

Rapid removal of terrigenous dissolved organic carbon over the Eurasian shelves of the Arctic Ocean

Robert T. Letscher*, Dennis A. Hansell, David Kadko

Rosenstiel School of Marine and Atmospheric Science, University of Miami, Miami, FL 33149, USA

ARTICLE INFO

Article history:

Received 28 July 2010

Received in revised form 6 October 2010

Accepted 8 October 2010

Available online 21 October 2010

Keywords:

Arctic Ocean

DOC

Radium isotopes

Terrigenous DOC

ABSTRACT

The fate of terrigenous dissolved organic carbon (tDOC) delivered to the Arctic Ocean by rivers remains poorly constrained on both spatial and temporal scales. Early reports suggested Arctic tDOC was refractory to degradation, while recent studies have shown tDOC removal to be an active but slow process. Here we present observations of DOC, salinity, $\delta^{18}\text{O}$, and $^{228}\text{Ra}/^{226}\text{Ra}$ in the Polar Surface Layer (PSL) over the outer East Siberian/Chukchi shelf and the adjacent Makarov and Eurasian basins of the eastern Arctic Ocean. This off-shelf system receives meteoric water, introduced by rivers, after a few years residence on the shelf. Elevated concentrations of DOC ($>120 \mu\text{M C}$) were observed in low salinity (~ 27) water over the Makarov Basin, suggesting inputs of tDOC-enriched river water to the source waters of the Transpolar Drift. The regression of DOC against salinity indicated an apparent tDOC concentration of $315 \pm 7 \mu\text{M C}$ in the river water fraction, which is significantly lower than the estimated DOC concentration in the riverine sources to the region ($724 \pm 55 \mu\text{M C}$). To obtain the timescale of removal, estimates of shelf residence were coupled with measurements of dissolved $^{228}\text{Ra}/^{226}\text{Ra}$, an isotopic tracer of time since shelf residence. Shelf residence time coupled with DOC distributions indicates a first order tDOC removal rate constant, $\lambda = 0.24 \pm 0.07 \text{ yr}^{-1}$, for the eastern Arctic, 2.5–4 times higher than rates previously observed in the western Arctic. The observed removal of tDOC in the eastern Arctic occurs over the expansive shelf area, highlighting the initial lability of tDOC upon delivery to the Arctic Ocean, and suggests that tDOC is composed of multiple compartments defined by reactivity. The relatively rapid remineralization of tDOC on the shelves may mitigate the strength of the Arctic Ocean atmospheric CO_2 sink if a projected increase in labile tDOC flux occurs.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

The Arctic Ocean represents 1% of the world ocean volume, yet receives $\sim 10\%$ of the global freshwater discharge from rivers (Dittmar and Kattner, 2003), a process that is intensifying under warming global temperatures (Peterson et al., 2002). Arctic rivers drain a catchment of $15.5 \times 10^6 \text{ km}^2$, carrying with them large amounts of terrigenous dissolved organic carbon (tDOC) to the Arctic basin, estimated at 25 to 36 Tg C a^{-1} (Raymond et al., 2007). The fate of tDOC within the Arctic Ocean is of importance for understanding the regional carbon cycle and budgets, with extrapolation to the role of tDOC in the global carbon cycle. Earlier Arctic studies addressing this issue suggested a largely refractory tDOC pool based on apparently conservative mixing behavior of tDOC across the Eurasian continental shelf in late summer (Cauwet and Sidorov, 1996; Kattner et al., 1999; Köhler et al., 2003; Amon and Meon, 2004), coupled with only small losses of tDOC observed in extended laboratory incubations (Köhler et al., 2003; Amon, 2004). However, with recent field campaigns capturing the historically under-

sampled Arctic spring freshet, new evidence has emerged for a more dynamic tDOC pool in terms of composition (Neff et al., 2006; Spencer et al., 2008), biolability (Holmes et al., 2008), and age (Raymond et al., 2007). Hansell et al. (2004) and Cooper et al. (2005) observed significant removal of tDOC within the Beaufort gyre of the western Arctic Ocean, based on interpretations of the DOC-salinity relationship and regional ocean circulation. These new insights warrant a reexamination of the fate of tDOC delivered to the Arctic Ocean.

River waters delivered to the Arctic Ocean first encounter shallow shelf seas overlying the continental shelves. Here the dynamics of dissolved organic carbon (DOC) in near surface waters are complex owing to transport, production, consumption, and sea ice processes (Amon, 2004; Mathis et al., 2005). The fate of tDOC is in part controlled by its residence time over the shelf, which is in turn dependent on the rate of exchange of shelf water with the ocean interior. The western Arctic (i.e., the Canada Basin and adjacent shelf seas), with relatively narrow continental shelves, is dominated by the anticyclonic circulation of the Beaufort gyre, allowing for long-term retention of surface waters. There, the slow decay of tDOC in surface waters was observed over the decade long timescale of circulation as determined by use of a dissolved Ra-age model (Hansell et al., 2004). The eastern Arctic (i.e., the Eurasian Basins and adjacent continental

* Corresponding author. Tel.: +1 305 421 4727.

E-mail address: rlscheser@rsmas.miami.edu (R.T. Letscher).

shelf seas), in contrast, is dominated by the inflow of Atlantic water over the shelf seas, which is then exported as the return flow of the Transpolar Drift (TPD) towards Fram Strait following a multiyear residence overlying broad shelves (Schlosser et al., 1994; Ekwurzel et al., 2001; Karcher and Oberhuber, 2002). While tDOC removal in the west largely occurs offshore over the deep basin where surface waters are retained during circulation within the Beaufort gyre, the expansive shelf area present in the eastern Arctic, and the variable residence of water in that system, may provide the environment necessary for removal of tDOC prior to its export from the basin, as has been observed in other shelf environments (Moran et al., 1999; Raymond and Bauer, 2000; Hopkinson et al., 2002).

Having previously examined the fate of tDOC delivered to the western Arctic (Hansell et al., 2004; Cooper et al., 2005), our primary goal here is to identify the fate of tDOC delivered to the eastern Arctic system. We investigated the surface layer distribution of DOC over a large extent of the summertime Arctic Ocean, including the shelf break and ocean interior to the Beaufort gyre west to the Laptev Sea. Included are measurements of salinity and stable oxygen isotope ratios, the latter useful for tracing the sources of freshwater, whether meteoric or from sea-ice melt (SIM), within surface waters (e.g. Ostlund and Hut, 1984; Bauch et al., 1995; Macdonald et al., 1995). The distribution and transport pathways of freshwater are important for interpreting the DOC pool in the context of regional hydrography (Cooper et al., 2005; Mathis et al., 2005). In addition, dissolved radium isotopes are employed here to trace the extent and rate of exchange between shelf waters and the ocean interior, as applied previously in the Arctic (Rutgers van der Loeff et al., 1995, 2003; Kadko and Muench, 2005). Combining the DOC distribution with knowledge of water mass origins and transport gained from the isotopic tracers, we determine the rate of removal of tDOC from the surface waters of the eastern Arctic.

2. Regional hydrography

Our focus is on the eastern Arctic system, defined here as the region from 0°–180°E. The region from 180°W–0° defines the western Arctic. Runoff from the major Siberian watersheds empty into the shelf seas, whereupon surface flow is generally along shelf to the east (Fig. 1). Runoff from the Ob and Yenisey rivers enters the Kara Sea, passing through the Vilkitsky Strait into the Laptev Sea, where it mixes with runoff from the Lena River (Guay et al., 2001). The direction of surface flow and the geographic position for detachment of the fluvial discharge from the shelf to enter the Transpolar Drift is influenced by the prevailing atmospheric conditions (Ekwurzel et al., 2001; Schlosser et al., 2002), represented by the sign of the Arctic Oscillation (AO) (Anderson et al., 2004). During negative phases of the AO, a stronger Beaufort high over the Arctic weakens the subpolar westerlies, shifting the axis of the TPD west towards the Eurasian Basins. Surface flow in the Laptev Sea follows a northerly route with the river runoff discharge crossing the Laptev shelf for export to the deep basin near the Lomonosov Ridge (Anderson et al., 2004). During the positive phase of the AO, a weaker Beaufort high intensifies the subpolar westerlies, shifting the axis of the TPD towards the Canada Basin. River runoff entering the Kara and Laptev seas flows strongly to the east, passing through the Sannikov and Dmitry Laptev straits before entering the East Siberian Sea, to mix with runoff from the Kolyma River (Dmitrenko et al., 2005; 2008). Once there, the fluvial waters cross the continental shelf, passing offshore with the river discharge entering the interior Arctic near the Mendeleyev Ridge (Guay et al., 2001; Anderson et al., 2004).

3. Methods

3.1. Field sampling

Dissolved isotopic tracer and biogeochemical samples were collected aboard the German icebreaker *FS Polarstern* during cruise

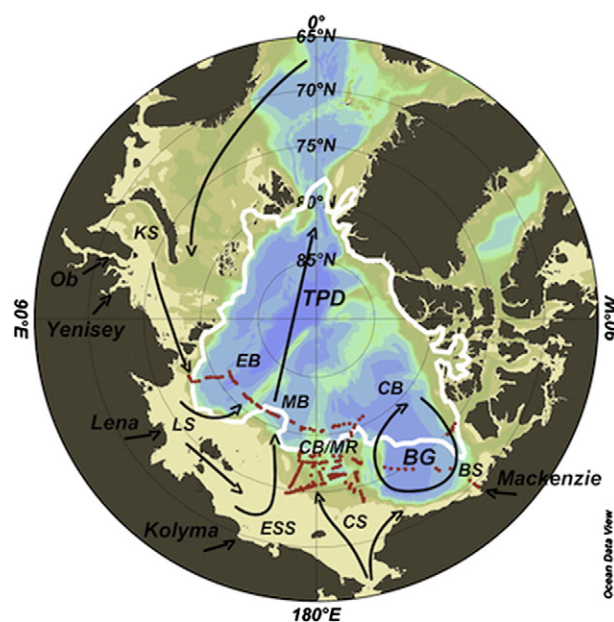


Fig. 1. Map showing station locations (red dots) in reference to generalized surface circulation and major river mouths (black arrows) of the Arctic Ocean. The large scale cyclonic circulation of the Eastern Arctic (0°–180°E) is dominated by the Transpolar Drift (TPD; originating at the shelf break of the Makarov Basin), contrasting the anticyclonic circulation of the Beaufort Gyre (BG) in the Western Arctic (180°W–0°). Shelf seas and deep basins are marked as follows: EB = Eurasian Basins, MB = Makarov Basin, CB = Canada Basin, KS = Kara Sea, LS = Laptev Sea, ESS = East Siberian Sea, CS = Chukchi Sea, CB/MR = Chukchi Borderland/Mendeleyev Ridge, and BS = Beaufort Sea. The solid white line approximates the minimum sea-ice extent during September 2008. This and Figs. 2 and 3 were created using Ocean Data View 4 (Schlitzer, 2010).

ARKXXIII/3 (12 Aug. to 17 Oct., 2008). The cruise circumnavigated the Arctic with extensive occupation of the western Chukchi/East Siberian Sea shelf break and adjacent Mendeleyev Ridge region (Fig. 1). In addition, a transect crossing the Canada, Makarov, and Eurasian basins at ~80°N was occupied, including the source waters of the Transpolar Drift in the Makarov Basin (Fig. 1). Sea-ice-free conditions were generally present south of 80°N in the study region with heavy ice conditions present to the north (white line, Fig. 1). Sampling of the Polar Surface Layer (PSL) was carried out through the ship's hull-mounted seawater intake line at a depth of ~10 meters. A total of 179 underway samples were collected for the analysis of DOC, with a subset (66) concomitantly collected for analysis of isotopic tracers $^{228}\text{Ra}/^{226}\text{Ra}$ and $\delta^{18}\text{O}$. Salinity was measured by conductivity using the ship's salinometer mounted at the seawater intake.

3.2. DOC

Samples were filtered for the removal of particulate organic carbon (POC) 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 clean seawater line using acid-cleaned, DOC-free silicon tubing. Samples were collected into preconditioned and acid-cleaned 60 mL HDPE bottles and immediately frozen upright at -20°C . New filters were loaded prior to each sample collection to ensure no contamination from previous filtrations.

Analyses of DOC were performed by high temperature combustion at our onshore laboratory using two Shimadzu TOC-V systems (Farmer and Hansell, 2007). Standardization was achieved using potassium hydrogen phthalate (KHP). Deep seawater and low carbon reference waters as provided by the Hansell CRM Program were measured every sixth analysis to assess the day-to-day and instrument-to-instrument variability. The precision of the DOC measurement was 2–3 μM or a CV of 3%–5%.

3.3. Isotopic tracers

Approximately 200-L samples for the detection of radium isotopes, ^{228}Ra and ^{226}Ra , were collected in 300-L plastic tanks using the ship seawater intake. The tanks were slowly drained ($\sim 300\text{ mL min}^{-1}$) using electric motors, passing the seawater through plastic cartridges containing Mn-coated acrylic fibers. Radium adsorbs to these fibers efficiently and without fractionation (Moore et al., 1985). Following filtration, the fibers were sealed and stored in plastic Petri dishes for subsequent analysis on land. The activities of ^{228}Ra and ^{226}Ra were measured from the activities of the radium daughters upon ingrowth using gamma ray spectrometry with a high purity germanium detector (Michel et al., 1981).

Samples for stable oxygen isotope measurements ($\delta^{18}\text{O}$) 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 the Rosenstiel School of Marine and Atmospheric Science, Miami, Florida, 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 $\delta^{18}\text{O}$ ‰ notation. Samples were analyzed in duplicate, with a precision of ± 0.08 ‰.

3.4. Calculating river and ice melt fractions in the polar surface layer

$\delta^{18}\text{O}$ and salinity data were used to calculate the fractions of marine water, river water and sea-ice melt (SIM) present in the PSL (e.g., Cooper et al. 2005; Mathis et al., 2007). Each end member was assigned characteristic $\delta^{18}\text{O}$ and salinity values and the fractions of each in a given sample were computed by solving a system of three equations. Oxygen isotope values of end members ($\delta^{18}\text{O}$) were assigned as follows: marine water $\delta^{18}\text{O} = +0.3$ ‰ (Bauch et al., 1995), SIM $\delta^{18}\text{O} = -1.9$ ‰ (Eicken et al., 2002), western Arctic river water $\delta^{18}\text{O} = -19.6$ ‰, and eastern Arctic river water $\delta^{18}\text{O} = -18.6$ ‰. Riverine end members were assigned using the flow weighted $\delta^{18}\text{O}$ values from Cooper et al. (2008) for the Mackenzie and Yukon rivers (western Arctic river water) and the Ob, Yenisey, Lena, and Kolyma rivers (eastern Arctic river water). Eastern hemisphere stations (i.e., west of 180°E) were assigned the eastern Arctic River water end

member value while western hemisphere stations (i.e., east of 180°E) were assigned the western Arctic River water end member. Salinity (S) values were assigned as follows: eastern Arctic marine (Atlantic) water $S = 34.9$, western Arctic marine (Pacific/Anadyr) water $S = 33$ (Coachman et al., 1975), SIM $S = 4.5$ (Mathis et al., 2007), and both western and eastern Arctic river water $S = 0$. Eastern and western Arctic marine end member salinities were assigned following the same hemisphere divisions as $\delta^{18}\text{O}$ and reflect the Atlantic influence in the eastern Arctic and Pacific influence of the western Arctic. Fractions were calculated by simultaneous solutions to the equations below:

$$S = (S' \times \text{SW}) + (0 \times \text{RW}) + (4.5 \times \text{SIM}) \quad (1)$$

$$\delta^{18}\text{O} = (+0.3\text{‰} \times \text{SW}) + (\delta^{18}\text{O}' \times \text{RW}) + (-1.9\text{‰} \times \text{SIM}) \quad (2)$$

$$1 = \text{SW} + \text{RW} + \text{SIM} \quad (3)$$

where S = salinity of sample, $S' = S$ for western (33) or eastern (34.9) Arctic marine water, $\delta^{18}\text{O}$ = oxygen isotope composition of sample, $\delta^{18}\text{O}' = \delta^{18}\text{O}$ for western (-19.6 ‰) or eastern (-18.6 ‰) Arctic river water, and SW, RW, and SIM are fractions of marine water, river water, and SIM, respectively.

4. Results

4.1. Salinity and DOC

The surface distributions of salinity and DOC are shown in Fig. 2a and b, respectively. Salinity in the PSL was generally low (<33) due to the presence of freshwater from both river runoff and SIM. A salinity front was observed just east of 180°E (Fig. 2a), separating the fresher (<29) western Arctic waters from the saltier (>29) eastern Arctic waters. An exception was where the cruise track crossed an ice-free region centered at $\sim 160^\circ\text{E}$ over the Makarov Basin (indicated by an arrow, Fig. 2a), characterized by reduced salinity (<29) relative to surrounding waters.

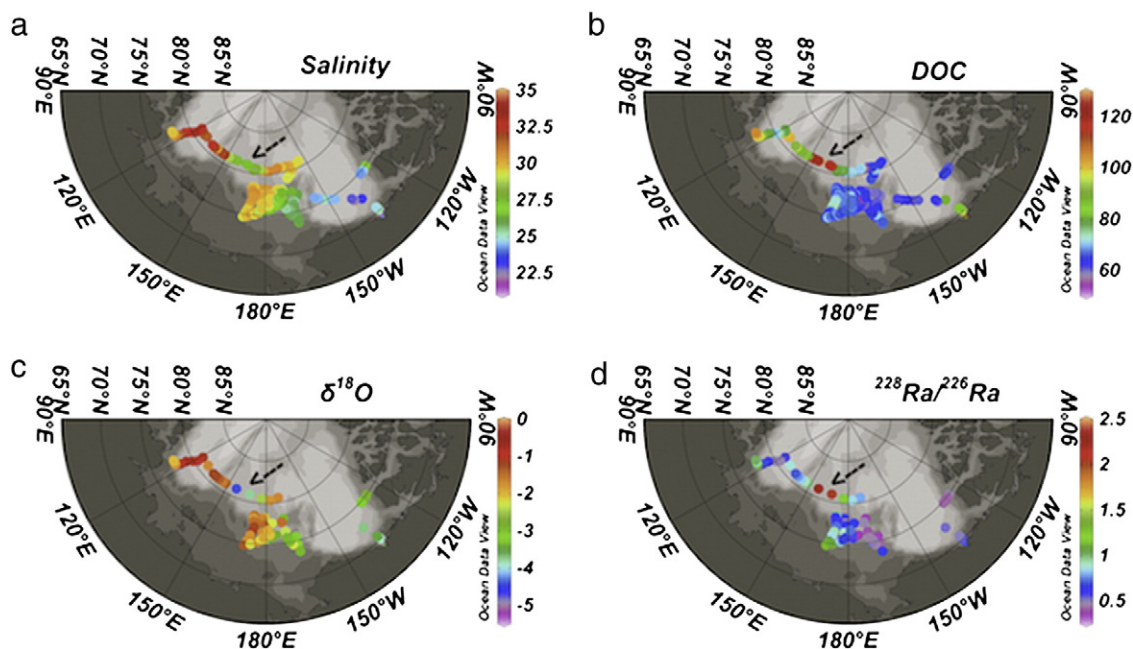


Fig. 2. Surface distribution of (a) salinity, (b) DOC ($\mu\text{M C}$), (c) $\delta^{18}\text{O}$ (‰), and (d) $^{228}\text{Ra}/^{226}\text{Ra}$ activity ratio. The black arrow denotes relatively fresh, shelf-water dominated stations in the Makarov Basin described in the text.

Surface DOC concentrations over the deep basins were generally lower in the western Arctic (60–65 μM) than in the eastern Arctic (60–120 μM) (Fig. 2b). In the western Arctic, DOC concentrations were highest (> 100 μM) at the few stations located near the mouth of the Mackenzie River, with much lower concentrations found offshore

over the Beaufort gyre. The highest DOC concentrations in the eastern Arctic (> 100 μM) coincided with low salinity water located over the Makarov Basin (indicated by an arrow, Fig. 2b) and the adjacent Eurasian Basin, suggesting a stronger influence of river runoff there. Elsewhere, over the Chukchi Borderland/Mendeleyev Ridge region,

Table 1

Location, bottom depth, salinity, $\delta^{18}\text{O}$, $^{228}\text{Ra}/^{226}\text{Ra}$ activity ratio, DOC, and fractions of river water (RW) and sea ice melt water (SIM) measured at ~10-m depth. CB/MR = Chukchi Borderland/Mendeleyev Ridge.

Location	Latitude °N	Longitude °E	Water depth (m)	Salinity	$\delta^{18}\text{O}$ ‰	$^{228}\text{Ra}/^{226}\text{Ra}$ AR	DOC [$\mu\text{M C}$]	RW	SIM
Beaufort Shelf	69.50	-136.01	71	24.41	-2.97	0.69 ± 0.06	89.4	0.15	0.13
Beaufort Shelf	69.74	-136.11	117	21.54	-5.01	0.70 ± 0.06	123.0	0.26	0.11
Beaufort Shelf	70.00	-136.23	105	25.30	-3.85	0.54 ± 0.01	94.1	0.21	0.03
Canada Basin	74.92	-127.00	409	26.70	-2.87	0.48 ± 0.07	60.5	0.16	0.04
Canada Basin	74.86	-128.38	826	27.27	-2.70	0.43 ± 0.10	60.7	0.15	0.03
Canada Basin	74.81	-129.76	1555	26.49	-2.68	0.40 ± 0.01	61.5	0.14	0.06
Canada Basin	74.78	-129.39	1932	24.61	-2.73	0.42 ± 0.01	63.9	0.14	0.14
Canada Basin	74.80	-130.67	2459	24.40	-2.89	0.40 ± 0.12	64.9	0.15	0.13
Canada Basin	74.82	-131.25	3071	24.21	-3.22	0.42 ± 0.06	64.7	0.16	0.12
Canada Basin	70.52	-136.43	1006	24.79	-3.47	0.50 ± 0.04	85.9	0.18	0.08
Canada Basin	72.50	-138.10	3061	23.07	-3.74	0.52 ± 0.07	88.0	0.19	0.13
Chukchi Sea	75.54	-165.71	452	25.94	-3.07	0.34 ± 0.06	63.6	0.16	0.06
Chukchi Sea	74.57	-165.60	366	25.76	-3.10	0.43 ± 0.02	67.7	0.16	0.07
Chukchi Sea	73.63	-165.49	118	26.39	-2.90	0.66 ± 0.09	67.5	0.16	0.05
Chukchi Sea	74.65	-167.69	231	25.93	-2.21	0.46 ± 0.04	63.5	0.11	0.12
Chukchi Sea	75.05	-168.93	228	26.22	-2.88	0.53 ± 0.05	67.8	0.15	0.06
Chukchi Sea	75.24	-168.55	279	25.96	-3.02	0.48 ± 0.09	64.6	0.16	0.06
CB/MR	78.00	-170.09	2301	28.98	-2.93	0.39 ± 0.02	59.6	0.16	0.01
CB/MR	78.25	179.37	1785	30.52	-2.06	0.48 ± 0.05	61.4	0.12	0.00
CB/MR	78.15	177.47	1801	30.52	-1.67	0.62 ± 0.05	66.1	0.10	0.03
CB/MR	78.47	173.00	1942	29.76	-1.44	0.97 ± 0.12	64.3	0.08	0.07
CB/MR	78.19	172.73	1369	29.91	-1.78	0.64 ± 0.07	67.8	0.10	0.04
CB/MR	77.67	173.10	1125	30.66	-1.50	0.66 ± 0.02	64.5	0.09	0.04
CB/MR	77.60	178.47	1489	30.07	-1.64	0.46 ± 0.11	64.3	0.10	0.05
CB/MR	77.59	-171.34	2265	28.72	-1.49	0.49 ± 0.11	65.0	0.08	0.05
CB/MR	77.60	-176.66	820	29.82	-2.26	0.65 ± 0.06	62.3	0.13	0.02
CB/MR	77.31	179.05	1228	30.23	-1.41	0.62 ± 0.25	67.8	0.08	0.06
CB/MR	77.61	174.54	1260	30.76	-1.50	0.59 ± 0.22	68.6	0.09	0.03
CB/MR	77.06	173.71	865	30.42	-1.24	0.73 ± 0.16	70.0	0.07	0.06
CB/MR	75.61	179.72	990	28.21	-2.41	0.50 ± 0.17	66.1	0.13	0.07
CB/MR	75.80	-177.63	1179	27.33	-2.75	0.59 ± 0.07	66.2	0.15	0.03
CB/MR	76.13	-174.87	2206	27.31	-2.79	0.37 ± 0.02	62.5	0.15	0.02
CB/MR	76.40	-170.14	2314	26.48	-2.37	0.40 ± 0.03	63.4	0.13	0.08
CB/MR	75.59	-169.82	1129	25.44	-2.93	0.46 ± 0.05	62.6	0.16	0.13
CB/MR	76.46	178.13	1228	29.72	-1.72	0.90 ± 0.09	68.1	0.10	0.06
CB/MR	75.84	178.76	983	29.66	-1.88	0.68 ± 0.06	66.4	0.11	0.05
CB/MR	76.15	-178.07	1243	29.17	-2.10	0.57 ± 0.06	67.6	0.12	0.05
CB/MR	76.75	-178.91	1161	29.70	-1.97	0.73 ± 0.05	66.9	0.11	0.04
East Siberian Sea	76.47	172.85	323	30.43	-1.11	0.93 ± 0.12	71.5	0.07	0.07
East Siberian Sea	75.98	172.16	234	30.33	-1.71	0.85 ± 0.11	73.5	0.10	0.03
East Siberian Sea	75.25	170.98	131	29.72	-1.72	1.06 ± 0.06	63.9	0.10	0.06
East Siberian Sea	74.67	170.07	61	29.18	-1.35	1.31 ± 0.05	64.5	0.08	0.10
East Siberian Sea	74.92	172.83	117	29.86	-2.20	1.09 ± 0.04	68.1	0.13	0.02
East Siberian Sea	75.36	177.20	353	30.19	-1.40	1.01 ± 0.10	62.6	0.08	0.06
East Siberian Sea	75.31	176.25	266	29.78	-1.84	0.83 ± 0.06	65.1	0.11	0.05
East Siberian Sea	75.57	177.48	478	28.91	-2.19	0.67 ± 0.05	65.0	0.12	0.06
Makarov Basin	80.56	-171.21	3373	30.69	-1.67	0.80 ± 0.10	70.6	0.10	0.02
Makarov Basin	80.32	-177.35	1427	30.72	-1.76	0.85 ± 0.05	70.0	0.11	0.02
Makarov Basin	80.51	176.70	2289	28.69	-2.48	1.24 ± 0.11	80.2	0.14	0.04
Makarov Basin	80.87	167.62	2856	27.41	-3.76	2.04 ± 0.12	117.5	0.21	0.00
Makarov Basin	81.00	157.06	2836	26.56	-4.42	2.24 ± 0.21	124.0	0.25	-0.01
Eurasian Basin	80.98	148.00	2473	32.37	-1.46	0.97 ± 0.03	91.6	0.10	-0.03
Eurasian Basin	81.02	145.05	2047	31.81	-1.58	0.91 ± 0.06	92.0	0.10	-0.01
Eurasian Basin	80.97	142.05	1627	31.94	-1.36	0.83 ± 0.09	89.7	0.09	0.00
Eurasian Basin	80.98	139.01	1703	31.98	-1.24	0.78 ± 0.06	89.6	0.08	0.00
Eurasian Basin	81.01	136.09	3035	32.39	-1.25	0.71 ± 0.03	91.5	0.08	-0.01
Eurasian Basin	81.17	128.79	3927	31.64	-1.68	0.87 ± 0.09	101.5	0.11	-0.01
Eurasian Basin	81.24	121.22	4242	32.94	-1.13	0.56 ± 0.03	78.6	0.08	-0.02
Eurasian Basin	80.48	121.48	3399	32.85	-1.02	0.49 ± 0.09	76.0	0.07	-0.01
Eurasian Basin	79.95	119.95	3355	33.01	-0.84	0.49 ± 0.02	71.0	0.06	-0.01
Eurasian Basin	79.24	118.11	3026	32.40	-0.75	0.58 ± 0.07	79.8	0.05	0.02
Eurasian Basin	78.54	117.77	2337	31.70	-0.99	0.69 ± 0.07	91.4	0.06	0.03
Eurasian Basin	77.95	116.64	1156	30.74	-1.70	1.10 ± 0.10	98.8	0.10	0.02
Laptev Sea	77.92	115.22	374	29.89	-1.91	0.93 ± 0.05	102.6	0.11	0.03
Laptev Sea	77.91	114.00	217	29.71	-2.04	1.02 ± 0.10	105.8	0.12	0.03

DOC concentrations were reduced at both the western and eastern Arctic stations (due to mixing with SIM; evidence given below).

4.2. Isotopic tracers

Surface distributions of $\delta^{18}\text{O}$ and $^{228}\text{Ra}/^{226}\text{Ra}$ activity ratios are shown in Fig. 2c and d, respectively (data for oxygen and radium tracers are given in Table 1). Values of $\delta^{18}\text{O}$ were depleted across the study region due to the presence of freshwater from both rivers and sea-ice melt, both of which have depleted $\delta^{18}\text{O}$ signatures (Fig. 2c). The most depleted values ($<-4.0\text{‰}$) in the east coincided with the low salinity region in the Makarov Basin (indicated by an arrow, Fig. 2c). Elsewhere in the eastern Arctic, $\delta^{18}\text{O}$ values typically ranged between -2.5‰ and -1.5‰ . The western Arctic stations showed slightly depleted values relative to the eastern Arctic, with typical values between -3.0‰ and -2.0‰ , reflecting freshwater storage in the upper Canada Basin (Aagaard and Carmack, 1989).

The $^{228}\text{Ra}/^{226}\text{Ra}$ activity ratios, with lower values indicating greater time since a water mass left the shelf, showed marked differences between the two systems owing to the contrasting circulation patterns (Fig. 2d). In the western Arctic, where the anticyclonic gyre circulation allows for significant decay of ^{228}Ra during the recirculation of surface waters (Kadko and Muench, 2005), activity ratios were reduced and nearly constant, averaging 0.45 ± 0.06 , $n=13$ (Fig. 2d). In the eastern Arctic, where circulation is dominated by shelf transport and cross basin transport via the Transpolar Drift, activity ratios were more varied, ranging from 0.4 to >2.0 . The highest ratios were observed offshore over the Makarov and Eurasian basins, corresponding with the low salinity, high DOC water (indicated by arrow, Fig. 2d). Ratios were reduced over the outer East Siberian shelf and Mendeleyev Ridge region (1.0–1.5), possibly due to mixing with western Arctic waters near the salinity front or, perhaps, due to simple aging.

4.3. Distributions of river and ice melt fractions in the polar surface layer

The fractional distributions of river water (RW) and SIM are shown in Fig. 3a and b, respectively. River water is ubiquitous in the PSL with fractions reaching 20% in the western Arctic and 25% in the low

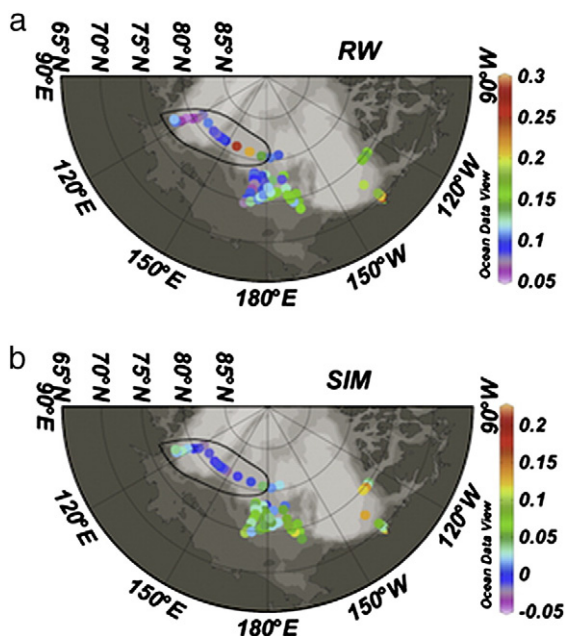


Fig. 3. Surface distribution of calculated freshwater fractions. (a) River water. (b) Sea-ice melt water. Dotted black circle denotes stations overlying the Makarov and Eurasian basins (110–180°E) used for DOC-salinity regressions described in text.

salinity region over the Makarov Basin. The distribution of SIM shows a larger influence in the western Arctic, reaching 12% in the Beaufort Sea. Contributions of freshwater due to SIM were small in the eastern Arctic, with $\sim 5\%$ at stations located at the shelf break of the East Siberian/Chukchi Sea, decreasing to negligible amounts at stations located over the Eurasian Basins. These distributions of SIM likely reflect the dominant flow systems: SIM is retained in the gyre circulation of the Beaufort gyre while in the east it is removed from the regions of formation with sea ice flow off the shelf and across the shelf break.

5. Discussion

5.1. Geographic distribution of river discharge in the eastern Arctic

Taken together, the distributions of both RW and SIM in the eastern Arctic indicate a large riverine influence in the PSL overlying the deep basins (dotted outline, Fig. 3). The low salinity region over the Makarov Basin near $\sim 160^\circ\text{E}$ coincides with the highest DOC concentration (129 μM), lowest $\delta^{18}\text{O}$ value (-4.42‰), highest $^{228}\text{Ra}/^{226}\text{Ra}$ activity ratio (2.24), and largest RW fraction (25%) measured. The results agree with the findings of Jones et al. (2008), who reported a large influence of fluvial water over the central Makarov Basin during the 2005 Arctic Ocean Section. In addition, the elevated surface DOC concentrations measured over the Makarov and Eurasian basins are consistent with previous measurements in the same region (Wheeler et al., 1997; Bussmann and Kattner, 2000; Amon and Benner, 2003). Working with a simple parameterization of tDOC concentrations in river runoff to the Arctic Ocean within an ocean general circulation model, Manizza et al. (2009) predicted the highest concentrations of riverine DOC to be in the nearshore Siberian seas (Kara, Laptev, East Siberian), with the river discharge crossing and detaching from the shelf at $\sim 150\text{--}180^\circ\text{E}$, coincident with the low salinity region observed over the Makarov Basin in this study.

The geographical position of the Eurasian river discharge detachment from the shelf is known to be variable (Guay et al., 2001; Schlosser et al., 2002) and dependent on the prevailing summertime atmospheric wind conditions, represented by the sign of the Arctic Oscillation (Anderson et al., 2004; Dmitrenko et al., 2005). AO was negative during the summer of 2008, following a three-year period of predominantly positive phase (CPC, 2009). The data presented here provide evidence that the 80°N transect in this study crossed the Eurasian River runoff discharge during the summer of 2008 as it joined the Transpolar Drift. The location of the river discharge sampled in 2008 midway between the Mendeleyev and Lomonosov Ridges in the Makarov Basin ($\sim 150\text{--}170^\circ\text{E}$) may be explained by a shift in the axis of the Transpolar Drift from near the Mendeleyev Ridge during the positive AO phase (Anderson et al., 2004) toward the Lomonosov Ridge in summer 2008.

5.2. Non-conservative behavior of tDOC

DOC-salinity plots have been commonly used to discern the controls exerted by Arctic hydrography on DOC distributions (Cauwet and Sidorov, 1996; Kattner et al. 1999; Bussmann and Kattner, 2000; Köhler et al., 2003; Hansell et al. 2004; Cooper et al., 2005; Mathis et al., 2005). It has been assumed in these analyses that sea ice formation and melt leave permanent imprints on the DOC-salinity relationship such that careful use of data allows its interpretation. If the DOC-enriched brine formed during sea ice formation (Giannelli et al., 2001) is dense enough to penetrate the pycnocline, a physical mechanism for tDOC removal from the PSL exists, thereby permanently affecting the DOC-salinity relationship in surface waters. There are few analyses on the export of DOC to the subpycnocline with brine formation. Amon (2004) reported that low-salinity, tDOC-rich shelf water in the Kara Sea does not become dense enough, following sea

ice formation to penetrate the pycnocline. Schauer (1997) reached a similar conclusion for the Laptev Sea, whereby the resulting increase in shelf water salinity post-sea-ice formation in winter was insufficient to mix with the underlying halocline waters. These results suggest that DOC and salinity concentrations in the PSL may be impacted by ice formation on the short term, but not necessarily over the full annual scale. The extent to which sea ice formation and brine export affect the DOC-salinity relationship over the multi-year residence of Eurasian shelf waters (Ekwurzel et al., 2001; Karcher and Oberhuber, 2002) needs to be ascertained, since small changes could accumulate to a larger impact over several freeze/thaw cycles. However, for the purposes of this study and employing judicious use of the data (favoring waters less impacted by SIM and for which SIM corrections can be made) we assume these processes to have modest impacts.

A plot of DOC versus salinity (Fig. 4) reveals mixing between three end members present in the PSL during the summer of 2008: low salinity/DOC-enriched riverine water, high salinity/intermediate DOC marine water, and low salinity/DOC-poor SIM. The presence of SIM during the summer months has been shown to dilute salinity and DOC concentrations in the PSL (Mathis et al., 2005). This dilution of the DOC signal is apparent during the time of our study, as evidenced by the low DOC concentrations at low salinities (Fig. 4), thereby complicating analyses of mixing between marine and river waters. The reduced DOC concentrations observed over the Beaufort gyre of the western Arctic (Fig. 4, crosses) also reflect “aged” river water (Hansell et al., 2004), whose tDOC has degraded over its decade long recirculation. Those data fitting the mixing line between the riverine and marine end members (Fig. 4, open circles) coincided with river water influenced stations overlying the Makarov and Eurasian basins with negligible influence from SIM, and are used for the subsequent DOC-salinity regressions below (Fig. 3a and b, indicated by a dotted outline). These data are the focus of the following analysis.

If tDOC in eastern Arctic River water behaved conservatively across the estuarine salinity gradient, its mixing with marine water would be approximated by the dotted line in Fig. 5a. The net loss of DOC across the salinity gradient would follow the curved dashed line. However, in this study only salinities >25 are sampled in the PSL, where the loss curve fits a straight line. The regression of this line can be used to infer the DOC concentration of the river water fraction from the zero salinity intercept, as has been done previously for the western Arctic (Hansell et al., 2004; Cooper et al., 2005). Plots of DOC concentration

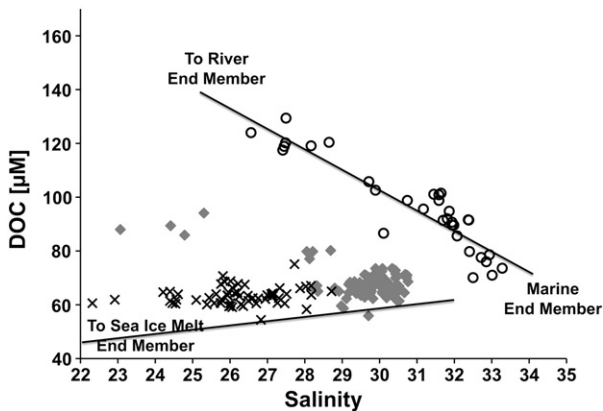


Fig. 4. Plot of DOC (µM) versus salinity showing apparent mixing lines between three end members present in the PSL during summer 2008. Stations from the Beaufort gyre (crosses) contain “aged” river water (Hansell et al., 2004) whose DOC concentrations have degraded over the decade long recirculation of surface waters and have been diluted due to summer-time sea ice melt. Stations over the Makarov and Eurasian basins (west of 180°E) show mixing between river and marine end members with negligible contributions from sea ice melt (open circles). Stations located in the Chukchi Borderland–Mendeleyev Ridge region exhibit intermediate influence of all three end members (gray diamonds). See Fig. 1 for regional reference.

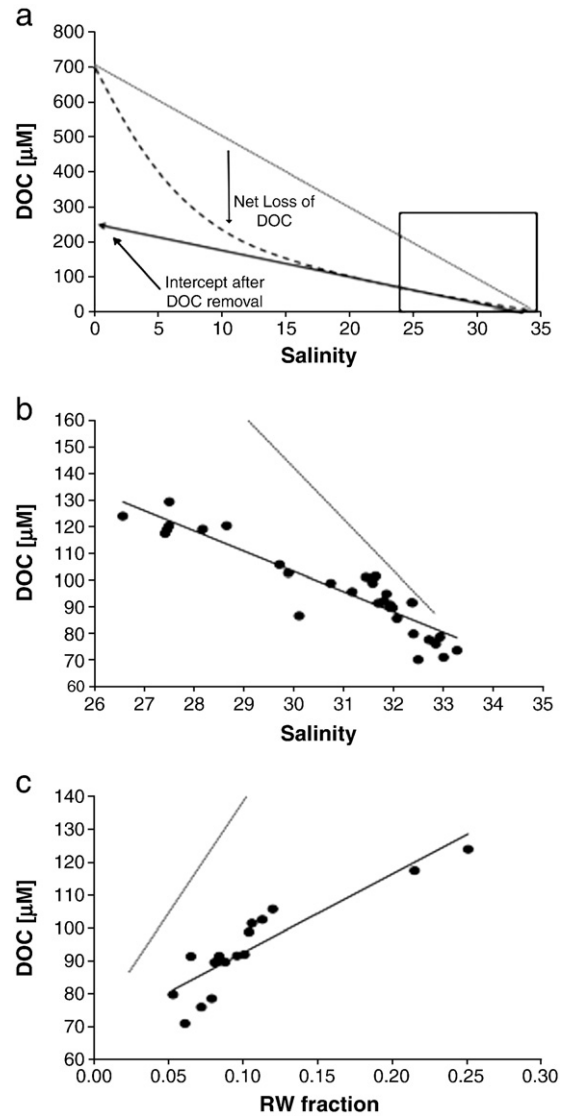


Fig. 5. Theoretical and observed correlations of DOC and salinity. (a) Theoretical mixing lines for DOC between eastern Arctic river and marine waters: conservative (dotted line); non-conservative with net loss of DOC (curved dashed line); and the zero salinity intercept (solid, arrowed line) based on correlations observed at high salinities (in the box). (b) Observed correlation between DOC (µM) and salinity ($DOC = -7.60 \times salinity + 331$; $R^2 = 0.84$; $n = 32$; solid line) for stations from the Makarov and Eurasian Basins outlined in Fig. 3. (c) Plot of DOC (µM) versus river water fraction ($DOC = 239.49 \times RW + 69$; $R^2 = 0.80$; $n = 16$; solid line). Theoretical conservative mixing (dotted lines in (b) and (c)) is shown for reference.

versus salinity, SIM-corrected salinity, and RW fraction for the Makarov and Eurasian basins are shown in Fig. 5b and c. The regression of DOC concentrations versus measured salinity indicates an apparent river water tDOC concentration (\pm SE) of $331 \pm 7 \mu\text{M C}$, while DOC versus SIM-corrected salinity and RW fraction returned apparent river water DOC values of 309 and $308 \pm 7 \mu\text{M C}$, respectively. Here we take the average zero-salinity (100% river water) DOC value from the three regressions, $315 \pm 7 \mu\text{M C}$, as representative of the tDOC concentration in the eastern Arctic river fraction located over the basins.

The apparent tDOC concentration in the eastern Arctic River water fraction reported here is reduced relative to the DOC concentrations in Eurasian rivers (Cooper et al., 2008), suggesting that significant removal of tDOC occurs over the Siberian Arctic shelves. In order to quantify tDOC removal there, tDOC concentrations in the rivers that drain into the eastern Arctic basins need to be established. Cooper et al. (2008) provide annual flow weighted estimates of concentrations for

DOC and other tracers in six major Arctic rivers. Of those six rivers, Ob, Yenisey, Lena, and Kolyma empty into the eastern Arctic basin, to eventually join the Transpolar Drift. The annual flow weighted DOC concentration taken for these four rivers yields a mean eastern Arctic river water tDOC concentration (\pm SE) of $724 \pm 55 \mu\text{M C}$ ($799 \pm 24 \mu\text{M C}$ if only the Lena and Kolyma rivers are considered, as they are the major rivers local to the East Siberian Shelf). Although there are many small rivers that drain into the eastern Arctic, these are assumed here to not have a significant impact on our river runoff end member estimate. Stable oxygen isotope data from this study fell along a mixing line between the flow weighted eastern Arctic river water ($\delta^{18}\text{O} = -18.6\%$, $S = 0$) and marine water ($\delta^{18}\text{O} = 0.3\%$, $S = 34.9$) (not shown), providing evidence that the mean character of Ob, Yenisey, Lena, and Kolyma provide a reasonable estimate for the cumulative eastern Arctic river runoff end member. The difference in DOC concentrations measured in the eastern Arctic rivers and the apparent DOC concentration in the river water fraction inferred from the regressions observed offshore implies tDOC loss of $409 \pm 55 \mu\text{M C}$ from the freshwater river component over the eastern Arctic shelf system.

5.3. tDOC removal rate estimates

River water entering the eastern Arctic has a multiyear residence overlying the continental shelf (Schlosser et al., 1994; Ekwurzel et al., 2001; Karcher and Oberhuber, 2002) before being transported into the interior Arctic Ocean to join the Transpolar Drift (Guay et al. 2001; Anderson et al., 2004). The dissolved $^{228}\text{Ra}/^{226}\text{Ra}$ activity ratio of seawater is a useful tracer of the timescale of shelf to deep basin interaction because it provides information on the time since a parcel of water was last in contact with the continental shelf (Rutgers van der Loeff et al., 1995). Here we combine the timescale for shelf-to-basin exchange at the East Siberian Sea shelf break–Makarov/Eurasian basins, as gauged using measurements of $^{228}\text{Ra}/^{226}\text{Ra}$, with the available estimates of shelf residence time in the Eurasian Arctic to arrive at an estimate for the timescale of tDOC removal in the eastern Arctic system.

The residence time of river water on the Eurasian shelves has been estimated previously using a variety of techniques. Early estimates for the Kara Sea were 2.5 years (Hanzlick and Aagaard, 1980) and 3.5 years (Pavlov et al., 1993) based on the mass balance of water. Schlosser et al. (1994) and Ekwurzel et al. (2001) estimated residence times of 3.5 ± 2 years and 2–5 years, respectively, for the Eurasian shelves using a $\text{He}/^3\text{H}$ technique. A recent modeling study by Karcher and Oberhuber (2002) places the residence time on the shelf at 2–3 years, with a total residence time of 4.1–6.5 years for river runoff in the eastern Arctic before exiting at Fram Strait. Based on these estimates we assign a Eurasian shelf residence time for the river runoff fraction of 3.5 ± 1.5 years. Assuming that the removal of tDOC occurs predominately during the residence time of river water on the Eurasian shelves, we can calculate the tDOC removal rate. If the $724 \pm 55 \mu\text{M C}$ of tDOC entering the eastern Arctic is reduced to $315 \pm 7 \mu\text{M C}$ on the timescale of 3.5 ± 1.5 years, a first order tDOC decay constant, $\lambda = 0.24 \pm 0.07 \text{ yr}^{-1}$, is calculated for the region. The loss of $409 \pm 55 \mu\text{M C}$ occurred almost entirely over the shelves such that $>50\%$ of tDOC entering the Eurasian shelf seas is removed from the water column before transit to the Arctic Ocean interior.

The measurements of DOC assessed here were made over the deep basin, and we assumed above that removal of tDOC occurred over the shelves and that subsequent transfer of tDOC-enriched shelf water to the basin site was essentially instantaneous. To test this assumption, we collected measurements of dissolved $^{228}\text{Ra}/^{226}\text{Ra}$ from the PSL to estimate the timescale of shelf-to-basin exchange of shelf water. Measurements of $^{228}\text{Ra}/^{226}\text{Ra}$ in surface waters have been used previously in the Arctic Ocean to infer rates of shelf-basin exchange (Rutgers van der Loeff et al., 1995; 2003; Kadko and Muench, 2005; Kadko and Aagaard, 2009) and to study tDOC removal in the western

Arctic (Hansell et al., 2004). Rapid mixing between high $^{228}\text{Ra}/^{226}\text{Ra}$, low salinity shelf water and low $^{228}\text{Ra}/^{226}\text{Ra}$, high salinity marine water results in conservative linear mixing trends, thus defining the “zero-age” trend for a region. Lower than expected $^{228}\text{Ra}/^{226}\text{Ra}$ values based on the zero-age trend for a given salinity indicate “aging” of that water parcel relative to when it left the shelf. High $^{228}\text{Ra}/^{226}\text{Ra}$ ratios have been reported in surface waters in the eastern Arctic (Rutgers van der Loeff et al., 1995; 2003), indicating rapid transport [<3 years; uncertainty of $^{228}\text{Ra}/^{226}\text{Ra}$ measurement (Rutgers van der Loeff et al., 1995)] of waters overlying the Eurasian shelves into the central Arctic Ocean. In contrast, low $^{228}\text{Ra}/^{226}\text{Ra}$ ratios found in the western Arctic [i.e., at Ice Station T3 (Kaufman et al., 1973) and at the Chukchi shelf break (Kadko and Muench, 2005)] indicate “aging” of those waters during recirculation within the Beaufort gyre.

The $^{228}\text{Ra}/^{226}\text{Ra}$ ratios from this study are plotted by region against SIM-corrected salinity in Fig. 6. Data from the western Arctic largely fell along the line indicating “aged” water over the Beaufort gyre (Kadko and Muench, 2005) while data from the Makarov and Eurasian basins (open circles, Fig. 6) fit a linear mixing trend (line Siberian–Makarov, Fig. 6), suggesting rapid exchange of Eurasian shelf waters at the shelf break with the ocean interior. Rapid mixing of Eurasian shelf waters with PSL waters over the Makarov and Eurasian Basins precludes significant aging of surface waters during the transit from the shelf break to the offshore sampling location at $\sim 80^\circ\text{N}$, within the uncertainty of the $^{228}\text{Ra}/^{226}\text{Ra}$ dating technique of <3 years (Rutgers van der Loeff et al., 1995); thus, the removal of tDOC occurs almost entirely over the expansive shelf area in the eastern Arctic system.

5.4. Lability and multi-compartment fractions of Arctic tDOC

Recent analyses point to a significant sink of tDOC over the continental shelves of the eastern Arctic, supporting the view that Arctic tDOC is initially labile. Cooper et al. (2005) suggested that $\sim 30\%$ of tDOC initially entering the Eurasian Arctic is removed on the shelves. Field studies capturing the traditionally undersampled spring thaw period of greatest river flow have highlighted a more dynamic tDOC pool in the Arctic than previously believed. Studies by Neff et al. (2006) and Raymond et al. (2007) have shown that the tDOC transported during the spring flood, when up to 60% of annual tDOC discharge occurs, is young in radiocarbon age, most likely comprising

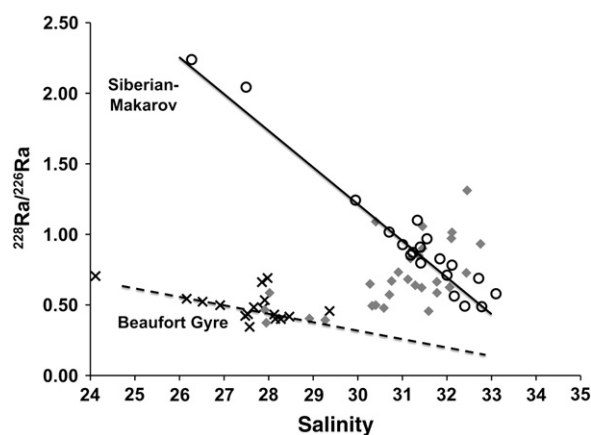


Fig. 6. Plot of $^{228}\text{Ra}/^{226}\text{Ra}$ activity ratio versus sea ice melt corrected salinity showing data collected in the western Arctic, i.e., Beaufort gyre and Beaufort Sea (crosses), Chukchi Borderland/Mendeleyev Ridge region (gray diamonds), and Makarov and Eurasian Basins of the eastern Arctic (open circles) (see Fig. 1 for reference). Stations in the western Arctic largely fall along the “aged” line for recirculated waters in the Beaufort gyre (Kadko and Muench, 2005) (dashed line). Stations overlying the Makarov and Eurasian Basins fit a conservative mixing line (line Siberian–Makarov) suggesting rapid (<3 years) mixing of Siberian shelf water with central Arctic Ocean water. Chukchi Borderland/Mendeleyev Ridge stations lie geographically between the Beaufort gyre-dominated western Arctic and shelf-dominated eastern Arctic and likely represent mixing of waters between the two systems.

recently fixed carbon present in surface leaf litter and soils. Of this tDOC transported in spring, ~50% is 1–5 years in age and ~35% aged 6–20 years (Raymond et al., 2007). Holmes et al. (2008) found that 20%–40% of the tDOC delivered during the spring freshet in Alaskan rivers is labile on the timescale of months, while DOC present during lower flow summer periods was more resistant to degradation. Similarly, van Dongen et al. (2008) estimated 20% of terrestrially-derived TOC (POC + DOC) delivered to the sub-Arctic Kalix River estuary was degraded over the timescale of days. As lability (or reactivity) negatively correlates with age (Raymond and Bauer, 2000), each DOC age cohort should exhibit a unique removal constant, with the youngest material being removed most rapidly upon export to the coastal system.

These findings of age fractionated tDOC pools in Arctic rivers (Neff et al., 2006; Raymond et al., 2007) indicate that the Arctic tDOC pool is made up of multiple fractions characterized by their lability, as is characteristic of both soil organic matter on land (Six and Jastrow, 2006; Deneff et al., 2009) and marine DOC in the world oceans (Kirchman et al., 1993; Carlson and Ducklow, 1995; Hansell et al., submitted for publication). The most labile tDOC fraction delivered after spring freshet (Holmes et al., 2008) is likely rapidly removed nearshore by microbial remineralization processes as has been observed in other estuarine environments (Moran et al., 1999; Raymond and Bauer, 2000; Hopkinson et al., 2002; Hernes and Benner, 2003), with the less labile fractions removed over longer timescales offshore. These multiple tDOC fractions or compartments, coupled with the contrasting shelf area and freshwater circulation between the eastern and western Arctic systems, influence the calculated tDOC removal rates for each region. The first order tDOC decay constant, λ , obtained here for the eastern Arctic ($0.24 \pm 0.07 \text{ yr}^{-1}$) is 2.5 times higher than that reported for the western Arctic ($0.097 \pm 0.004 \text{ yr}^{-1}$) (Hansell et al., 2004) or 4 times that rate (0.06 yr^{-1}) as revised by Cooper et al. (2005). This difference is most likely due to an observational bias arising from the timescale of observation between the two systems. River runoff delivered to the eastern Arctic has 2–5 years of shelf residence time before passing offshore to join the Transpolar Drift. The decay constant calculated here for the eastern Arctic ($0.24 \pm 0.07 \text{ yr}^{-1}$) captures the rapid removal of the young, relatively labile Arctic tDOC pool that occurs on the continental shelves. By contrast, tDOC delivered in river runoff to the western Arctic transits relatively narrow continental shelves, quickly passing offshore to mix with older waters that have recirculated within the Beaufort gyre for a decade (Hansell et al., 2004). This rapid mixing of the labile tDOC fraction into the older waters of the Beaufort gyre containing less labile tDOC biases the calculated decay constant towards slower rates. The most refractory tDOC is likely removed over longer timescales in the halocline and deep waters, though at an as yet undetermined rate. The timescales of the tDOC removal processes is illustrated in Fig. 7.

5.5. Relevance to the cycling of carbon in the surface Arctic Ocean

The mineralization of tDOC over the shelves impacts air-sea exchange of CO_2 in the system, and these impacts should vary as land-to-ocean transfer of water and organic matter changes with a changing climate at these high latitudes. Hansell et al. (2004) found approximate mass balance for carbon, where the decrease in tDOC was matched by an increase of dissolved inorganic carbon (DIC) in the PSL, suggesting that microbial degradation and photo-oxidation predominate as tDOC removal mechanisms. Consistent with this, Anderson et al. (2009) attributed an excess of DIC over the East Siberian and Laptev shelves to the microbial remineralization of terrigenous organic matter. The remineralization of terrigenous organic matter and accompanying increase in DIC of shelf waters likely counters enhancement of the Arctic Ocean CO_2 sink resulting from reduced sea ice extent (Bates et al. 2006). As the amount of river

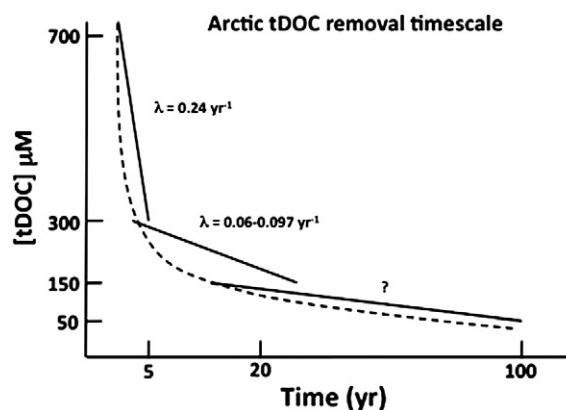


Fig. 7. Schematic for the timescale of the removal of Arctic tDOC illustrating multi-compartment fractions along with the inferred first order decay rate constants. Relatively labile tDOC is rapidly removed over the Eurasian shelves in less than 5 years time at a rate of $\lambda = 0.24 \text{ yr}^{-1}$ found in this study. tDOC delivered to the western Arctic is mixed with older Beaufort gyre waters and removed over decades, yielding an integrated rate of $\lambda = 0.06\text{--}0.097 \text{ yr}^{-1}$ (Cooper et al., 2005; Hansell et al., 2004). More refractory tDOC is removed over longer timescales in the halocline and deep waters at an undetermined rate. The distinct labilities of Arctic tDOC suggest its removal can best be described by a multi-compartment model as compared to a reactivity continuum model (dashed line).

discharge continues to increase (Peterson et al., 2002), along with increasing DOC export due to climatic warming and permafrost thawing (Spencer et al., 2009), the remineralization of terrigenous organic matter over the Arctic shelves should reduce the Arctic Ocean's ability to absorb atmospheric carbon dioxide.

Using the flow-weighted DOC concentrations and annual fluvial discharges from Cooper et al. (2008), total annual delivery of DOC into the Arctic Basin from the six largest Arctic rivers is $\sim 17.6 \text{ Tg C a}^{-1}$. Of this, 2.8 Tg C a^{-1} is delivered to the western Arctic (via the Mackenzie and Yukon rivers) and the remaining 14.8 Tg C a^{-1} empties into the eastern Arctic (via the Ob, Yenisey, Lena, and Kolyma rivers). If western Arctic tDOC decays at the rate representative of that system ($0.06\text{--}0.097 \text{ yr}^{-1}$) over a residence time estimated at 11 to 15 years (Bauch et al., 1995) or 12 to 14 years (Karcher and Oberhuber, 2002), then the initial 2.8 Tg C will be reduced to $0.7\text{--}1.5 \text{ Tg C}$ by the time it exits the Arctic. A similar calculation using the decay rate found here (0.24 yr^{-1}) for the eastern Arctic follows that the 14.8 Tg C entering the eastern Arctic will be reduced to $3.1\text{--}5.7 \text{ Tg C}$ over 4 to 6.5 years of residence time of river water in the Eurasian Arctic (Karcher and Oberhuber, 2002). This estimate provides an upper limit for tDOC decay in the eastern Arctic because the decay rate (0.24 yr^{-1}) only applies to waters overlying the shelf with slower rates offshore. Therefore, the 17.6 Tg C of tDOC that enter the Arctic Basin annually via the six largest rivers will be reduced to $3.1\text{--}5.7 \text{ Tg C}$ (215–41% of input) by the time it reaches Fram Strait. If this analysis of the six largest rivers can be extrapolated to include all river runoff to the Arctic Basin, then the total tDOC input of 25 Tg C a^{-1} (Raymond et al., 2007) will be reduced to $5.3\text{--}10.3 \text{ Tg C}$ before subsequent export to the North Atlantic. By comparison, the analysis of lignin content, a biomarker for terrestrially derived carbon, indicated that 12%–40% of Arctic tDOC is exported via the East Greenland Current at Fram Strait (Opsahl et al., 1999) or 20%–50% as estimated using DOM fluorescence (Amon et al., 2003).

6. Conclusions

In this study we observed the removal of a significant fraction of tDOC delivered to the eastern Arctic system. This removal occurred largely over the Eurasian shelf seas such that the source waters of the Transpolar Drift contain <50% of eastern Arctic tDOC concentrations originally added to the system. The tDOC decay constant calculated

here, $\lambda = 0.24 \pm 0.07 \text{ yr}^{-1}$, reflects the rapid removal of a relatively labile Arctic tDOC pool over a multi-annual (2–5 years) Eurasian shelf residence time. This tDOC decay constant agrees well with that found for the western East Siberian Arctic shelf of $\lambda = 0.3 \text{ yr}^{-1}$ (Alling et al., *in press*). These results reinforce the idea of a dynamic tDOC pool in the Arctic, consisting of biolabile components supporting the microbial loop in the Arctic Ocean. Remineralization of terrigenous organic matter over the shelves mitigates the air–sea disequilibrium of CO_2 , with implications for the net air-to-sea flux of atmospheric CO_2 over the Arctic Ocean that warrants further investigation. The decay constants for tDOC found in this and earlier studies for the Arctic Ocean can be incorporated into regional biogeochemical models to represent the dynamic tDOC pool within the Arctic carbon cycle. Further studies in the more temperate regions of the globe are needed to accurately include tDOC dynamics in global biogeochemical models.

Acknowledgements

The authors received support for this work from the National Science Foundation, Grant No. OPP-0822429 to DK and DAH. We thank C. Farmer and W. Chen for the DOC analyses, P. Swart and the University of Miami Stable Isotope Laboratory for the $\delta^{18}\text{O}$ analyses, M. Stephens for the 228-, 226-Ra analyses, and M. Rutgers van der Loeff for providing sampling equipment. We would also like to thank the crew and science party aboard the FS Polarstern for inclusion and support of our water sampling program during expedition ARKXXIII/3.

References

- Aagaard, K., Carmack, E.C., 1989. The role of sea ice and other fresh water in the Arctic circulation. *J. Geophys. Res.* 94, 14485–14498.
- Alling, V., Sanchez-Garcia, L., Porcelli, D., Pugach, S., Vonk, J.E., van Dongen, B., Mörth, C.-M., Anderson, L.G., Sokolov, A., Andersson, P., Humborg, C., Semiletov, I., Gustafsson, O., *in press*. Non-conservative behavior of dissolved organic carbon across the Laptev and East Siberian Seas. *Global Biogeochemical Cycles* (accepted 27 Sept 2010). doi:10.1029/2010GB003834.
- Amon, R.M.W., 2004. The role of dissolved organic matter for the organic carbon cycle in the Arctic Ocean. In: Stein, R.S., Macdonald, R.W. (Eds.), *The organic carbon cycle in the Arctic Ocean*. Springer, New York, pp. 83–99.
- Amon, R.M.W., Benner, R., 2003. Combined neutral sugars as indicators of the diagenetic state of dissolved organic matter in the Arctic Ocean. *Deep Sea Res.* 50, 151–169.
- Amon, R.M.W., Meon, B., 2004. The biogeochemistry of dissolved organic matter and nutrients in two large Arctic estuaries and potential implications for our understanding of the Arctic Ocean system. *Mar. Chem.* 92, 311–330.
- Amon, R.M.W., Budéus, G., Meon, B., 2003. Dissolved organic carbon distribution and origin in the Nordic Seas: Exchanges with the Arctic Ocean and the North Atlantic. *J. Geophys. Res.* C: Oceans 108, 3221.
- Anderson, L.G., Jutterström, S., Kallin, S., Jones, E.P., Björk, G., 2004. Variability in river runoff distribution in the Eurasian Basin of the Arctic Ocean. *J. Geophys. Res.* C: Oceans 109, C01016.
- Anderson, L.G., Jutterström, S., Hjalmarsson, S., Wählström, I., Semiletov, I.P., 2009. Outgassing of CO_2 from Siberian Shelf seas by terrestrial organic matter decomposition. *Geophys. Res. Lett.* 36, L20601.
- Bates, N.R., Moran, S.B., Hansell, D.A., Mathis, J.T., 2006. An increasing CO_2 sink in the Arctic Ocean due to sea-ice loss. *Geophys. Res. Lett.* 33, C10013.
- Bauch, D., Schlosser, P., Fairbanks, R.G., 1995. Freshwater balance and the sources of deep and bottom waters in the Arctic Ocean inferred from the distribution of H_2^{18}O . *Prog. Oceanogr.* 35, 53–80.
- Bussmann, I., Kattner, G., 2000. Distribution of dissolved organic carbon in the central Arctic Ocean: The influence of physical and biological properties. *J. Mar. Syst.* 27, 209–219.
- Carlson, C.A., Ducklow, H.W., 1995. Dissolved organic carbon in the upper ocean of the central equatorial Pacific Ocean, 1992: Daily and finescale vertical variations. *Deep Sea Res.* II 42, 639–656.
- Cauwet, G., Sidorov, I., 1996. The biogeochemistry of Lena River: Organic carbon and nutrients distribution. *Mar. Chem.* 53, 211–227.
- Climate Prediction Center, National Weather Service, NOAA, 2009. Standardized 3-month running mean AO Index. http://www.cpc.naa.gov/products/precip/CWlink/daily_ao_index/month_ao_index.shtml. (Accessed 19 November 2009).
- Coachman, L.K., Aagaard, K., Tripp, R.B., 1975. Water masses, in *Bering Strait: The Regional Physical Oceanography*. University of Washington Press, USA, pp. 11–43.
- Cooper, L.W., Benner, R., McClelland, J.W., Peterson, B.J., Holmes, R.M., Raymond, P.A., et al., 2005. Linkages among runoff, dissolved organic carbon, and the stable oxygen isotope composition of seawater and other water mass indicators in the Arctic Ocean. *J. Geophys. Res. Biogeosci.* 110, G02013.
- Cooper, L.W., McClelland, J.W., Holmes, R.M., Raymond, P.A., Gibson, J.J., Guay, C.K., et al., 2008. Flow-weighted values of runoff tracers ($\delta^{18}\text{O}$, DOC, Ba, alkalinity) from the six largest Arctic rivers. *Geophys. Res. Lett.* 35, L18606.
- Denef, K., Plante, A.F., Six, J., 2009. Characterization of soil organic matter. In: Kutsch, W.L., Bahn, M., Heinemeyer, A. (Eds.), *Soil Carbon Dynamics: An Integrated Methodology*. Cambridge University Press, New York, pp. 91–126.
- Dittmar, T., Kattner, G., 2003. The biogeochemistry of the river and shelf ecosystem of the Arctic Ocean: A review. *Mar. Chem.* 83, 103–120.
- Dmitrenko, I., Kirillov, S., Eicken, H., Markova, N., 2005. Wind-driven summer surface hydrography of the eastern Siberian shelf. *Geophys. Res. Lett.* 32, 1–5.
- Dmitrenko, I.A., Kirillov, S.A., Bruno Tremblay, L., 2008. The long-term and interannual variability of summer fresh water storage over the eastern Siberian shelf: Implication for climatic change. *J. Geophys. Res.* C Oceans 113, C03007.
- Eicken, H., Krouse, H.R., Kadko, D., Perovich, D.K., 2002. Tracer studies of pathways and rates of meltwater transport through Arctic summer sea ice. *J. Geophys. Res.* C: Oceans 107, 8046.
- Ekwrusel, B., Schlosser, P., Mortlock, R.A., Fairbanks, R.G., Swift, J.H., 2001. River runoff, sea ice meltwater, and Pacific water distribution and mean residence times in the Arctic Ocean. *J. Geophys. Res.* C Oceans 106, 9075–9092.
- Epstein, S., Mayeda, T., 1953. Variation of O^{18} content of waters from natural sources. *Geochim. Cosmochim. Acta* 4, 213–224.
- Farmer, C., Hansell, D.A., 2007. Determination of dissolved organic carbon and total dissolved nitrogen in sea water: Guide to best practices for ocean CO_2 measurements. *PICES Special Publication*, 3, p. 91.
- Giannelli, V., Thomas, D.N., Haas, C., Kattner, G., Kennedy, H., Dieckmann, G.S., 2001. Behaviour of dissolved organic matter and inorganic nutrients during experimental sea-ice formation. *Ann. Glaciol.* 33, 317–321.
- Guay, C.K.H., Falkner, K.K., Muench, R.D., Mensch, M., Frank, M., Bayer, R., 2001. Wind-driven transport pathways for Eurasian Arctic river discharge. *J. Geophys. Res.* C: Oceans 106, 11469–11480.
- Hansell, D.A., Kadko, D., Bates, N.R., 2004. Degradation of terrigenous dissolved organic carbon in the western Arctic Ocean. *Science* 304, 858–861.
- Hansell, D.A., Carlson, C.A., Schlitzer, R., submitted. Removal of major marine dissolved organic carbon fractions in the deep ocean. *Nature Geoscience*, 2010.
- Hanzlick, D., Aagaard, K., 1980. Freshwater and Atlantic water in the Kara Sea. *J. Geophys. Res.* 85, 4937–4942.
- Hernes, P.J., Benner, R., 2003. Photochemical and microbial degradation of dissolved lignin phenols: Implications for the fate of terrigenous dissolved organic matter in marine environments. *J. Geophys. Res.* C: Oceans 108, 3291.
- Holmes, R.M., McClelland, J.W., Raymond, P.A., Frazer, B.B., Peterson, B.J., Stieglitz, M., 2008. Lability of DOC transported by Alaskan rivers to the Arctic Ocean. *Geophys. Res. Lett.* 35, L03402.
- Hopkinson Jr., C.S., Vallino, J.J., Nolin, A., 2002. Decomposition of dissolved organic matter from the continental margin: Deep-sea res. Part II top. *Stud. Oceanogr.* 49, 4461–4478.
- Jones, E.P., Anderson, L.G., Jutterström, S., Mintrop, L., Swift, J.H., 2008. Pacific freshwater, river water and sea ice meltwater across Arctic Ocean basins: Results from the 2005 Beringia Expedition. *J. Geophys. Res.* C: Oceans 113, C08012.
- Kadko, D., Aagaard, K., 2009. Glimpses of Arctic Ocean shelf-basin interaction from submarine-borne radium sampling. *Deep Sea Res.* I 56, 32–40.
- Kadko, D., Muench, R., 2005. Evaluation of shelf-basin interaction in the western Arctic by use of short-lived radium isotopes: The importance of mesoscale processes—Deep-sea res.: Part II top. *Stud. Oceanogr.* 52, 3227–3244.
- Karcher, M.J., Oberhuber, J.M., 2002. Pathways and modification of the upper and intermediate waters of the Arctic Ocean. *J. Geophys. Res.* C: Oceans 107, 3049.
- Kattner, G., Lobbes, J.M., Fitznar, H.P., Engbrodt, R., Nöthig, E., Lara, R.J., 1999. Tracing dissolved organic substances and nutrients from the Lena River through Laptev Sea (Arctic). *Mar. Chem.* 65, 25–39.
- Kaufman, A., Trier, R.M., Broecker, W.S., Feely, H.W., 1973. Distribution of ^{228}Ra in the world ocean. *J. Geophys. Res.* 78, 8827–8848.
- Kirchman, D.L., Lancelot, C., Fasham, M., Legendre, L., Radach, G., Scott, M., 1993. Dissolved organic matter in biogeochemical models of the ocean. In: Evans, G.T., Fasham, M.J.R. (Eds.), *Towards a Model of Ocean Biogeochemical Processes*. Springer-Verlag, Berlin Heidelberg, pp. 209–225.
- Köhler, H., Meon, B., Gordeev, V., Spitz, A., Amon, R., 2003. Dissolved organic matter (DOM) in the estuaries of Ob and Yenisei and the adjacent Kara Sea, Russia. In: Stein, R., Fahl, K., Fütterer, D.K., Galimov, E.M., Stepanets, O.V. (Eds.), *Siberian river run-off in the Kara Sea: Proc. Mar. Sci.*, 6, pp. 281–308.
- Macdonald, R.W., Paton, D.W., Carmack, E.C., Omstedt, A., 1995. The freshwater budget and under-ice spreading of Mackenzie River water in the Canadian Beaufort Sea based on salinity and $^{18}\text{O}/^{16}\text{O}$ measurements in water and ice. *J. Geophys. Res.* 100, 895–919.
- Manizza, M., Follows, M.J., Dutkiewicz, S., McClelland, J.W., Menemenlis, D., Hill, C.N., et al., 2009. Modeling transport and fate of riverine dissolved organic carbon in the Arctic Ocean. *Glob. Biogeochem. Cycles* 23, GB4006.
- Mathis, J.T., Hansell, D.A., Bates, N.R., 2005. Strong hydrographic controls on spatial and seasonal variability of dissolved organic carbon in the Chukchi Sea—Deep-sea res.: Part II top. *Stud. Oceanogr.* 52, 3245–3258.
- Mathis, J.T., Hansell, D.A., Kadko, D., Bates, N.R., Cooper, L.W., 2007. Determining net dissolved organic carbon production in the hydrographically complex western Arctic Ocean. *Limnol. Oceanogr.* 52, 1789–1799.
- Michel, J., Moore, W.S., King, P.T., 1981. γ -ray spectrometry for determination of radium-228 and radium-226 in natural waters. *Anal. Chem.* 53, 1885–1889.
- Moore, W.S., Key, R.M., Sarmiento, J.L., 1985. Techniques for precise mapping of ^{226}Ra and ^{228}Ra in the ocean. *J. Geophys. Res.* 90, 6983–6994.

- Moran, M.A., Sheldon Jr., W.M., Sheldon, J.E., 1999. Biodegradation of riverine dissolved organic carbon in five estuaries of the southeastern United States. *Estuaries* 22, 55–64.
- Neff, J.C., Finlay, J.C., Zimov, S.A., Davydov, S.P., Carrasco, J.J., Schuur, E.A.G., et al., 2006. Seasonal changes in the age and structure of dissolved organic carbon in Siberian rivers and streams. *Geophys. Res. Lett.* 33, L23401.
- Opsahl, S., Benner, R., Amon, R.M.W., 1999. Major flux of terrigenous dissolved organic matter through the Arctic Ocean. *Limnol. Oceanogr.* 44, 2017–2023.
- Ostlund, H.G., Hut, G., 1984. Arctic ocean water mass balance from isotope data. *J. Geophys. Res.* 89, 6373–6381.
- Pavlov, V.K., Kulakov, M.Y., Stanovoy, V.V., 1993. Oceanographical description of the Kara and Barents seas. Rep. IAEA 133.
- Peterson, B.J., Holmes, R.M., McClelland, J.W., Vörösmarty, C.J., Lammers, R.B., Shiklomanov, A.I., et al., 2002. Increasing river discharge to the Arctic Ocean. *Science* 298, 2171–2173.
- Raymond, P.A., Bauer, J.E., 2000. Bacterial consumption of DOC during transport through a temperate estuary. *Aquat. Microbiol. Ecol.* 22, 1–12.
- Raymond, P.A., McClelland, J.W., Holmes, R.M., Zhulidov, A.V., Mull, K., Peterson, B.J., et al., 2007. Flux and age of dissolved organic carbon exported to the Arctic Ocean: A carbon isotopic study of the five largest arctic rivers. *Glob. Biogeochem. Cycles* 21, GB4011.
- Rutgers van der Loeff, M.M., Key, R.M., Scholten, J., Bauch, D., Michel, A., 1995. ^{228}Ra as a tracer for shelf water in the arctic ocean—Deep-sea res.: Part II top. *Stud. Oceanogr.* 42, 1533–1553.
- Rutgers van der Loeff, M., Kühne, S., Wahsner, M., Hölzner, H., Frank, M., Ekwurzel, B., et al., 2003. ^{228}Ra and ^{226}Ra in the Kara and Laptev seas. *Cont. Shelf Res.* 23, 113–124.
- Schauer, U., 1997. Impact of eastern Arctic shelf waters on the Nansen Basin intermediate layers. *J. Geophys. Res. C: Oceans* 102, 3371–3382.
- Schlitzer, R., 2010. Ocean Data View 4. <http://odv.awi.de>.
- Schlösser, P., Bauch, D., Fairbanks, R., Bonisch, G., 1994. Arctic river-runoff: Mean residence time on the shelves and in the halocline. *Deep Sea Res. I* 41, 1053–1068.
- Schlösser, P., Newton, R., Ekwurzel, B., Khatriwala, S., Mortlock, R., Fairbanks, R., 2002. Decrease of river runoff in the upper waters of the Eurasian Basin, Arctic Ocean, between 1991–1996: Evidence from $\delta^{18}\text{O}$ data. *Geophys. Res. Lett.* 29, 1289.
- Six, J., Jastrow, J.D., 2006. Soil organic matter turnover. In: Lal, R. (Ed.), *Encyclopedia of Soil Science*. Aylor and Francis Group, New York, pp. 1210–1214.
- Spencer, R.G.M., Aiken, G.R., Wickland, K.P., Striegl, R.G., Hernes, P.J., 2008. Seasonal and spatial variability in dissolved organic matter quantity and composition from the Yukon River basin, Alaska. *Glob. Biogeochem. Cycles* 22, GB4002.
- Spencer, R.G.M., Aiken, G.R., Butler, K.D., Dornblaser, M.M., Striegl, R.G., Hernes, P.J., 2009. Utilizing chromophoric dissolved organic matter measurements to derive export and reactivity of dissolved organic carbon exported to the Arctic Ocean: A case study of the Yukon River, Alaska. *Geophys. Res. Lett.* 36, L06401.
- Swart, P.K., 2000. The oxygen isotopic composition of interstitial waters: Evidence for fluid flow and recrystallization in the margin of the Great Bahama Bank. *Proc. Ocean Drilling Program. Sci. Res.* 166, 91–98.
- van Dongen, B.E., Zencak, Z., Gustafsson, Ö., 2008. Differential transport and degradation of bulk organic carbon and specific terrestrial biomarkers in the surface waters of a sub-arctic brackish bay mixing zone. *Mar. Chem.* 112, 203–214.
- Wheeler, P.A., Watkins, J.M., Hansing, R.L., 1997. Nutrients, organic carbon and organic nitrogen in the upper water column of the Arctic Ocean: Implications for the sources of dissolved organic carbon. *Deep Sea Res. II* 44, 1571–1592.