shelf residence time of 3.5 ± 1.5 years. Using this residence time with the estimated tDON loss within the river water fraction yields a first-order decay constant, $\lambda = 0.15 \pm 0.07$ yr$^{-1}$, if all four Siberian Arctic rivers are considered or essentially the same value, $\lambda = 0.16 \pm 0.07$ yr$^{-1}$, if only the Lena and Kolyma are selected as contributing riverine waters to the shelf water shelf residence time and the river runoff is of a more Paciﬁc origin (Kolyma, Indigirka). Our analysis indicates that 25–55% of Siberian Arctic river tDON is removed during transit of the Eurasian shelves over a 2–5 year timescale.

5.2. Non-conservative behavior of tDON within the Beaufort Gyre of the western Arctic

Data from spring and summer cruises within the SBI 2002 field season allow comparison of the DON distribution between pre- and post-bloom conditions in the NE Chukchi Sea and Beaufort Gyre. The DON-salinity plot for the SBI 2002 spring (May–early June) cruise is shown in Fig. 4b. Higher river water fractions were present at lower salinities, yet [DON] at lower salinities during the summer remains relatively unchanged from its spring value (3.8 ± 0.5 μM N at salinities < 28). Again the contribution of a sea ice melt end member to [DON] within the region is likely negligible owing to its similar [DON] to winter marine water [DON] (see Section 5.5). The samples with high river water fractions and 3.8 μM DON (the lower salinities within Fig. 4c) correspond to stations within the Beaufort Gyre (see Fig. 2b for reference), which has been shown to retain western Arctic river water for several years (Macdonald et al., 2002; Kadko and Muench, 2005). Hansell et al. (2004) used measurements of dissolved radium isotopes to estimate the residence time of western Arctic river water within the PSL of the

Table 2

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<thead>
<tr>
<th>System</th>
<th>AR rivers</th>
<th>[DON]$^a$ river</th>
<th>[DON]$^b$ aged RW</th>
<th>[DON]$^c$ lost$^d$</th>
<th>RW res. time</th>
<th>$\lambda$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eastern Ob + Yenisey + Lena + Kolyma</td>
<td>15.2 ± 0.8</td>
<td>9.1 ± 1.0</td>
<td>6.1 ± 1.3</td>
<td>3.5 ± 2 yr$^{-1}$</td>
<td>0.15 ± 0.07 yr$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>Eastern Lena + Kolyma</td>
<td>15.7 ± 0.9</td>
<td>9.1 ± 1.0</td>
<td>6.6 ± 1.3</td>
<td>3.5 ± 2 yr$^{-1}$</td>
<td>0.16 ± 0.07 yr$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>Western Mackenzie + Yukon</td>
<td>11.0 ± 0.6</td>
<td>3.8 ± 0.5</td>
<td>7.2 ± 0.8</td>
<td>13 ± 1 yr$^{-1}$</td>
<td>0.08 ± 0.01 yr$^{-1}$</td>
<td></td>
</tr>
</tbody>
</table>

a Initial river DON concentration (μM ± SE).

b Aged river DON concentration (μM ± SE).

c Difference between initial and aged river DON concentrations (μM ± SE).

d Residence time for river water on the Eurasian shelves (eastern Arctic) was estimated from He$^{33}$H ages (Schlosser et al., 1994; Ekwurzel et al., 2001).
Beaufort Gyre, arriving at a mean age of 13 ± 1 years. As noted above, the absence of a DON concentration gradient with salinity during spring, as well as the continued low values at low salinity during summer, suggests that the river and marine fractions during spring have essentially equal concentrations of DON. Aged Beaufort Gyre river water with a mean [DON] of 3.8 ± 0.5 μM can be compared with [DON] of the western Arctic rivers. The mean annual flow weighted [DON] within the Yukon and Mackenzie Rivers (from Holmes et al., 2012) yielded a value of 11.0 ± 0.6 μM N. Thus a net tDON loss of 7.2 ± 0.8 μM over a 13 ± 1 year timescale is indicated from the river water fraction of the Beaufort Gyre PSL, yielding a first-order decay constant, λ = 0.08 ± 0.01 yr⁻¹ (Table 2). This concentration change represents a 55–70% removal of tDON during the decadal timescale of Beaufort Gyre circulation.

5.3. Net production of marine DON over the Chukchi shelf

Nutrient-enriched Pacific waters entering the western Arctic at Bering Strait support summertime net community production (NCP) rates on the Chukchi Sea shelf of up to ~300 g C m⁻² yr⁻¹ (Bates et al., 2005; Mathis et al., 2009). Inspection of the spring and summer DON distributions within this region allows assessment of the fraction of this production that is released as DON. Spring (pre-bloom) [DON] within surface waters located over the Chukchi Shelf has a mean value of 4.0 ± 0.7 μM N (Fig. 4b). Concomitant [NO₃⁻] within the end of winter surface waters is correlated with salinity (Fig. 5a), ranging from ~14 μM NO₃⁻ at salinity = 33 in the southern Chukchi Sea near Bering Strait to near zero within the Beaufort Gyre PSL at salinity = 30–31. This surface layer nitrate is almost completely utilized in the summer season (Fig. 5b and Fig. 3b), fueling NCP over the Chukchi shelf. A portion of this NCP is released as DON, represented by the increase in summer season [DON] at salinities > 29 (Fig. 5b). Net production of marine DON over the Chukchi shelf above the end of winter 4.0 μM [DON] ranged from ~0 to 8.0 μM, with an average over the SBI region of 1.9 ± 1.1 μM. Taking summertime [NO₃⁻] to be essentially zero, the ratio of the slopes in Fig. 5b (0.377: 4.584) for marine DON (red line: showing DON accumulation between spring and summer) and winter ice-melt-corrected nitrate (dashed black line: which is a measure of NO₃⁻ utilized) indicates that 8 ± 1% of seasonal nitrate drawdown is converted to marine DON in the Chukchi Sea region. The contribution of urea to the observed seasonal increase in marine DON was low at 2–4% (urea data from the SBI program). As expected, net production of marine DON is not observed over the Beaufort Gyre where PSL [NO₃⁻] is low year-round.

5.4. Impact of fluvial inputs of dissolved N on Arctic ecosystem productivity

The riverine input of nitrate and ammonium, along with decay of tDON by remineralization to DIN, represents a source of allochthonous nitrogen to the Arctic shelf seas, thus supporting export production. Here we combine the fluxes of nitrate, ammonium, and DON from the six largest Arctic rivers reported by Holmes et al. (2012) with estimates of export production for the Arctic shelf seas to assess the impact of riverine delivery of bioavailable dissolved nitrogen on ecosystem productivity. The first-order decay constants determined for the Arctic tDON pool from this study are used to estimate the amount of DIN released from the decay of tDON over the residence time of the fluvial waters within each region. Table 3 lists the sum of nitrogen inputs to each Arctic region by the respective river(s) of influence. Estimates of export production are taken from Macdonald et al. (2010) with the exception of the eastern East Siberian Sea taken from Anderson et al. (2011). Values were converted from carbon to nitrogen units using a C:N molar ratio of 6.6. Fluvial inputs of dissolved nitrogen have the largest impact over the Siberian shelf seas (Kara, Laptev, and western East Siberian Seas), where they support ~7–14% of export production, with about half of terrigenous N inputs deriving from tDON decay. River N inputs had less of an impact in regions...
influenced by high-nutrient Pacific water, with ~2–8% of export production supported by fluvial N over the eastern East Siberian Sea, Beaufort Sea, and the Canada Basin.

5.5. Uncertainties

First, upon delivery of fluvial N to the shelf, biological conversion of riverine DIN to DON increases the [DON] within the river end member downstream of the river mouth, thereby altering apparent tDON removal estimates. Thus the removal of tDON observed within the river water fraction represents the net of tDON decay and DON production from riverine DIN. Therefore, the tDON removal rates calculated here from the net DON loss within the river water fraction are possible underestimates of the true removal rate for the exported Arctic river tDON. If we assume that ~8% of riverine DIN is converted to DON, then an additional 0.6 μM and 0.7 μM DON is added to the river water fraction in the eastern and western Arctic systems, respectively. If the DON originating from riverine DIN is fully conserved, the tDON removal rate constants must be adjusted upward ~10% to λ values of 0.16–0.17 ± 0.08 for the eastern Arctic and 0.09 ± 0.01 for the western Arctic.

Second, in the calculation of the removal rate constants, the removal of tDON is assumed to be a slow process occurring at a constant rate over the timescale of river water residence time in Arctic surface waters. However, there may exist multiple tDON removal rates if tDON removal is rapid upon initial delivery to Arctic shelves and then slows with aging towards the open ocean (Tank et al., 2012). For example, riverine DOM can be rapidly removed during estuarine mixing at low salinities via flocculation; however, the removal of DON via this physical process is small (<10% of total DOM) (Sholkovitz, 1976; Sholkovitz et al., 1978).

Third, dilution by sea ice melt freshwater in summer with an unknown [DON] could potentially alter the observed DON-salinity relationship, affecting interpretation of river water and marine end members. Sea ice melt has a [DON]=4.5±1.0 μM N (n=45), measured in sea ice cores collected from the SBI program in the NE Chukchi Sea (Mathis et al., 2007 for ice core locations and sampling details). It appears that sea ice forms with a [DON] not significantly different from the [DON] found in surface marine water. Upon sea ice melt in summer, the addition of freshwater containing DON to the PSL only acts to lower the salinity, while leaving the observed [DON] essentially unchanged, e.g. a ~15% addition of sea ice melt freshwater reduces the salinity of the western Arctic PSL by >4, while adding ~0.1 μM DON. This small effect is within the DON analytical error and does not significantly alter identification of end members.

Lastly, we assumed that the majority of tDON removal is in the surface layer, and that this material is kept there in support of export production. However, Dittmar (2004) observed evidence for tDON present in the deep Arctic Ocean, which he hypothesized was the result of entrainment of tDON within dense water formation on the Siberian shelves and subsequent advective transport to the deep ocean. This suggested sink of tDON will not affect the calculation of the removal rate constant, but failure to account for it results in overestimation of the mineralization sink (i.e., the mass of mineralized products available to support export production). Anderson et al. (1999) used CFC-12 and CCl₄ distributions to estimate the renewal rate of Arctic Ocean deep waters (>200 m) by the shelf water entrainment and advective transport process. The renewal rate for the Eurasian basin is ~2.5% per year, which when multiplied by the 2–5 year shelf water residence, yields a loss of 5–13% of shelf water with its enriched tDON content to the deep Arctic Ocean. The renewal rate and shelf water residence time for the western Arctic is much lower, with an estimated loss of tDON via dense water export of <1%.

Acknowledgments

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References


Table 3

<table>
<thead>
<tr>
<th>Arctic region</th>
<th>Export prod.</th>
<th>DIN from IDON</th>
<th>% Export prod. from remin. tDON</th>
<th>ΣN input</th>
<th>% Export prod. from ΣN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kara Sea</td>
<td>116</td>
<td>2.3±0.9</td>
<td>1–3%</td>
<td>12.1±0.9</td>
<td>10–11%</td>
</tr>
<tr>
<td>Laptev + west E. Siberian Sea</td>
<td>74</td>
<td>5.6±2.3</td>
<td>4–11%</td>
<td>7.9±2.3</td>
<td>7–14%</td>
</tr>
<tr>
<td>East E. Siberian Sea</td>
<td>76a</td>
<td>2.1±1.0</td>
<td>1–4%</td>
<td>2.6±1.0</td>
<td>2–5%</td>
</tr>
<tr>
<td>Beaufort Sea</td>
<td>27</td>
<td>0.2±0.1</td>
<td>-1%</td>
<td>2.1±0.1</td>
<td>7–8%</td>
</tr>
<tr>
<td>Canada Basin</td>
<td>56</td>
<td>3.6±0.1</td>
<td>6–7%</td>
<td>3.6±0.1</td>
<td>6–7%</td>
</tr>
</tbody>
</table>

* Export production estimates are from Macdonald et al. (2010).
† Rate for East Siberian Sea taken from Anderson et al. (2011).
* DIN released by tDON decay using calculated eastern and western Arctic decay constants, λ, and river water residence times.
* ΣN=(NO₃⁻)+([NH₄⁺])+([DIW DON released from tDON)).
* Uncertainties in the sum of nitrogen inputs reflect the propagated uncertainties in annual dissolved nitrogen delivery, tDON decay rate, and river water residence time.


Olsen, A., Johannessen, T., Rey, F., 2003. On the nature of the factors that control spring bloom development at the entrance to the Barents Sea and their interannual variabi-


