



The biogeochemistry of dissolved organic matter and nutrients in two large Arctic estuaries and potential implications for our understanding of the Arctic Ocean system[☆]

Rainer M.W. Amon^{a,b,*}, Benedikt Meon^{b,c}

^aTexas A&M University at Galveston, Department of Marine Sciences and Oceanography, Galveston, TX, USA

^bAlfred Wegener Institute for Polar and Marine Research, Department of Biological Oceanography, Bremerhaven, Germany

^cUniversity of Hamburg, Institute for Biogeochemistry and Marine Chemistry, Hamburg, Germany

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Abstract

The discharge, composition, and fate of dissolved organic matter (DOM) and nutrients was investigated in two of the largest Arctic rivers, Yenisei and Ob, in order to assess their role for the biogeochemistry of the Kara Sea, and the potential of terrestrial DOM as tracer for the Arctic Ocean. Ultrafiltered DOM (UDOM) from the two river–estuary systems was characterized by high C/N ratios (34–49), depleted $\delta^{13}\text{C}$ values ($< -26.5\text{‰}$), depleted $\delta^{15}\text{N}$ values (1.8–4.2‰), and enriched $\Delta^{14}\text{C}$ values (84–307‰). The distribution of DOM and its chemical properties indicated no major loss processes during estuarine mixing but showed considerable variability between the rivers and years, suggesting a variable input of plankton-derived DOM. The input of plankton-derived DOM was reflected in elevated neutral sugar yields, decreased C/N ratios, but variable $\delta^{13}\text{C}$ values. In contrast, $\delta^{15}\text{N}$ values appear to be more reliable indicators to distinguish terrestrial from plankton-derived DOM in this estuarine system. Based on $\delta^{15}\text{N}$ values, we estimate that between 6% and 16% of the DOM in the river and estuaries is of plankton origin. Clear differences were found in the chemical composition of DOM size fractions. Plankton-derived DOM was more abundant in the higher molecular weight fractions whereas terrestrial-derived DOM dominated the lower molecular weight fraction. This suggests a more heterogeneous origin of DOM than is revealed from looking at the composition of the bulk DOM. Photooxidation experiments indicated the potential photoreactivity of river DOM from those rivers. Compiling the information from this study with previous studies indicates that river input of DOM and nutrients is not the main driver of autotrophic and heterotrophic processes in the Kara Sea ecosystem. Consistent with previous reports, we found the terrestrial fraction of river DOM to be largely

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* Corresponding author. Texas A&M University at Galveston, Department of Marine Sciences and Oceanography, Fort Crockett Campus, 5007 Avenue U, Galveston, TX 77551, USA. Tel.: +1 409 740 4719; fax: +1 409 740 4787.

E-mail address: amonr@tamug.edu (R.M.W. Amon).

conservative in the estuaries underscoring the potential of terrestrial DOM as a tracer in the Arctic Ocean, especially when combined with standard hydrographic measurements.

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1. Introduction

The Arctic Ocean is greatly influenced by river run-off from the surrounding continents receiving approximately 10% of the global freshwater discharge (Shiklomanov et al., 2000). The large watersheds of the major Arctic rivers also store enough soil organic carbon to be of global significance (Stolbovoi, 2002, Tarnocai et al., 2003). The observed environmental changes in the Arctic over the last 15 years have increased the interest in Arctic river discharge and how environmental change affects the discharge of water and organic matter to the Arctic Ocean (Peterson et al., 2002; Benner et al., 2004). In order to detect changes, it is important to understand the natural variability of discharge and how it influences the Arctic Ocean in terms of physical processes and biogeochemistry. Most of the work on Arctic river discharge and coastal processes conducted in the last decade significantly improved our basic understanding of land–ocean systems in the Arctic. We now know that Arctic river discharge has very strong seasonal variability (Shiklomanov et al., 2000), that the rivers have a relatively high concentration of dissolved organic matter (DOM; Cauwet and Sidorov, 1996; Lobbes et al., 2000; Anderson, 2002; Köhler et al., 2003), and that signs of river water and its organic constituents can be found throughout Arctic Ocean surface waters (Opsahl et al., 1999; Benner et al., 2004). Although we have developed a general appreciation of the important role that large river input plays for physical and biogeochemical processes in the Arctic Ocean, we still have a very limited understanding of how the different physical and biogeochemical processes link into each other and how those interactions might be affected by environmental change.

The Yenisei and Ob contribute about 34% to the total Arctic river discharge and about 40% (666–750 Gmol C year⁻¹ or 8–9 Tg C year⁻¹) to the total DOM discharge (Gordeev and Rachold, 2003). These two

rivers drain vast areas of the Eurasian continent (5.43×10^6 km²) including the worlds largest peat bog system and extended permafrost areas in the north. Both are important pools of organic carbon that could be mobilized under different climatic conditions. The Yenisei, Ob, and the Kara Sea have been the focus of a Russian–German project which in the last 6 years has gathered valuable background information (Stein et al., 2003) on the biology, chemistry, and biogeochemistry of the water column and sediments in this region. Some of the open questions that we tried to address in this project included the importance of river discharge for biological processes in the Kara Sea, the chemical composition and origin of DOM in the rivers, the fate and transformations of terrestrial DOM in the estuaries, and the potential of terrestrial organic matter to be used as a tracer for water mass distribution and modification on the Eurasian shelf and in the open Arctic Ocean, and as an indicator of environmental change.

This study contains new information on the elemental, isotopic and molecular level composition of DOM and its size fractions in the rivers Yenisei and Ob and their estuaries. It also contains new information on the photochemical reactivity of high latitude terrestrial DOM under natural conditions. The new information will be presented in a wider context together with a summary of information that has been presented before in order to create a general overview of the role of river discharge for the Arctic Ocean system and how terrestrial organic tracers might aid us in the future to better understand the complex interaction of physical and biogeochemical processes on the Eurasian shelf.

2. Materials and methods

As part of the bilateral Russian–German “Siberian River Run-off (SIRRO)” project, water samples for

nutrients and dissolved organic matter were collected in and off the river mouths of Ob and Yenisei and in the Kara Sea during cruises on the Russian research vessel “Akademik Boris Petrov.” Additionally, we collected samples from a tundra lake near Murmansk and obtained one sample from the Mackenzie River, Canada.

Large volume samples (10–200 L) were collected either with Niskin bottles mounted onto a CTD rosette or with a large-volume (200 L) stainless-steel water-sampler. The water samples were filtered through a 0.2- μm polycarbonate filter (Nuclepore) immediately after sampling. Samples were ultrafiltered on board, or stored (in polypropylene bottles at 4 °C in the dark) until processing at the home laboratory. DOC concentrations in the stored samples did not indicate DOC losses or contamination during storage ($\leq 5\%$ variation).

2.1. Isolation of DOM samples

Ultrafiltration was performed with an Amicon Proflex M 30 system with two spiral-wound polysulfone filter cartridges (S10N1; 1000 Dalton cutoff). After concentration of the initial volume (30–200 L) to ~ 1 L, the sample was diafiltered with 12–18 L of Milli-Q water to remove inorganic salts (to salinity < 0.2). The diafiltered sample, typically 1.0–1.8 L, was stored in a polycarbonate bottle and frozen until further processing. The volume of the diafiltered concentrate was reduced to about 75 ml by rotary evaporation. The samples were dried in a Savant SVC200 SpeedVac concentrator and the dry samples were stored in precombusted glass vials until further analysis. For further details on the ultrafiltration procedures, see Benner et al. (1987).

For comparison to the main sample set collected by ultrafiltration, we also isolated a number of DOM samples by vacuum evaporation from several river end-members including samples from the Mackenzie River and from a tundra lake. Vacuum evaporation was performed using a rotoevaporator with automatic vacuum control and a chilled condensation coil. The high vacuum allowed a relatively low evaporation temperature of 45 °C. Seven to sixteen liters of sample were concentrated down to about 75 ml and subsequently dried as described above. In those samples, essentially all

DOM and dissolved inorganic matter were recovered as a dried powder.

2.2. Measurements

Dissolved organic carbon (DOC) was measured by the high temperature combustion method and either a Shimadzu TOC 5000 analyzer (Benner and Strom, 1993) or MQ-Scientific 1001 TOC analyzer (Qian and Mopper, 1996). Samples for DOC determinations were filtered through precombusted Whatman GF/F filters and stored frozen in sealed glass ampoules until analysis at the home laboratory. To assure quality control, we routinely determined deep-sea DOC standards supplied by J. Sharp (University of Delaware) or our own from Arctic Ocean deep water (50.5 μM , calibrated with the standard supplied by J. Sharp). The standards were used approximately every second analysis day and averaged $47.5 \pm 0.7 \mu\text{M C}$ ($n=5$) for the Shimadzu TOC 5000, and $45.4 \pm 1.4 \mu\text{M C}$ ($n=8$) for the MQ-1001 Analyzer. The deep water standard from the Arctic Ocean had an average DOC concentration of $51.1 \pm 2 \mu\text{M C}$ ($n=27$) which was within the margin of error compared to cross calibration with Sharp’s deep-sea standard. The vast majority of the samples were measured with the MQ-1001 analyzer. With this instrument, the relative standard deviation at the 80 μM DOC level was on average 1.6% ($n=200$).

Samples for nutrient analysis were either poisoned with HgCl_2 and stored in the refrigerator or frozen until analysis (Kattner, 1999). Nutrients were analyzed using a Technicon Autoanalyzer II system following the method outlined by Kattner and Becker (1991). Oxygen concentrations were determined by Winkler titration using an autotitration system (Mettler Toledo) with potentiometric equivalence point determination (Graneli and Graneli, 1991). Samples for oxygen determination were incubated in acid-washed and rinsed quartz BOD bottles (115 ml). Oxygen consumption rates were calculated between the initial and final time points.

The concentrations of individual neutral sugars (fucose, rhamnose, arabinose, galactose, glucose, mannose, and xylose) in hydrolyzed ultrafiltered DOM (UDOM) and rotor evaporated (RDOM) samples were determined with a Dionex 500 anion-exchange chromatography system with pulsed

amperometric detection (PAD) following the procedure described by Skoog and Benner (1997) and Kaiser and Benner (2000). Briefly, 2-ml 12 M H₂SO₄ was added to dry UDOM samples (1–2 mg), mixed in an ultrasonic bath (15 min) and transferred to a glass ampoule. Sealed ampoules were placed in a water bath (100 °C) and hydrolyzed for 3 h. The hydrolyzed samples were neutralized in 4.5 ml of self-absorbed resin AG11 A8 (Bio-Rad; Kaiser and Benner, 2000). The neutralized samples were diluted 1:10–1:20 with Milli-Q water (Millipore) prior to analysis with the HPLC system. Deoxiribose was added to the ice-cooled hydrolysates as internal standard prior to the neutralization step. The residual standard deviation including sample preparation was between 2% and 10%.

Amino acids (DL-aspartic acid, DL-glutamic acid, L-serine, L-threonine, glycine, L-arginine, DL-alanine, γ -amino butyric acid, L-tyrosine, L-valine, L-phenylalanine, L-isoleucine, L-leucine) were determined by HPLC and precolumn derivatization with *o*-phthalaldehyde and *N*-isobutyrylcystein after hydrolysis following the procedure described by Fitznar et al. (1999). UDOM and RDOM samples were dissolved in 10 ml of MQ water, mixed with 10 ml HCl (32%) and hydrolyzed in sealed glass ampoules for 24 h at 110 °C. After hydrolysis, the samples were neutralized with 8.9 ml borate buffer (0.5 M) and the pH was adjusted to 8.5 with 32% NaOH. The residual standard deviation for this analysis typically lies between 1% and 8% for the individual amino acids.

Carbon and nitrogen concentrations of UDOM were determined with a Carlo Erba 1108 elemental analyzer after vapor phase acidification (Hedges and Stern, 1984). Stable carbon and nitrogen isotope ratios of dried UDOM were measured using a Finnegan Delta Plus system or an Europa Scientific ANCA SL system with in-line combustion. Stable isotope ratios were calculated using the equation $\delta^{NE} (\text{‰}) = [(R_{\text{sample}}/R_{\text{standard}}) - 1] \times 1000$, where ^{NE} is the heavy isotope of an element (¹³C or ¹⁵N) and *R* is the ratio of ¹³C/¹²C or ¹⁵N/¹⁴N in the sample and the standard (Pee Dee Belemite and atmospheric nitrogen, respectively).

Carbon-14 analyses were performed at the “Leibnitz Labor für Altersbestimmung und Isotopenforschung” at the University of Kiel (Germany). Dried samples of DOM were microscopically inves-

tigated for contamination, combusted at 900 °C to CO₂, reduced to graphite and analyzed for $\Delta^{14}\text{C}$ by accelerator mass spectrometry. Errors averaged ± 40 years for radiocarbon ages.

2.3. Photooxidation experiments

Filtered water samples (0.2 μm) were allowed to sit for at least 30 min in PP bottles before they were siphoned into 120 ml quartz BOD bottles carefully avoiding bubble formation. At least two bottle volumes of sample water were used to flush the BOD bottles before the stoppers were added. One set of replicates (usually 4) was immediately fixed with Winkler reagents followed by the determination of dissolved oxygen in the autotitrator using 0.0125 N thiosulfate as titrant solution for 50 ml of sample aliquots. A second set of replicates (dark control) was wrapped in aluminum foil. BOD bottles were exposed to ambient irradiation on deck of the ship. The maximum exposure periods were 6 and 12 days, respectively, for water from the Yenisei and 2.5 days for Ob water. One experiment with water from the tundra lake was conducted in a solar simulator using elevated UV-light levels similar to equatorial conditions. In this experiment, filtered lake water was exposed in quartz BOD bottles along with dark controls over 72 h of uninterrupted artificial light.

3. Results and discussion

3.1. Dissolved organic matter and nutrient discharge by the Ob and Yenisei

The Ob and Yenisei contribute about one third of the total freshwater discharge to the Arctic Ocean. The Yenisei, the largest Arctic river overall, contributes 620 km³ year⁻¹, and the Ob contributes about 482 km³ year⁻¹ (including Taz and Pur; Gordeev and Rachold, 2003). The concentration and elemental composition of bulk DOM in the Ob and Yenisei and the adjacent estuaries have been reported previously (Köhler et al., 2003; Amon, 2003), indicating that DOC concentrations in the rivers vary roughly between 400 and 1200 μM C mainly as a function of the hydrograph with elevated concentration during the spring (May and June) freshet and lower concen-

tration during base flow conditions in the winter (Köhler et al., 2003). Based on the known variations of water discharge and DOM concentrations, we estimated weighted average concentrations of DOC and DON for the two rivers to be 640 μM DOC for the Ob and 690 μM DOC L for the Yenisei (Table 1). Average concentrations of DON are more speculative with a rough estimate of 11 μM in the Ob and 13 μM in the Yenisei (Table 1). Based on the above assumptions, the annual discharge of DOC and DON from the Ob is 308 Gmol (3.7 Tg) and 5.0 Gmol (0.07 Tg), and from the Yenisei, 425 Gmol (5.1 Tg) and 7.8 Gmol (0.11 Tg), respectively (Table 1). DON is the dominant form of nitrogen discharged by the two rivers, about five times as large as dissolved inorganic nitrogen (DIN). DIN concentration and discharge from Siberian Rivers to the Arctic Ocean have been a matter of debate recently, leading to significantly lower current DIN estimates (Holmes et al., 2000, 2001). We sampled the rivers between July and October in 1997, 1999, 2000, and 2001 and found consistently low concentrations of DIN and relatively high concentrations of phosphate and silicate (Table 1). Averaged over the four sampling periods, nitrate and ammonia concentrations were 1.1 and 1.3 μM N in the River Ob and 0.4 and 0.5 μM in the River Yenisei. Silicate concentrations were much higher in the Yenisei (78 μM) than in the Ob (27 μM) and phosphate concentrations were between 0.3 and 0.7 μM in the rivers. The river values are in good agreement with recently published values by Holmes et al. (2001). Based on the DIN values reported here, the seasonal variations of nutrient concentrations reported by Holmes et al. (2000), and on seasonal variation of water discharge (Köhler et al., 2003), we can roughly estimate the annual DIN discharge to be approximately 1.4 Gmol N (0.02 Tg) for the Ob and 0.7 Gmol N (0.01 Tg) for the Yenisei (Table 1). This

is 25 times less than the value reported by Holmes et al. (2000) based on the long-term Russian data set.

3.2. DOM distribution and composition in the estuaries

The distribution of DOC and the elemental and stable carbon isotopic composition of bulk DOM along the salinity gradient indicated a largely conservative behavior of river DOM during the summer months (Köhler, 2003). C/N ratios averaged 45 in the rivers and conservatively declined to about 20 in the northern Kara Sea (Köhler et al., 2003). A similarly conservative distribution was observed for humic substances isolated from Ob and Yenisei estuaries by XAD resins (Köhler, 2003), a fraction usually more prone to precipitation due to its relatively higher hydrophobicity.

The distribution of ultrafiltered DOM (UDOM) along the salinity gradient (Fig. 1A–D) was more variable between the years and rivers than is bulk DOC. While UDOM and its chemical characteristics were distributed rather conservatively along the salinity gradient in 1997 (Fig. 1A,B), we found considerable variability of DOM recovery and composition in 1999 (Fig. 1C,D). Reasons for such variability are numerous and include the changing hydrograph, with associated but poorly understood changes in DOM, and changes in the relative contributions of terrestrially and algal-derived DOM. From the data presented in Fig. 1, it appears that UDOM is not lost to any significant extent during the estuarine mixing process and that the variability observed is a result of varying DOM inputs rather than DOM losses. The use of multiple organic biomarkers is very helpful to understand the sources of variability in such a dynamic system and ultra-filtration harvests enough organic material, free of

Table 1
Discharge and multi-annual average concentration (μM) of DOC, DON, and nutrients in Ob and Yenisei

	Discharge, $\text{km}^3 \text{ year}^{-1}$	DOC, μM	DOC, Gmol (Tg) year^{-1}	DON, μM	DON, Gmol (Tg) year^{-1}	NO_3^- , μM	NH_4^+ , μM	DIN, Gmol (Tg) year^{-1}	Si, μM	PO_4 , μM	$\text{NO}_3^-/\text{PO}_4$
Ob	482 ^a	640 ^b	308 (3.7)	11 ^b	5.0 (0.07)	1.1	1.3	1.4 (0.02)	27.0	0.7	1.9
Yenisei	620 ^a	690 ^b	425 (5.1)	13 ^b	7.8 (0.11)	0.4	0.5	0.7 (0.01)	77.9	0.3	1.6

^a From Gordeev and Rachold (2003), Ob estimate includes the discharge of Taz and Pur.

^b From Köhler et al., 2003.

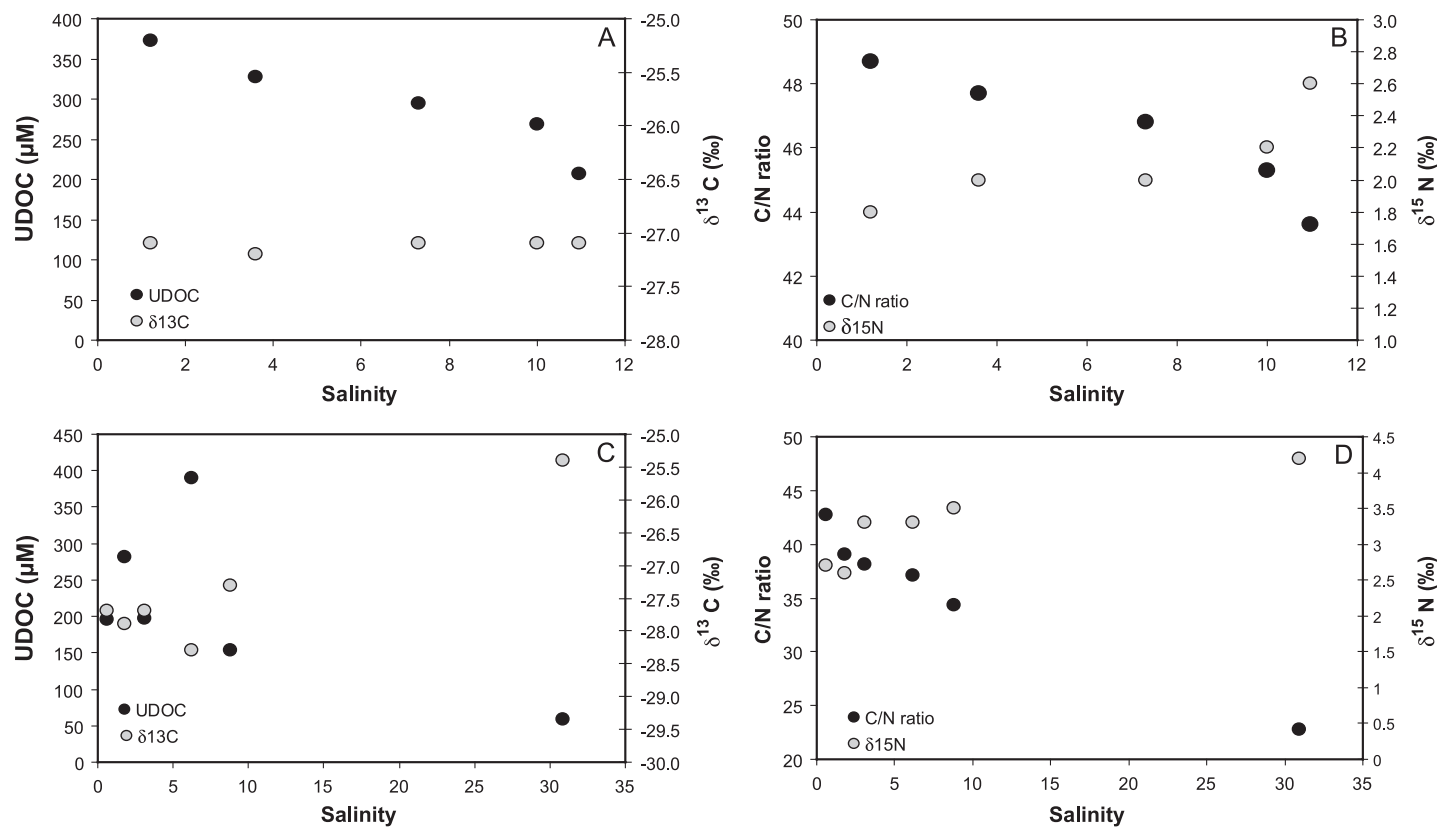


Fig. 1. Concentration, elemental and isotopic composition of ultrafiltered DOM along the salinity gradient in the Yenisei 1997 (AB), and in the Ob 1999 (CD).

inorganic salts, to run a variety of analyses on a single sample.

The DOM isolated from river and estuarine water samples by ultrafiltration in this study represents between 37% and 72% of the total DOM based on DOC mass balances (Table 2). In river samples with salinities below 5, the recovery of DOM by ultrafiltration was >60% (Table 2), showing that UDOM represents a major fraction of the total river DOM. DOC concentrations in the river end-member samples prior to DOM isolation ranged between 527 and 680 μM DOC in Ob and Yenisei as compared to 410 μM DOC in the Mackenzie River and 933 μM DOC in the tundra lake (Table 2). C/N ratios in UDOM ranged from 38 to 49 in Yenisei samples (salinity <10) and from 34 to 44 in Ob samples (salinity <10; Table 3), with average values being higher in 1997 than in 1999 in both rivers. The lower C/N ratios in 1999 are likely the result of increased inputs of plankton DOM with relatively low C/N values. This is consistent with much higher chlorophyll-*a* concentrations during the 1999 cruise (Nöthig et al.,

2003). Generally, the C/N values observed in UDOM are very consistent with the C/N ratios observed in bulk DOM (Köhler et al., 2003). C/N ratios in rotary evaporated DOM (RDOM) cannot directly be compared to UDOM values because of the presence of DIN in evaporated samples. Nonetheless, we observed the highest C/N ratio (53) in the tundra lake sample which contained DIN due to the isolation method.

Stable carbon isotope ratios in river and estuarine UDOM ranged between -26.7‰ and -27.7‰ in the Yenisei River and plume and between -27.3‰ and -28.3‰ in the Ob river and plume. As with C/N ratios, the stable carbon isotope values varied between the rivers and years with more depleted values in the Ob (-27.3‰ to -28.3‰) relative to the Yenisei (-26.7‰ to -27.7‰) and slightly more depleted values in 1999 than in 1997. In terms of stable carbon isotopes, the RDOM samples can be directly compared to UDOM values and are in fact very similar to UDOM values with a stable carbon isotope value of -27.5‰ for Yenisei and Ob RDOM, -26.7‰ for

Table 2
Sample locations and characteristics for ultrafiltered and vacuum evaporated samples

Sample origin—type	Date	Latitude	Longitude	Salinity	Depth, m	DOC, μM	UDOC, μM	DOC, %
Yenisei 1—UDOM	Sept. 18, 97	72°0535" N	81°2852" E	1.2	0–2	537	373	61
Yenisei 2—UDOM	Sept. 19, 97	72°3031" N	80°1943" E	3.6	0–2	534	328	64
Yenisei 3—UDOM	Sept. 17, 97	72°5321" N	80°0533" E	7.3	0–2	520	294	56
Yenisei 4—UDOM	Sept. 20, 97	73°4051" N	80°3639" E	10	0–2	503	269	54
Yenisei 5—UDOM	Aug. 26, 99	74°0060" N	79°5948" E	6	0–2	632	355	59
Yenisei 6—UDOM	Aug. 27, 99	72°2010" N	79°5936" E	2.6	0–2	680	422	72
Yenisei 7—UDOM	Aug. 29, 99	74°2983" N	78°0000" E	8.8	0–3	620	310	60
Ob 1—UDOM	Sept. 14, 97	72°3010" N	74°0451" E	2.4	0–2	528	299	68
Ob 2—UDOM	Sept. 15, 97	72°1013" N	74°1737" E	3.4	0–2	520	282	53
Ob 3—UDOM	Sept. 15, 97	72°4119" N	73°4350" E	7.0	0–2	493	267	56
Ob 4—UDOM	Aug. 24, 99	74°3040" N	73°5940" E	6.2	0–2	725	390	59
Ob 5—UDOM	Aug. 31, 99	72°1998" N	74°0000" E	1.8	0–2	536	281	65
Ob 6—UDOM	Aug. 31, 99	72°0010" N	73°4769" E	0.6	0	527	195	62
Ob 7—UDOM	Sept. 1, 99	72°3081" N	74°4390" E	3.1	0–2	504	197	45
Ob 8—UDOM	Sept. 2, 99	73°1479" N	74°0201" E	8.8	0–2	521	154	37
Kara Sea 1—UDOM	Sept. 16, 97	73°5742" N	76°0819" E	11.0	0–2	423	207	47
Kara Sea 2—UDOM	Aug. 25, 99	74°3060" N	75°5530" E	30.9	26	154	59	38
Kara Sea 3—UDOM	Sept. 13, 97	73°5438" N	73°1059" E	12.7	0–2	458	245	48
Yenisei >100 kDa	Aug. 27, 99	72°2010" N	79°5936" E	2.6	0–2	630	5	1.1
Yenisei 30–100 kDa	Aug. 27, 99	72°2010" N	79°5936" E	2.6	0–2	630	7	2.2
Yenisei 1–30 kDa	Aug. 27, 99	72°2010" N	79°5936" E	2.6	0–2	630	373	64
Yenisei—RDOM	Sept. 12, 99	69°5886" N	83°2719" E	0	0	640	343	na
Ob—RDOM	Aug. 31, 99	72°0010" N	73°4769" E	0.6	0	527	198	na
Mackenzie—RDOM	July 31, 99	69°0010" N	134°3000" W	0	0	410	222	na
Tundra Lake—RDOM	Sept. 12, 99	68°5900" N	55°0800" E	0	0	933	722	na

Table 3
Chemical composition of DOM isolated by ultrafiltration and vacuum evaporation

Sample origin—type	Salinity	C/N _(a)	$\delta^{13}\text{C}$, ‰	$\delta^{15}\text{N}$, ‰	$\Delta^{14}\text{C}$, ‰	Neutral sugars, nM L ⁻¹	Amino acids, nM L ⁻¹	NS, %OC	AA, %OC
Yenisei 1—UDOM	1.2	48.7	-27.1	1.8	150	1101	819	1.7	1.4
Yenisei 2—UDOM	3.6	47.7	-27.2	2	nd	1047	828	1.8	1.6
Yenisei 3—UDOM	7.3	46.8	-27.1	2	nd	985	699	1.9	1.7
Yenisei 4—UDOM	10	45.3	-27.1	2.2	nd	913	961	1.9	2.5
Yenisei 5—UDOM	6	37.7	-26.7	3	nd	3688	1180	6.0	1.2
Yenisei 6—UDOM	2.6	42.3	-27.7	2.6	nd	1536	1078	2.1	0.9
Yenisei 7—UDOM	8.8	38.1	-27.5	2.9	nd	2685	672	5.0	0.7
Ob 1—UDOM	2.4	43.9	-27.6	2.5	84	1823	969	3.5	1.7
Ob 2—UDOM	3.4	43.2	-27.6	2.4	nd	1357	739	2.8	1.4
Ob 3—UDOM	7.0	41.7	-27.5	2.8	nd	1308	893	2.8	2.1
Ob 4—UDOM	6.2	37.1	-28.3	3.3	nd	nd	816	nd	0.7
Ob 5—UDOM	1.8	39	-27.9	2.6	nd	1913	1565	3.9	2.0
Ob 6—UDOM	0.6	42.7	-27.7	2.7	nd	1571	477	4.7	1.0
Ob 7—UDOM	3.1	38.1	-27.7	3.3	nd	1399	559	4.1	1.0
Ob 8—UDOM	8.8	34.3	-27.3	3.5	nd	1024	531	3.8	1.1
Kara Sea 1—UDOM	11.0	43.6	-27.1	2.6	nd	913	739	2.5	2.3
Kara Sea 2—UDOM	30.9	22.8	-25.4	4.2	nd	nd	1237	nd	0.3
Kara Sea 3—UDOM	12.7	41.6	-27.1	3.1	nd	1320	770	3.1	1.6
Yenisei >100 kDa	2.6	17.3	-24.7	4.8	nd	123	nd	14.2	4.0
Yenisei 30–100 kDa	2.6	22	-27.2	4.4	nd	108	nd	11.0	1.0
Yenisei 1–30 kDa	2.6	46.8	-27.7	2.1	nd	670	nd	1.0	4.3
Yenisei—RDOM	0	36.2*	-27.5	2*	108	830	1555	1.4	1.7
Ob—RDOM	0.6	29.1*	-27.5	1.5*	307	1142	313	3.7	0.7
Mackenzie—RDOM	0	31.3*	-26.7	2.4*	nd	nd	670	nd	1.4
Tundra Lake—RDOM	0	53.3*	-27.6	0.7*	156	2441	nd	1.5	ND

* These values include inorganic nitrogen and cannot directly be compared to UDOM samples.

Mackenzie RDOM and -27.6‰ in the tundra lake sample.

C/N and $\delta^{13}\text{C}$ values in estuaries have both been used previously to distinguish between marine and terrestrial DOM in the Arctic Ocean (Opsahl et al., 1999; Anderson, 2002); however, in the presented set of samples, there is no apparent relationship between C/N ratios and $\delta^{13}\text{C}$ values of river and river plume UDOM. This suggests additional DOM sources in the system with different elemental and $\delta^{13}\text{C}$ composition. The obvious sources of DOM in this area are terrigenous DOM with high C/N (>40) and depleted $\delta^{13}\text{C}$ values (< -25‰) and marine-phytoplankton-derived DOM with lower C/N (<20) and relatively higher $\delta^{13}\text{C}$ values (around -21‰). There are some consistent and interesting differences in this data set when compared in a property–property plot of the two parameters (Fig. 2A). In 1997, the UDOM collected from the Ob had consistently lower C/N ratios but lighter $\delta^{13}\text{C}$ values relative to the Yenisei samples (Table 3; Fig. 1A). This could be caused either by a

different elemental and $\delta^{13}\text{C}$ composition of allochthonous DOM coming off the two rivers, or by an autochthonous input of phytoplankton DOM in the Ob river with lower C/N values (as expected for phytoplankton DOM) but more depleted $\delta^{13}\text{C}$ values. Depleted $\delta^{13}\text{C}$ values (< -30‰) have been reported for phytoplankton abundant in the Ob and Yenisei at the time the DOM samples were collected (Kodina, 2001, 2002). The abundance of $\delta^{13}\text{C}$ depleted phytoplankton and their contribution to the DOM pool seems to be a possible explanation for the weak relationship between C/N ratios and $\delta^{13}\text{C}$ values, suggesting that in this system $\delta^{13}\text{C}$ values might not be the best indicator to distinguish terrestrial and plankton-derived DOM. More support for the importance of fresh, plankton-derived DOM for the variations in the elemental and isotopic composition of UDOM comes from the neutral sugar data. Concentrations of neutral sugars varied by a factor of 4 from 900 to 3700 nM L⁻¹ representing between 1.7% and 6% of the UDOM carbon (Table 3). Neutral

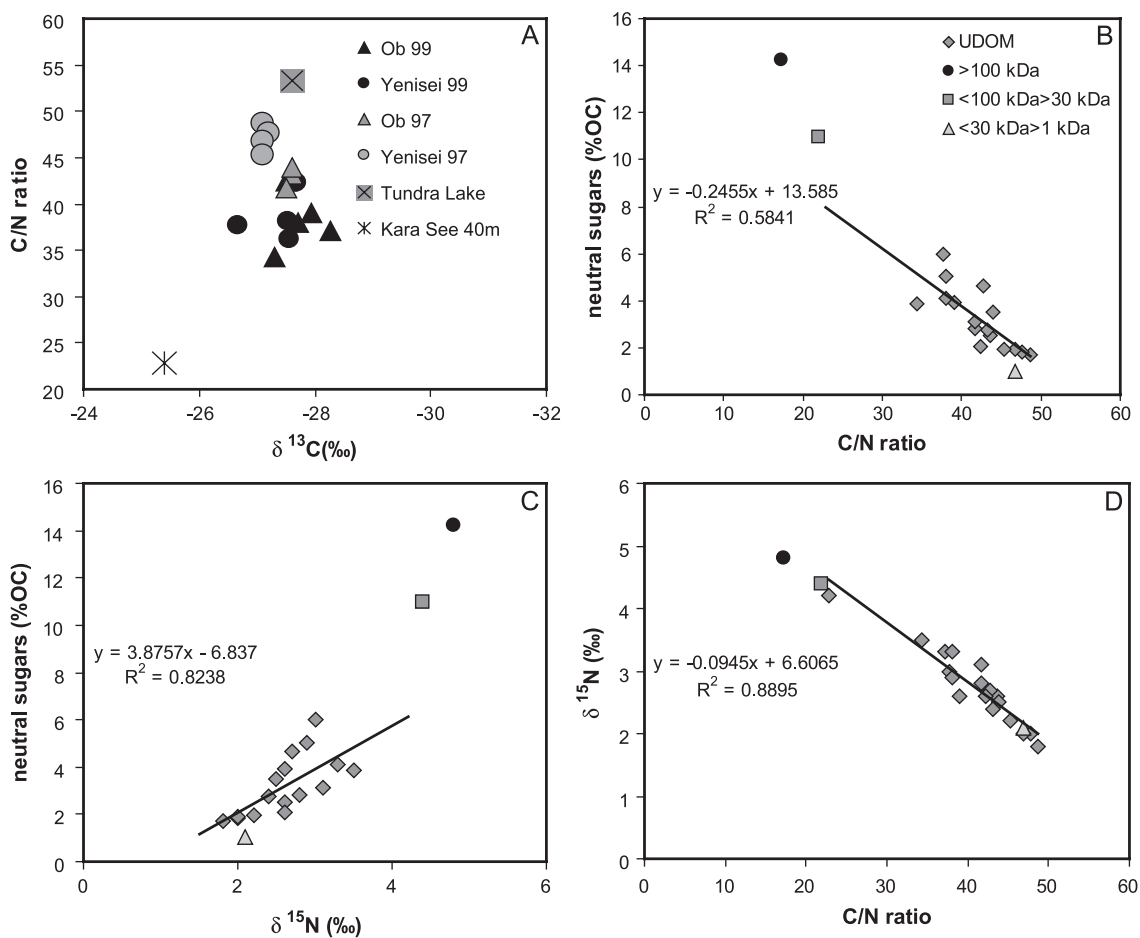


Fig. 2. Relationships among the elemental, isotopic and molecular composition of UDOM in samples from different locations and years.

sugar yield (%OC) is an established indicator of the amount of fresh and labile DOM in aquatic environments (Cowie and Hedges, 1984; Skoog and Benner, 1997; Amon et al., 2001; Meon and Kirchman, 2001; Amon and Benner, 2003) and can be used as an independent parameter to estimate the contribution of fresh, plankton-derived DOM in this system. The neutral sugar yield of the river and river plume UDOM was poorly related to salinity and $\delta^{13}\text{C}$ values (data not shown) but was strongly related to C/N ratios (Fig. 2B), reflecting the relatively lower C/N ratios in samples with higher neutral sugar yields (higher proportion of phytoplankton DOM). The different C/N values in Ob and Yenisei samples from 1997 are also reflected in the neutral sugar yield. Higher yields were observed in the Ob (3.0%) relative

to the Yenisei (1.8%) consistent with the lower C/N values observed in the Ob relative to the Yenisei (Table 3), indicating that in 1997 the Ob samples had a larger contribution of plankton-derived DOM than the Yenisei samples. The stable carbon isotope ratio of DOM is also affected by the chemical composition of organic matter. Carbohydrates, for example, are usually enriched in ^{13}C relative to bulk organic matter (Benner et al., 1987), suggesting that enriched $\delta^{13}\text{C}$ values could be a result of the elevated carbohydrate concentrations. However, in our samples, we did not see a relationship between carbohydrate concentrations and $\delta^{13}\text{C}$ values.

$\delta^{15}\text{N}$ values in river and estuarine UDOM varied between +1.8‰ and +4.2‰ and showed a weak relationship to salinity, but a strong positive correla-

tion with neutral sugar yield (Fig. 2C) and an even stronger and negative correlation with C/N ratios (Fig. 2D). Nitrogen isotopes are not well understood in any estuarine system, especially at high northern latitudes, but it appears from the relationships of $\delta^{15}\text{N}$ to neutral sugar yields and C/N ratios that nitrogen isotopes might be a useful indicator to distinguish terrestrial and plankton DOM in these relatively undisturbed river systems. The strong correlation with C/N values suggests that DOM coming off the Ob and Yenisei carries a low $\delta^{15}\text{N}$ signal (around or below $+2\text{‰}$) consistent with reports on soil DOM from lower latitudes (Kalbitz et al., 2000), while plankton-derived DOM appears to have a $\delta^{15}\text{N}$ value around 7‰ which is consistent with $\delta^{15}\text{N}$ values of Arctic phytoplankton using nitrate as a N-source (Schubert and Calvert, 2001). $\delta^{15}\text{N}$ values around 7‰ were also detected in organic matter from surface sediments and in suspended matter in the northern Kara Sea (Gaye-Haake, personal communication) and in other Siberian coastal sediments (Guo et al., 2004). Low values of $\delta^{15}\text{N}$ were observed in DOM from the tundra lake, a typical oligotrophic blackwater system, with a value of 0.7‰ . This sample seems to resemble the terrestrial end-member the closest among the samples presented here. Guo et al. (2004) identified very similar $\delta^{15}\text{N}$

values for the terrestrial and marine end-members in Eurasian shelf sediments and also observed a very strong relationship between $\delta^{15}\text{N}$ and C/N ratios in sediment organic matter, consistent with what we observed for DOM.

Based on a terrestrial end-member of 0.7‰ with a C/N ratio of 54 and a plankton end-member of 7‰ with an average C/N ratio of 14, we derived a relationship between $\delta^{15}\text{N}$ and the estimated amount of autochthonous carbon (Fig. 3). For example, a 50:50 mix based on nitrogen isotopes would contain 54 equivalents of terrestrial carbon and 14 equivalents (or $\sim 21\%$) of plankton carbon. From this relationship, we estimated that the river and river plume UDOM samples contained between 6% and 16% of autochthonous or plankton-derived DOC. We realize that this is a rough estimate and that the end-members are not well constrained in terms of C/N values at the moment, especially the plankton-derived DOM; however, we think that our choice of end-members is realistic and based on actual data from the tundra lake as the terrestrial end-member and data from the deep Kara Sea (salinity >33) for the plankton end-member. Fresh phytoplankton DOM has an average C/N ratio of ~ 8 (Biddanda and Benner, 1997); however, in order to also account for background plankton DOM in the

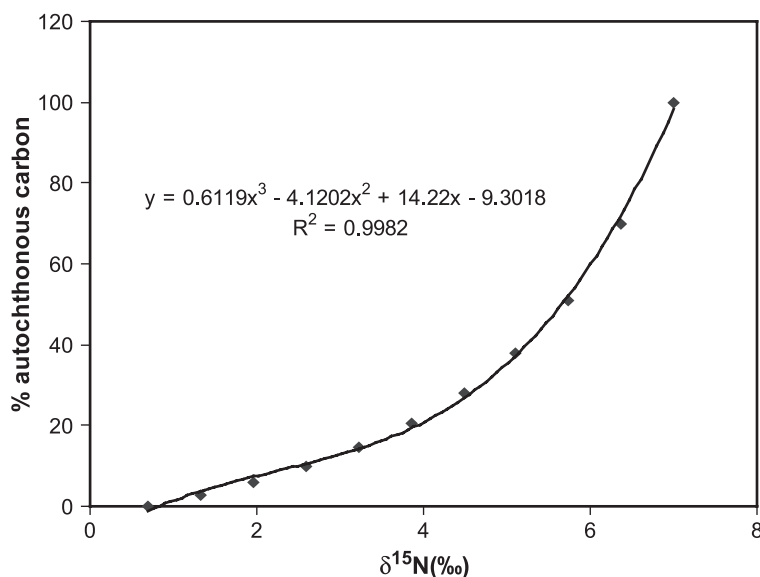


Fig. 3. Theoretical relationship between $\delta^{15}\text{N}$ values and the percentage of autochthonous organic carbon in DOM assuming a terrigenous end-member with a $\delta^{15}\text{N}$ of 0.7‰ and a C/N ratio of 54, and an autochthonous end-member with a $\delta^{15}\text{N}$ of 7.0‰ and a C/N ratio of 14.

estuaries, we choose 14 as an average C/N ratio for plankton DOM. Using a $\delta^{15}\text{N}$ value of 14 as opposed to 8 as plankton end-member yields relatively high estimates for the autochthonous contribution to DOC. The distinction between terrestrial and plankton-derived DOM is helpful in interpreting the elemental and isotopic composition of river DOM, particularly for the interpretation of apparent ^{14}C ages of bulk river DOM.

We determined the concentration of ^{14}C in a few samples from the Ob, Yenisei, and the tundra lake to determine the potential contribution of old peat and permafrost derived organic matter to the river DOM. In all of the five samples analyzed, UDOM as well as RDOM, we found $\Delta^{14}\text{C}$ values indicative of a modern origin. Values ranged from 84‰ to 307‰ with no consistent differences between the UDOM and RDOM fractions (Table 3). The two riverine UDOM samples dated, represented 61% and 68% of total DOC while RDOM samples represented essentially 100% of DOC, indicating that there was no significant difference in average age between the high and low molecular weight fraction of DOM sampled during the summer–fall period. It is difficult to place an exact age on such samples but it is obvious that all of them contained a significant amount of bomb ^{14}C , suggesting that most of the DOM coming off the Ob and Yenisei was produced by plants sometime in the past 100 years. A similar young age of UDOM from other Arctic rivers, draining mainly tundra areas, was recently reported by Guo et al. (2003) and Benner et al. (2004). In contrast to our findings, Guo et al. (2003) reported significant differences between organic matter size fractions, with a modern average age in the UDOM fraction but an older average age (~600 years BP) in the low molecular weight fraction (<1 kDa). Different average ages for river DOM have been reported for a set of North American rivers (Raymond and Bauer, 2001; Raymond et al., 2004), indicating the potential influence of organic deposits and mineralogy in the watershed. The young average age of DOM in this study is not surprising considering the extensive drainage basins of these large Siberian rivers reaching as far south as 46°N resulting in a DOM load that represents an integrated average of different vegetation zones. Most of the DOM found in these large rivers likely represents surface runoff, rich in plant litter and surface soil organic matter which is characterized by abundant

“under-decomposed” organic matter (Stolbovoi, 2002). Our results indicate that by looking at bulk DOM, there is no evidence for aged permafrost or peat carbon in the DOM fractions coming off the rivers during the summer–fall period. From the stable nitrogen isotope values of the dated samples (Table 3; Fig. 3), it appears that the contribution of autochthonous DOC is too small (<10%) to account for the relatively young ages, indicating that most of the young material is in fact of terrestrial origin. This is consistent with the enriched $\Delta^{14}\text{C}$ values found in terrestrial DOM in the central Arctic Ocean. On the other hand, however, it is theoretically possible that a fraction of riverine DOM is actually several 100 years old, despite the young average ^{14}C age of the bulk DOC. More detailed studies looking at ^{14}C concentrations in different DOM fractions and at different stages of the hydrograph are needed to fully exploit the potential of the ^{14}C tracer.

The molecular level composition of UDOM in the rivers and estuaries was quite uniform between the rivers and between the years (Fig. 4A–D). The amino acid composition in the rivers was dominated by glycine and alanine, contributing 22–23 and 16–17 mol%, respectively (Fig. 4A,B). Followed by approximately equimolar contributions of aspartic acid, threonine, and serine, each at about 10 mol% (Fig. 4A,B). The amino acid composition is very similar to the one reported from other Siberian rivers by Dittmar et al. (2001). The neutral sugar composition was equally similar between the rivers and the different years (Fig. 4C,D). The only difference in the neutral sugar composition was the slightly higher abundance of glucose in Yenisei samples during 1999, reflecting the elevated neutral sugar yield (Table 3) which is sometimes associated with higher concentrations of glucose (Amon and Benner, 2003; Meon and Kirchman, 2001). As noted previously (Cowie and Hedges, 1984), the molecular level composition of carbohydrates and amino acids appear very similar in organic matter of different origin and represent poor source indicators.

3.3. Chemical characteristics of different molecular weight fractions

The general trends in the elemental and isotopic composition seen in UDOM samples were also observed in different molecular size fractions of river

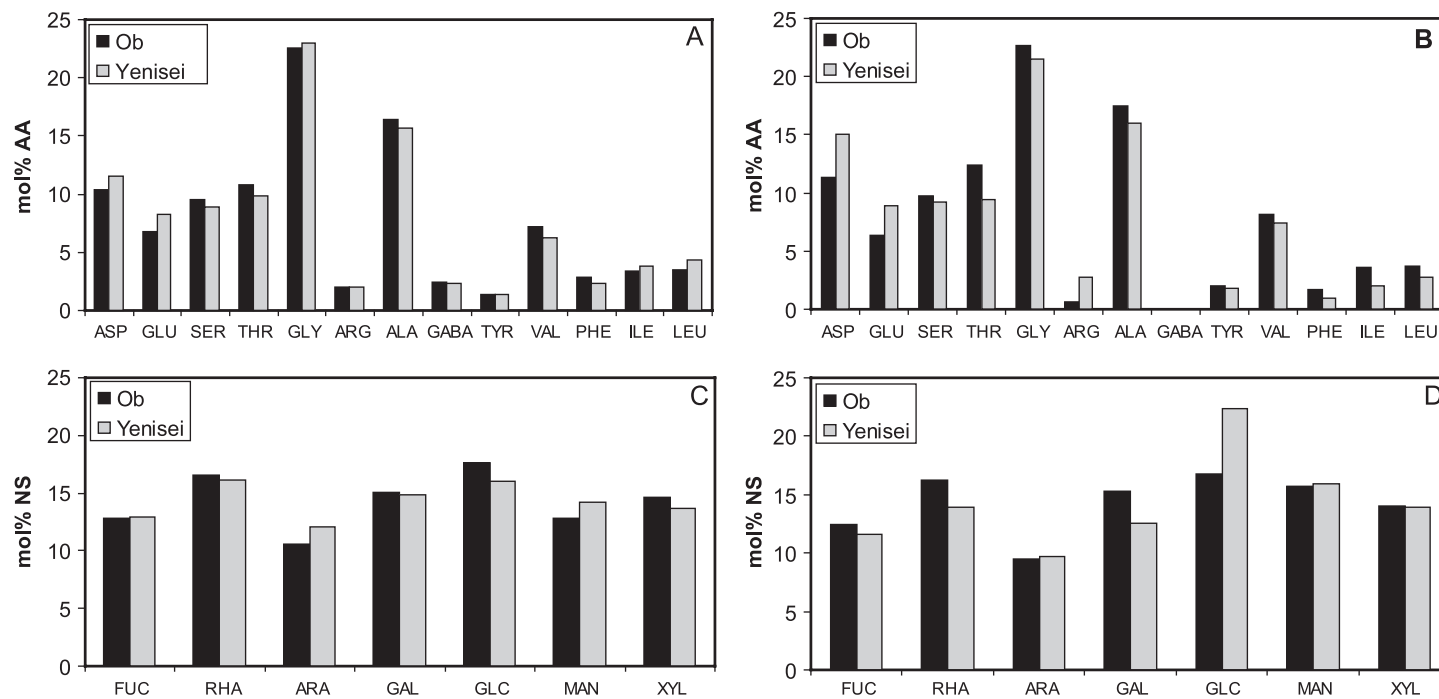


Fig. 4. Amino acid composition of UDOM from the Yenisei and Ob in 1997 (A) and 1999 (B), and neutral sugar composition of Yenisei and Ob in 1997 (C) and 1999 (D).

DOM. One of the Yenisei samples was fractionated into three different molecular size fractions (>100, 30–100, and 1–30 kDa) and the fractions were subjected to the same suite of analysis as the other UDOM samples. The highest molecular weight fraction (>100 kDa) represented 1.1% of the DOC, the 30–100 kDa fraction represented 2.2% of DOC, and the 1–30 kDa fraction represented 60% of total

DOC. The highest molecular weight fraction (>100 kDa) had the lowest C/N ratio (17) and the highest neutral sugar yield (>14%), both indicating the relatively larger contribution of fresh plankton-derived DOM to the highest molecular weight fraction (Fig. 5A). This is consistent with the isotopic data which showed relatively enriched carbon ($-24.6‰$) and nitrogen ($+5‰$) isotope values (Fig. 5B). The 30–

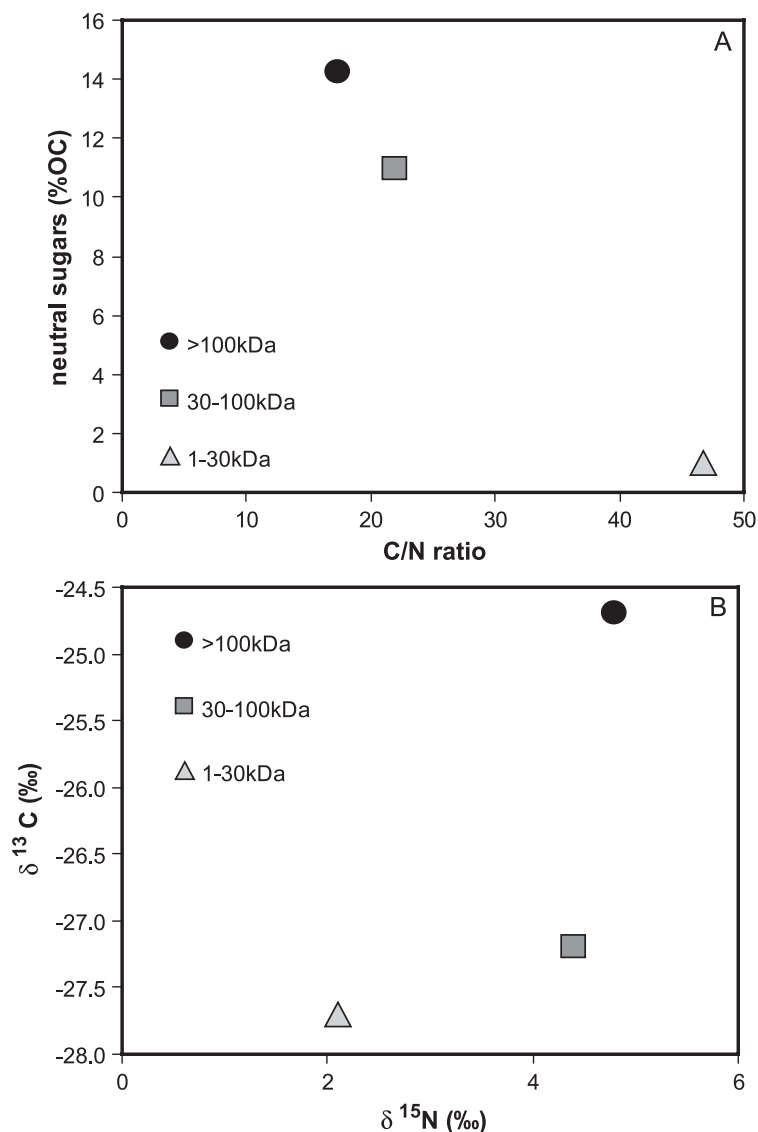


Fig. 5. Elemental (A), molecular (A) and isotopic (B) composition in different molecular weight fractions of UDOM sampled from the Yenisei River in 1999.

100 kDa fraction also had a relatively low C/N value (23) with a high neutral sugar yield (11%) and a relatively enriched $\delta^{15}\text{N}$ value of 4.4‰, all pointing to a significant plankton contribution. The $\delta^{13}\text{C}$ value, however, was relatively depleted in the 30–100 kDa fraction suggesting a different algal DOM source than in the >100 kDa fraction. The 1–30 kDa fraction which contributed 60% to the total DOC was dominated by a remote terrestrial DOM source as reflected in a high C/N ratio (47), low neutral sugar yield (1%), depleted $\delta^{13}\text{C}$ (−27.7‰) value, and depleted $\delta^{15}\text{N}$ (2.1‰) value (Fig. 5A,B). No significant differences were found in the molecular level composition of the three size fractions (data not shown). Similar compositional trends in C/N ratios of Yenisei DOM molecular weight fractions were observed in a different sample taken in 2001 (Köhler, 2003). Again, lower C/N values were typically associated with the high molecular weight fraction (Köhler, 2003). In this case, the DOM was fractionated in four fractions (>10, 1–10, 0.5–1, and 0.15–0.5 kDa) and the C/N ratio increased consistently with decreasing molecular size but the stable carbon isotope value was basically the same in the size fractions <10 kDa, indicating that in addition to different DOM sources, diagenesis and/or adsorption processes in soil probably contribute to elevated C/N ratios in smaller DOM size fractions (Köhler, 2003). Information on the origin and chemical composition of DOM fractions is scarce due to the laborious separation process, but results presented here indicate that much new information about DOM origin, age, and fate might be masked within the bulk DOM and need to be investigated further.

3.4. The fate of Ob and Yenisei river DOM in the Kara Sea

The two major sinks for river DOM in the coastal ocean are bacterial decomposition and photochemical degradation. The fate of Arctic river DOM and its role to support heterotrophic production in coastal Eurasian seas has only recently been addressed (Saliot et al., 1996; Meon and Amon, in press). We know that most Siberian river DOM, at least from Ob, Yenisei, and Lena mixes conservatively with minor apparent losses (<5%) due to flocculation (Cauwet and Sidorov, 1996; Kattner et al., 1999; Amon, 2003;

Köhler et al., 2003). However, from the conservative distribution of DOC alone, it is not possible to infer bacterial or photochemical degradation which likely happen over the entire salinity gradient and would not necessarily change the overall conservative distribution of DOC. Indirect information on the magnitude of river DOM losses in the Arctic Ocean comes from export estimates of terrestrial DOM through the Fram Strait (Opsahl et al., 1999; Amon et al., 2003). Amon et al. (2003) estimated that between 675 and 983 Gmol (8.1 and 11.8 Tg) terrestrial carbon are annually exported through Fram Strait. This compares to an annual DOC discharge from Eurasian rivers of 1617 Gmol (19.4 Tg) C year^{−1} (Gordeev and Rachold, 2003). Assuming that there is no export of North American river DOM through Fram Strait (Taylor et al., 2003) and ignoring the transfer of Eurasian river DOM into the Canada Basin (McLaughlin et al., 2004), between 44% and 65% of the annual Eurasian river DOC would be exported from the Arctic Ocean. Although these numbers are very rough estimates, they supply us with a ball-park figure of how much river DOM can be expected to be remineralized during the 12- to 14-year transit from the rivers to the Fram Strait (Karcher and Oberhuber, 2002). This suggests that between 35% and 55% of the Eurasian river discharge could be lost to photooxidation and bacterial respiration. The most critical unknown in this calculation is the likely, but poorly understood exchange of river DOM between the Eurasian and the Canadian Basin—a volume transport, equivalent to a river run-off of several hundred, perhaps 1000 km³ year^{−1} from the East Siberian Sea into the Canadian Basin was recently suggested for the early and mid-1990s (MacDonald et al., 2003). Taking this into account would significantly reduce the amount of river DOM lost within the Arctic Ocean to a range between 5% and 32%. The only direct evidence for bacterial degradation of river DOM comes from a long-term decomposition experiment with Yenisei river water performed in the dark which resulted in the loss of ~5% of DOC over a period of 21 month (Köhler et al., 2003). Additional evidence for the largely refractory nature of Siberian river DOM comes from addition experiments where either glucose was added to river water or sterile-filtered river water was added to estuarine water and water from the open Kara Sea. The glucose additions stimulated the

bacterial activity indicating carbon limitation in the river samples while addition of filtered river water to estuarine or Kara Sea samples had no effect on the bacterial activity relative to the controls (Meon and Amon, in press). The relatively refractory nature of river DOM observed in the Ob and Yenisei estuaries is consistent with the high concentrations of terrestrially derived DOM in the central Arctic Ocean surface waters (Opsahl et al., 1999).

The other loss mechanism that has to be considered for the fate of terrestrial DOM in the Arctic Ocean is photooxidation. River DOM has been shown to be very photoreactive and photochemical degradation of river DOM has been identified as a major sink for terrestrially derived DOM in the ocean (Mopper et al., 1991; Miller and Zepp, 1995; Amon and Benner, 1996; Opsahl and Benner, 1998). To test the potential of photochemical degradation of Arctic river DOM, we exposed river water to natural sunlight during the cruise in 2001. The three experiments lasted between 64 and 290 h covering exceptionally nice to cloudy conditions in the Ob and Yenisei estuaries. Under

sunny conditions, the photochemical oxygen consumption rate was $0.149 \mu\text{M h}^{-1}$, resulting in an overall oxygen consumption of $40 \mu\text{M}$ oxygen. Over the same period (290 h), about $40 \mu\text{M}$ DOC were photomineralized (Fig. 6A). Using the same Yenisei water sample under cloudy conditions, the photochemical consumption rate was $0.09 \mu\text{M oxygen h}^{-1}$ consuming $13 \mu\text{M}$ oxygen over the 144-h exposure time (Fig. 6B). In the third experiment conducted with water from the river Ob and under cloudy conditions, the oxygen consumption rate was $0.058 \mu\text{M h}^{-1}$ with an overall oxygen consumption of $3.5 \mu\text{M}$ (Fig. 6C). If we assume that photochemical oxygen and DOC losses are approximately equimolar (Fig. 6A; Amon and Benner, 1996), then 6% of the DOC was lost in the first experiment under sunny conditions, 2% in the second experiment, and 0.6% in the third experiment. Further consideration of experiments under cloudy conditions as representative would approximate a loss of about 1% of the DOC per week to photochemical processes in surface waters on the Eurasian shelf. However, these esti-

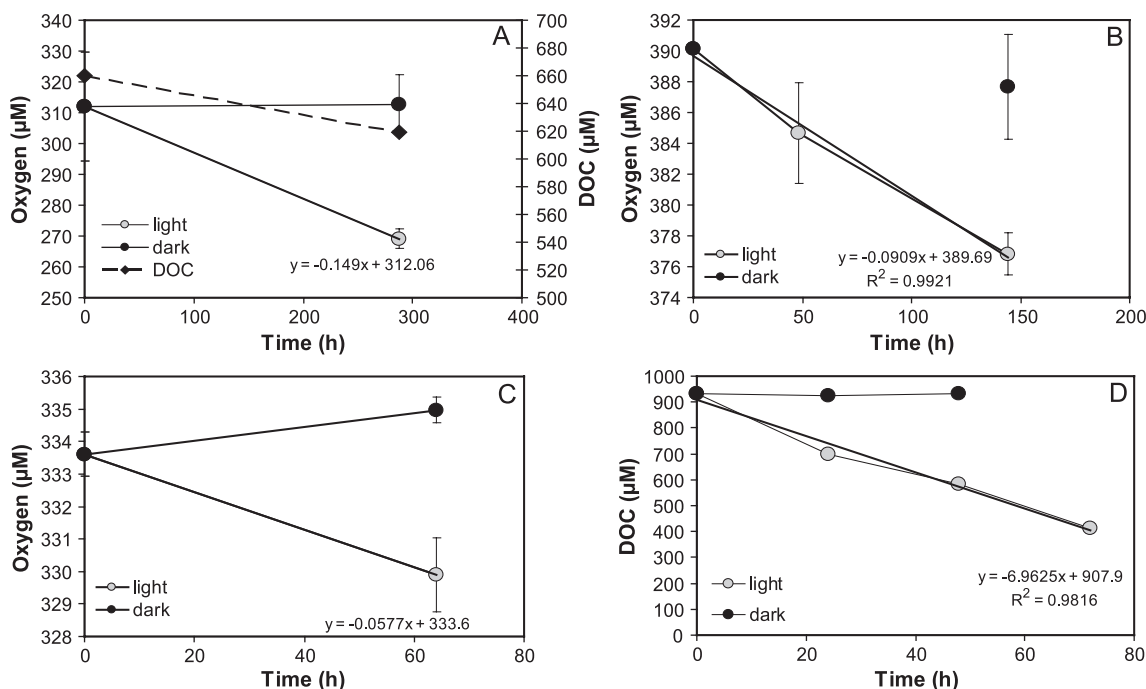


Fig. 6. Photochemical consumption of oxygen and carbon under natural light conditions in water from the Yenisei during nice (A) and cloudy (B) weather conditions, in water from the Ob under cloudy conditions (C) and under artificial light conditions in water from a tundra lake (D).

mates are only valid for the upper 5 cm of the water column since our measurements are based on the incubation of small volume bottles with a layer thickness of 5 cm. Because of the strong light attenuation in river and estuarine water, photooxidation effects related to the whole water column would be significantly smaller. To constrain the potential of photochemical degradation of DOM in the Arctic Ocean, photodegradation experiments with parallel irradiance measurements need to be conducted in the future to get a more realistic understanding of the underwater light conditions and how they relate to DOM photooxidation.

The high potential photoreactivity of DOM derived from high latitude soils was investigated in a separate laboratory experiment by exposing a water sample from the tundra lake to artificial sunlight in a solar simulator. In this experiment, we chose a light dose more typical for low latitudes. During this experiment (Fig. 6D), about 50% of the initial DOC was photochemically degraded during the 72 h of uninterrupted exposure at a rate of almost $7 \mu\text{M h}^{-1}$. This impressively demonstrates the photochemical reactivity of terrestrially derived DOM in Eurasian rivers and the potential role of photooxidation for the removal of terrestrial DOM from surface waters given the light dose is high enough.

The Arctic Ocean is unique in that it has much higher concentrations of terrestrially derived DOM in its surface waters relative to other ocean basins. The Arctic Ocean is also unique in having a permanent ice cover, prevailing cloudy conditions, and a low solar angle, all influencing the amount of sun light, in particular UV light, penetrating into surface waters. As a result of these conditions, photochemical processes are likely less important for the fate of river DOM in the Arctic Ocean than in other coastal seas which would explain the significant export of terrestrial DOM from the Arctic Ocean to the North Atlantic (Opsahl et al., 1999; Amon et al., 2003).

Generally, it seems that most of the DOM discharged by Yenisei and Ob is exported from the estuaries towards the Arctic Ocean or eastward along the Eurasian Shelf without major losses due to flocculation, bacterial degradation, and photooxidation. This makes terrestrial DOM, and compounds therein, a potential tracer, at least on a time scale relevant for the Arctic Ocean. However, the photo-

oxidation experiments also suggest that with reduced ice cover in the Arctic Ocean the fate of terrestrial DOM could be significantly different compared to the present situation.

3.5. The role of river discharge for carbon fluxes in the Kara Sea

Several lines of evidence (Amon, 2003; Köhler et al., 2003; Meon and Amon, *in press*) suggest that the riverine DOM discharged into the Kara Sea does not significantly contribute to heterotrophic processes during its passage through the coastal and northern Kara Sea. At the same time, we observe relatively high rates of bacterial production and respiration in the rivers and estuaries (Meon and Amon, *in press*) resulting in a bacterial carbon demand (BCD) that is higher than current estimates of primary production in the Kara Sea. Our estimate of BCD was calculated using conservative values for the leucine to carbon conversion and a relatively high bacterial growth efficiency (Meon and Amon, *in press*). On an annual basis and based on an area of 926,000 km² for the Kara Sea, we estimate the BCD to be about 3.83 Tmol (46 Tg) C year⁻¹ (Table 4). This compares to a current primary production estimate for the Kara Sea of 3.08 Tmol (37 Tg) C year⁻¹ (Sakshaug, 2003) with about 0.75 Tmol (9 Tg) C year⁻¹ as new production (Sakshaug, 2003; Table 4). If we include the estimated carbon demand of benthic communities in the Kara Sea at about 0.42–0.58 Tmol (5–7 Tg) C year⁻¹ (Klages et al., 2003), the primary production estimate appears insufficient to support the demand, even without the consideration of pelagic zooplankton. Although the rivers discharge about 0.67–0.75 Tmol (8–9 Tg) C year⁻¹ (Köhler et al., 2003; Gordeev and Rachold, 2003), this carbon does not

Table 4

Annual bacterial carbon demand (BCD), primary production, and new production in relation to river DOC discharge and to the PP that could be supported if all DIN discharged by the rivers would be utilized by phytoplankton assuming a C/N ratio of 7

BCD	PP	NP	River discharge of DOC	River DIN-based PP
3833 (46)	3083 (37)	750 (9)	667 (8)	14 (0.17)

All numbers are in Gmol C (Tg) C year⁻¹.

help in this C-budget problem since most of the material is not readily available to bacteria. In terms of nitrogen input, the rivers also seem to be of minor importance. Based on the average concentrations of nitrate and ammonia in the rivers (Table 1), we estimate an annual DIN import of 1.71 Gmol (24 Gg) N year⁻¹ which would translate to 14.2 Gmol (0.17 Tg) C if all river DIN would be used for primary production (PP; assuming Redfield ratio; Table 4). From the numbers compared in Table 4, it appears that PP estimates in the Kara Sea are underestimated by at least 1.25 Tmol (15 Tg) C year⁻¹. However, the PP estimate of 3.08 Tmol (37 Tg) C year⁻¹ does not include dissolved organic matter production (Sakshaug, 2003). In order to meet all the carbon demands in the Kara Sea, there has to be a so far unconsidered production of DOM on the order of 1.25–2.08 Tmol (15–25 Tg) C year⁻¹ which would represent about 40% of the total PP, provided that the existing estimates of PP in the Kara Sea are valid. The riverine DIN input would support <0.5% of the total primary production and <2% of the estimated new production in the system indicating that there needs to be an additional outside source of nitrogen to the Kara Sea and that most of the PP in the system represents recycled production. An important but poorly understood source of new DIN for the Kara Sea is Atlantic water entering through the Kara Strait and from the north. The Kara Strait inflow of Atlantic water is estimated between 0.2 and 0.6 Sv (Karcher et al., 2003) which with a DIN concentration of 4.5 μM (Fransen et al., 2001) could represent an annual DIN import of about 71 Gmol (1 Tg) DIN. Much remains to be investigated in terms of carbon and nitrogen fluxes in the Kara Sea, but it seems that the river discharge of organic matter and inorganic nutrients is not the main driver of the observed biological activity in this system.

3.6. River constituents as tracers for the Arctic Ocean system and environmental change

The largely conservative nature of river DOM in the Arctic Ocean has important implications for their use as tracers (Amon et al., 2003). DOM as well as dissolved inorganic constituents discharged by Arctic Rivers have great potential as biomarkers and tracers for biogeochemical processes, water

mass formation and distribution, and environmental change in the Arctic Ocean. Several studies in the past have used nutrient ratios (Codispoti and Richards, 1968; Jones et al., 1998), barium (Guay and Falkner, 1997; Guay et al., 2001; Taylor et al., 2003), and organic matter (Guay et al., 1999; Opsahl et al., 1999; Amon et al., 2003; Benner et al., 2004) along with hydrographic information to improve our understanding of biogeochemical fluxes and physical processes. However, the tracers have not been used to their full potential which lies in a combined utilization of several organic and inorganic constituents. One example is the nutrient ratio which has been used in the past to characterize Arctic Ocean surface waters. One important observation from the nutrient data presented in this study is that the ratio of nitrate to phosphate in the rivers and Kara Sea surface waters is typically below 2 (Table 1). Similar values have been reported for the Lena River (Lara et al., 1998) indicating that the three largest Arctic rivers discharge nitrate and phosphate in a ratio similar to the nitrate/phosphate ratios found in “Pacific-derived” Arctic Ocean surface waters (Jones et al., 1998). Based on nitrate to phosphate ratios alone, a significant contribution of Eurasian river water to Arctic Ocean surface layers would go unnoticed in the Pacific sector of the Arctic Ocean as well as in the Fram Strait, potentially distorting our understanding of water mass formation and distribution in the Arctic Ocean. This is especially critical for our understanding of the formation of the Arctic halocline, which plays an important role for the heat exchange of Arctic Ocean surface layers. A significant intrusion of Eurasian shelf-derived water into the Canada Basin halocline has recently been suggested by McLaughlin et al. (2004). The use of organic tracers or proxies like in situ fluorescence along with barium and other hydrographic information along the Arctic shelf break and in the central Arctic Ocean will be very informative for our understanding of Arctic halocline formation, and the role of sea ice formation in general. A recent study has demonstrated the important role of sea ice formation and brine rejection for the intermediate ventilation of the North Pacific (Shcherbina et al., 2003). The role of sea ice formation on the extended Eurasian Shelves for water mass modifi-

cation and deep water formation in the Arctic Ocean are still not well understood; however, with the high concentrations of river water and terrestrial DOM on those shelves and the fact that river DOM behaves like salt during sea ice formation (Amon, 2003), we have a valuable tracer on hand for further investigation. While elevated levels of terrigenous DOM have been suggested for the Arctic Halocline (Amon et al., 2003; Benner et al., 2004), samples from central Arctic Ocean deep waters show no indication of terrestrial DOM (Opsahl et al., 1999). However, more recent studies suggest the vertical export of terrigenous DOM to intermediate depth in the Arctic Ocean (Dittmar, 2004; Benner et al., in preparation). Whether these varying levels of terrigenous DOM in intermediate and deep waters of the Arctic Ocean reflect environmental change in the Arctic remains to be seen but could be linked to increased sea ice production in coastal flaw leads in the Laptev and East Siberian Seas during periods with a high Arctic Oscillation (AO) index (MacDonald et al., 2003). The combined use of several organic and inorganic tracers with higher resolution should significantly improve our understanding of how physical processes link into biogeochemical fluxes in the Arctic Ocean system.

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