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Combined neutral sugars as indicators of the diagenetic state of dissolved organic matter in the Arctic Ocean

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Abstract

Dissolved organic matter (DOM) was sampled by tangential flow ultrafiltration from different basins in the central Arctic Ocean, the Greenland, Iceland and Norwegian (GIN) Seas, and the estuaries of the Ob and Yenisei Rivers. Dissolved organic carbon (DOC) concentrations ranged from more than 500 μM C in the rivers to about 50 μM C in the deep basins. Arctic Mediterranean Sea (AMS) surface water DOC concentrations ranged from 66 to 137 μM C. High concentrations in surface waters were due mainly to river discharge of terrigenous DOC, while elevated concentrations in AMS deep water likely reflect downwelling of DOM in this system. Total hydrolyzable neutral sugar concentrations were ~7-fold higher in ultrafiltered DOM (UDOM) from estuaries (1200 nM) than in Arctic ocean surface waters (160 nM), but carbon-normalized neutral sugar yields (% OC) were lower in the estuaries indicating that marine DOM sources were relatively rich in neutral sugars. Depth profiles of neutral sugar concentrations and carbon-normalized yields indicated that carbohydrates were produced and consumed largely in surface waters of the AMS. These observations were consistent with rapid bacterial degradation of neutral sugars during decomposition experiments. The molecular composition of neutral sugars was very similar among AMS surface samples and showed only minimal differences between terrestrial and marine UDOM, indicating that the neutral sugar composition is not useful for distinguishing these sources. It appears diagenetic processes rather than sources are primarily responsible for determining neutral sugar compositions in UDOM. Neutral sugar compositions in all of the UDOM samples analyzed in this study were indicative of heteropolysaccharides. The strong relationship between neutral sugars and the diagenetic state of DOM was best represented by neutral sugar yields (% OC), which were used as a quantitative indicator for the amount of labile DOM in the AMS. Based on the low average neutral sugar yield (5.5% OC) in UDOM from AMS surface waters, we estimated that only ~2.2% of the DOC was of labile nature. This value was lower than for surface waters of the Ross Sea and Atlantic and Pacific Oceans suggesting DOM is less bioavailable and the microbial loop is less active in AMS surface waters.

Keywords: Dissolved organic matter; DOC; Carbohydrates; Neutral sugars; Diagenesis; Arctic Ocean; Gin Sea

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1. Introduction

Biological oceanography in the Arctic Ocean has blossomed during the past 10 years with numerous advances in understanding the structure and function of food webs. The view of the Arctic as a biological desert was modified by the realization that the Arctic Ocean supports an active autotrophic and heterotrophic community (Wheeler et al., 1996; Pomeroy, 1997; Rich et al., 1997; Sherr et al., 1997). In addition to marine production in the water column and in sea ice, the Arctic Ocean receives a disproportionately large amount of terrestrially derived organic matter (Aagaard and Carmack, 1989; Gordeev et al., 1996; Guay et al., 1999; Macdonald et al., 1998; Anderson et al., 1998; Opsahl et al., 1999; Köhler et al., in press) from Arctic rivers. This diversity of organic matter sources and perennial ice cover make the Arctic Ocean a particularly interesting environment to study the biogeochemistry of dissolved organic matter (DOM).

DOM has been the focus of numerous studies because of its significant role as an energy and carbon source for the microbial food web and its role in the global carbon cycle. Despite the importance of DOM we still have a limited understanding of its composition, sources, and fates in aquatic systems. A major fraction of DOM has escaped chemical characterization because of its dilute nature and the high salt content in marine samples. With a better understanding of the largely elusive chemical composition of DOM, we will have a better grasp on the multiple roles DOM plays in the environment (Benner, 2002a).

Carbohydrates are important structural and storage compounds in marine and terrestrial organisms, and they represent the most abundant class of biochemicals in the biosphere. Carbohydrates account for 20–30% of dissolved organic carbon (DOC) in marine surface waters (Pakulski and Benner, 1994), and up to 50% of ultrafiltered DOC (UDOC) in marine surface waters (Benner et al., 1992). Several recent studies investigated the distribution and molecular composition of hydrolyzable neutral sugars in the marine environment (McCarthy et al., 1996; Aluwihare et al., 1997; Skoog and Benner, 1997; Borch and Kirchman, 1997) revealing strong vertical gradients that indicate the reactive nature of this compound class. Subsequently, neutral sugars were proposed as indicators of the bioreactivity and the diagenetic state of natural DOM (Skoog and Benner, 1997; Amon et al., 2001).

We used ultrafiltration to isolate 61 DOM samples from various locations in the Arctic Ocean and adjacent seas as part of an international cooperation investigating the biogeochemistry of DOM in the Arctic Mediterranean Sea (AMS). This multiyear sampling effort has harvested the largest set of ultrafiltered DOM (UDOM) samples ever collected from a single ocean basin. In this study we report the distribution and composition of neutral sugars within this sample set to learn more about the biogeochemical cycle of DOM in the AMS. The large sample set facilitates larger scale comparisons to show how organic matter from different environments can be related through their neutral sugar composition.

2. Materials and methods

2.1. Study area and sampling

A large number (61) of ultrafiltered DOM samples were isolated from various locations and depths in the Arctic Ocean, Fram Strait, Greenland, Iceland, and Norwegian Sea (GIN Sea), and the southern Kara Sea during cruises on the US Navy submarines *USS Pogy* (1996), *USS Archerfish* (1997) and *USS Hawkbill* (1998), the German ice breaker *FS Polarstern* (*ARK XIII/3*, 1997 and *ARK XIV/2b*, 1998) and the Russian research vessel "*Akademik Boris Petrov*," 1997 (Fig. 1, Table 1). Stations in the Fram Strait and GIN Sea were chosen to represent different water masses flowing in and out of the Arctic Ocean. Inflowing Atlantic water represents an important source for DOM to the Arctic Ocean. Samples of outflowing water masses included Fram Strait deep water originating in the Eurasian Basin, Fram Strait intermediate water originating in the Canada Basin, and Fram Strait surface water from the East Greenland Current (EGC) originating in the Transpolar Drift. The EGC was sampled at

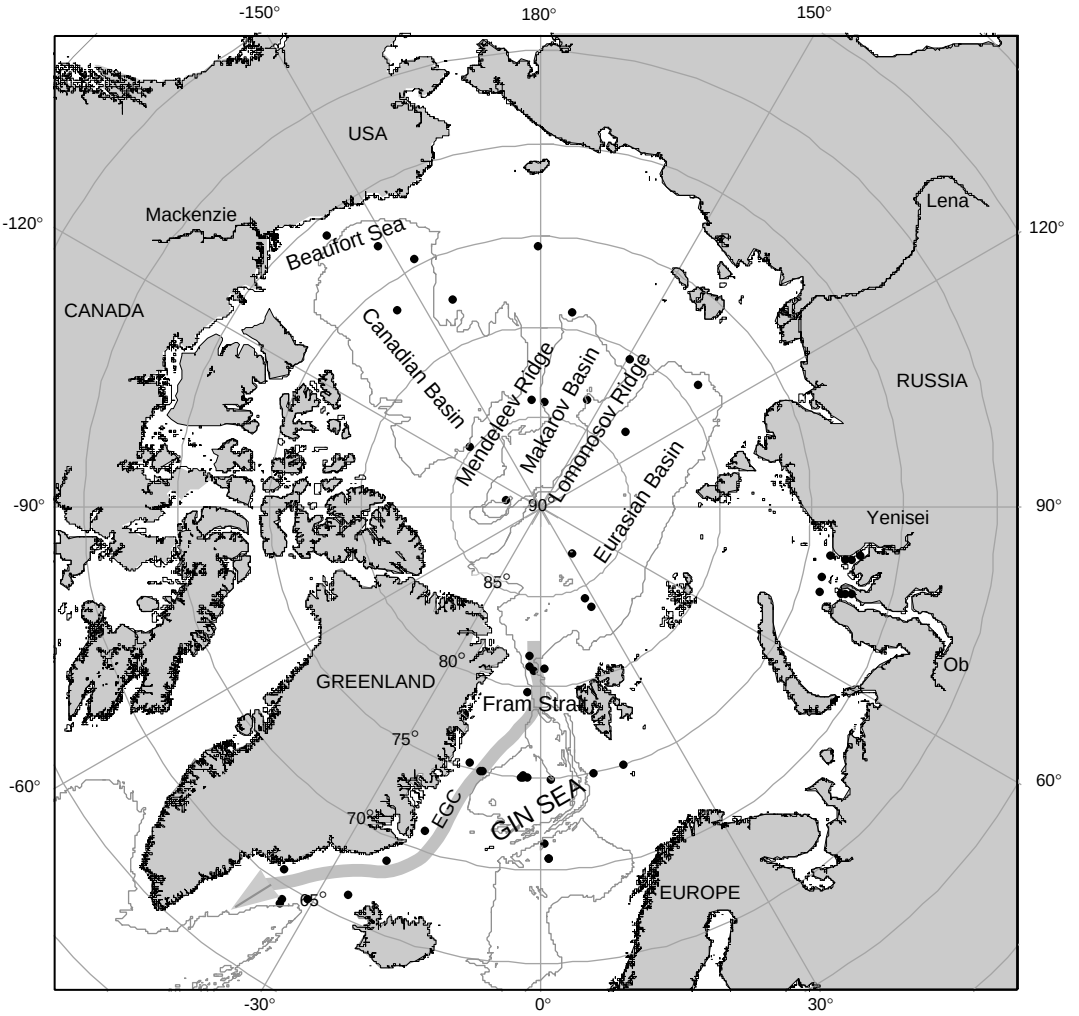


Fig. 1. Map of the study area showing the sampling locations for UDOM. Samples were collected during six different expeditions. More detailed information on the sampling locations is given in Table 1. Gray contour line represents the 2500 m isobath. GIN Sea, Greenland, Iceland, Norwegian Sea; EGC, East Greenland Current.

several locations from 81°N to 66°N to trace the export of Arctic DOM to the North Atlantic (Fig. 1). Additionally, we collected depth profile samples in the central Arctic Ocean, the Greenland Gyre, the Norwegian Sea and the Iceland Sea. Surface samples in the southern Kara Sea were collected across salinity gradients from the mouths of two major Russian rivers (Ob and Yenisei). One multiyear ice floe was recovered in the Fram Strait to obtain a sample of DOM in sea ice. Most of the samples from the central Arctic were collected from submarines between 35 and 236 m, with the exception of one depth profile between 10 and 1600 m over the Mendeleyev Ridge between the Makarov and Canada Basins and two discrete deep-water samples in the Nansen Basin and the Makarov Basin, respectively (Table 1).

Large volume samples (30–200 l) were collected either with Niskin-bottles mounted onto a CTD rosette or with a large-volume (200 l) stainless-steel water sampler (Kara Sea). On the submarine cruises samples were either taken from a through-hull water inlet system, a rosette-CTD system lowered from the surface, or from the sea

Table 1
Sample location and description including salinity, temperature and dissolved organic carbon (DOC) concentrations at the sampling site, as well as concentrations of ultrafiltered organic carbon (UDOC), and neutral sugars (NS) in ultrafiltered DOM (UDOM)

Sample identification	Sampling date	Latitude	Longitude	Depth (m)	Salinity (psu)	Temp. (C°)	DOC (μM C)	UDOC (μM C)	NS (nM)	NS (% OC)
Yenisei 1	September 18, 1997	72°05′35N	81°28′52E	0–2	1.211	7.798	537	373	1102	1.70
Yenisei 2	September 19, 1997	72°30′31N	80°19′43E	0–2	3.600	7.280	534	328	1048	1.84
Yenisei 3	September 17, 1997	72°53′21N	80°05′33E	0–2	7.300	6.577	520	294	985	1.92
Yenisei 4	September 20, 1997	73°40′51N	80°36′39E	0–2	10.000	5.857	503	269	913	1.95
Kara Sea	September 16, 1997	73°57′42N	76°08′19E	0–2	10.963	5.424	423	207	912	2.53
Ob 1	September 14, 1997	72°30′10N	74°04′51E	0–2	2.440	6.266	528	299	1823	3.50
Ob 2	September 15, 1997	72°10′13N	74°17′37E	0–2	3.400	6.081	520	282	1357	2.76
Ob 3	September 15, 1997	72°41′19N	73°43′50E	0–2	6.975	5.410	493	267	1308	2.82
Ob 4	September 13, 1997	73°54′38N	73°10′59E	0–2	12.682	5.412	458	245	1320	3.10
Icefloe	August 31, 1997	80°53′53N	02°35′16W	0	2.510	nd	107	15	558	21.91
EGC 1	August 21, 1997	81°41′20N	04°33′20W	80	33.968	−1.690	75	27	76	1.63
EGC 2	September 15, 1997	75°16′00N	15°30′10W	50	33.251	−1.666	85	30	101	1.96
EGC 3	September 21, 1998	75°00′00N	12°22′00W	50	34.134	−1.579	67	21	113	3.03
EGC 4	October 03, 1998	70°59′40N	19°44′20W	85	33.320	−1.673	86	25	118	2.70
EGC 5	October 05, 1998	68°53′20N	23°36′01W	72	33.425	−1.560	79	26	98	2.19
EGC 6	October 10, 1998	65°43′49N	35°16′43W	40	33.022	0.950	79	22	163	4.36
Atl. Water	August 18, 1997	81°01′50N	01°26′10E	250	34.926	1.900	61	17	48	1.58
Atl. RW	September 15, 1997	74°59′40N	12°33′30W	149	34.905	2.406	65	17	62	2.05
Atl. Water	September 26, 1998	75°00′40N	11°17′00E	100	35.043	3.632	54	20	102	3.02
Atl. Water	October 08, 1998	64°59′90N	30°41′70W	95	35.098	7.247	62	17	60	2.10
FS-CBIW	August 26, 1997	79°40′50N	03°56′40W	1820	34.924	−0.541	53	16	31	1.12
FS-EBDW	August 19, 1997	81°03′90N	03°29′60W	3600	34.934	−0.699	49	18	35	1.13
Greenl. Gyre	September 24, 1998	75°00′20N	02°17′00W	12	34.652	4.259	72	18	194	6.36
Greenl. Gyre	September 23, 1998	75°03′00N	02°51′00W	12	34.635	3.646	67	24	409	9.64
Greenl. Gyre	September 19, 1997	75°04′80N	03°29′10W	200	34.855	−0.542	58	16	54	2.00
Greenl. Gyre	September 17, 1997	74°59′90N	03°30′90W	1800	34.906	−0.878	54	14	32	1.37
Greenl. Gyre	August 14, 1997	74°58′90N	04°20′00W	3200	34.902	−0.967	50	18	41	1.31

Norweg. Sea	September 30, 1998	71°24′00N	00°40′60W	70	35.130	6.350	61	18	71	2.25
Norweg. Sea	September 30, 1998	70°35′40N	01°22′30E	1500	34.904	−0.669	53	16	45	1.64
Norweg. Sea	September 30, 1998	70°35′40N	01°22′30E	3100	34.909	−0.843	55	15	39	1.49
Barents Sea	September 27, 1998	75°00′00N	18°01′00E	50	34.480	3.353	70	22	165	4.25
Denmark St.	October 06, 1998	66°14′80N	26°30′20W	569	34.888	−0.296	60	17	52	1.76
Labrador Sea	October 08, 1998	64°00′60N	33°14′90W	2413	34.871	1.068	56	16	67	2.43
Labrador Sea	October 08, 1998	64°00′60N	33°14′90W	1705	34.852	2.962	54	15	46	1.77
Eurasian B.	September 21, 1997	78°54′00N	127°55′70E	35	34.219	nd	76	15	96	3.70
Eurasian B.	September 03, 1997	84°15′30N	26°16′40E	55	34.295	nd	66	14	75	3.10
Eurasian B.	July 07, 1998	83°45′50N	26°43′12E	4080	34.941	−0.668	56	17	63	2.13
Eurasian B.	October 18, 1996	86°50′10N	35°31′10E	132	34.332	nd	77	14	64	2.70
Eurasian B.	October 22, 1996	83°38′10N	131°11′30E	132	34.302	nd	71	16	96	3.50
Mendeleev R.	August 26, 1998	84°01′80N	175°03′20W	10	29.74	nd	137	33	219	3.9
Mendeleev R.	August 26, 1998	84°02′00N	175°08′00W	55	33.22	nd	104	25	136	3.16
Mendeleev R.	August 26, 1998	84°02′00N	175°08′00W	100	33.71	nd	90	18	74	2.35
Mendeleev R.	August 26, 1998	84°02′00N	175°08′00W	132	34.14	nd	77	16	71	2.53
Mendeleev R.	August 26, 1998	84°02′00N	175°08′00W	180	34.44	nd	76	16	55	1.94
Mendeleev R.	August 26, 1998	84°02′00N	175°08′00W	226	34.67	nd	65	13	57	2.48
Mendeleev R.	August 26, 1998	84°01′70N	175°03′80W	300	34.82	nd	62	14	59	2.37
Mendeleev R.	August 26, 1998	84°01′50N	175°03′30W	600	34.87	nd	59	13	49	2.21
Mendeleev R.	August 25, 1998	84°01′10N	175°05′30W	1000	34.9	nd	58	13	57	2.58
Mendeleev R.	August 25, 1998	84°01′00N	175°04′00W	1600	34.95	nd	54	13	67	2.93
Makarov B.	July 10, 1998	87°59′20N	102°28′10W	3200	34.953	−0.334	53	18	48	1.54
Makarov B.	September 16, 1997	75°30′80N	179°34′40W	132	34.2	nd	75	16	88	3.30
Makarov B.	September 25, 1997	84°08′00N	177°28′60E	236	34.809	nd	69	13	49	2.10
Makarov B.	September 18, 1997	79°00′90N	170°25′70E	132	34.250	nd	67	15	73	2.80
Makarov B.	October 22, 1996	83°28′20N	156°54′80E	132	34.492	nd	73	14	75	3.20
Makarov B.	September 20, 1997	80°26′60N	148°57′50E	55	33.689	nd	79	18	104	3.30
Canada B.	September 25, 1996	84°50′90N	130°04′60W	132	33.010	nd	74	16	97	3.50
Canada B.	October 08, 1996	74°38′30N	152°54′40W	132	32.703	nd	78	17	89	3.10
Canada B.	October 03, 1996	76°31′70N	144°00′60W	165	33.067	nd	nd	15	79	3.00
Beaufort Sea	September 12, 1997	70°53′50N	141°49′60W	55	32.042	nd	80	18	125	4.10
Canada B.	September 12, 1997	72°59′60N	148°14′60W	132	33.046	nd	79	20	177	5.20
Canada B.	September 27, 1997	77°28′00N	157°07′90W	236	34.564	nd	62	14	59	2.40

EGC, East Greenland Current; Atl. RW, Atlantic Return Water; FS-CBIW, Fram Strait-Canada Basin Intermediate Water, FS-EBDW, Fram Strait-Eurasian Basin Deep Water.

ice surface, by lowering the sampling equipment through a hole in the ice. The water samples (30–200 l) were filtered through a 0.2 μm polycarbonate filter (Nuclepore) immediately after sampling or preserved with $HgCl_2$ in the case of the submarine samples. Kara Sea samples and samples taken on the submarines were stored until processing at the home laboratory. All other samples were ultrafiltered on board, immediately after sampling. DOC concentrations in the Kara Sea and submarine samples did not indicate DOC losses or contamination during storage. Preserved ($HgCl_2$) replicates had DOC values and neutral sugar concentrations indistinguishable from their fresh and unpreserved counterparts.

2.2. Ultrafiltration and sample dry down

Ultrafiltration was performed either with an Amicon DC-10 or with an Amicon Proflux M 30 system with two spiral-wound polysulfone filter cartridges (S10N1; 1000 D cutoff). Prior to ultrafiltration the water samples were filtered through 0.2 μm pore size polycarbonate filters. 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. (1997).

2.3. Measurements

Dissolved organic carbon was measured by the high temperature combustion method and either a Shimadzu TOC 5000 analyzer (Benner and Strom, 1993) or MQ-Scientific Inc. 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.

The concentrations of individual neutral sugars (fucose, rhamnose, arabinose, galactose, glucose, mannose, and xylose) in hydrolyzed UDOM 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, 1 ml 12 M H_2SO_4 was added to dry UDOM samples (1–10 mg) and mixed in an ultrasonic bath (15 min). After 2 h at room temperature, each sample received 9 ml of water (Milli-Q-UV Plus) and was 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 self-absorbed resin AG11 A8 (Bio-Rad); 3–4 ml of resin was used to neutralize 1 ml of hydrolyzed sample (Kaiser and Benner, 2000). The residual standard deviation including sample preparation was between 2% and 10%.

3. Results and discussion

3.1. Distribution of dissolved organic carbon

Concentrations of DOC were variable among sampling locations and depth horizons (Table 1, Table 2, Fig. 2A). High concentrations (423–537 μM C) of DOC in the Kara Sea were associated with low-salinity water discharged by the Ob and Yenisei rivers. The high lignin phenol content and high C/N ratios (>40) of DOM collected from the Kara Sea indicate a predominantly terrestrial origin (Opsahl et al., 1999; Köhler et al., in press).

Samples from surface waters (⩽55 m) of the central Arctic Ocean and the Greenland, Iceland, Norwegian (GIN) Sea had DOC concentrations more typical for oceanic samples but with high spatial variability (Fig. 2A). Arctic Ocean surface waters are also quite variable in terms of salinity and temperature (Table 1), indicating a large and geographically variable contribution of freshwater. The potential sources of freshwater include rivers, melting sea ice, and inflowing Pacific water (Bauch et al., 1995; Rudels et al., 1996), all of them influencing DOC concentrations. Generally, DOC

Table 2
Hydrographic and chemical characteristics of grouped samples from the Arctic Mediterranean Sea

Group	Depth (m)	Salinity (psu)	DOC (μM)	NS (nM)	NS (% OC)	TDOC (%)
Estuarine	0–2	1.20–12.70	502 (423–537)	1196 (912–1823)	2.5 (1.7–3.5)	>90
Ocean-surface	< 55	29.74–34.65	82 (66–137)	158 (75–409)	4.2 (2.0–9.6)	2.4–37.2
Terrestrial	< 55	29.74–33.69	97 (79–137)	145 (101–219)	3.3 (2.0–4.4)	>10
Marine	< 55	32.04–34.65	71 (66–80)	194 (75–409)	5.5 (3.1–9.6)	<8
Ocean-interm.	60–600	32.70–35.13	70 (54–90)	76 (48–177)	2.6 (1.6–5.2)	2.2–25.1
Terrestrial	60–600	32.70–34.87	76 (59–90)	82 (49–118)	2.5 (1.6–3.3)	>10
Marine	60–600	33.01–35.13	65 (54–79)	73 (48–177)	2.5 (1.6–5.2)	<8
Ocean-deep	⩾1000	34.85–34.95	54 (49–58)	48 (31–67)	1.8 (1.1–2.9)	1.5–7.1
Fresh	12–132	32.04–34.65	74 (67–80)	214 (125–409)	5.9 (4.1–9.6)	2.4–7.0
Old	70–4080	34.44–35.10	59 (49–76)	51 (31–71)	1.8 (1.1–2.4)	1.5–7.7

DOC, dissolved organic carbon; NS, neutral sugars, TDOC, terrigenous dissolved organic carbon. The percentage of terrigenous DOC was estimated from dissolved lignin concentrations as presented in Opsahl et al. (1999).
Estuarine and oceanic samples were separated based on salinity. Oceanic samples were further grouped according to depth (surface ⩽55 m, intermediate = 60–600 m, and deep ⩾1000 m), content of terrigenous DOM (terrestrial ⩾10% TDOC, marine ⩽8% TDOC), and freshness (fresh⩾4% OC as neutral sugars, old ⩽2.5% OC as neutral sugars). Mean values (range).

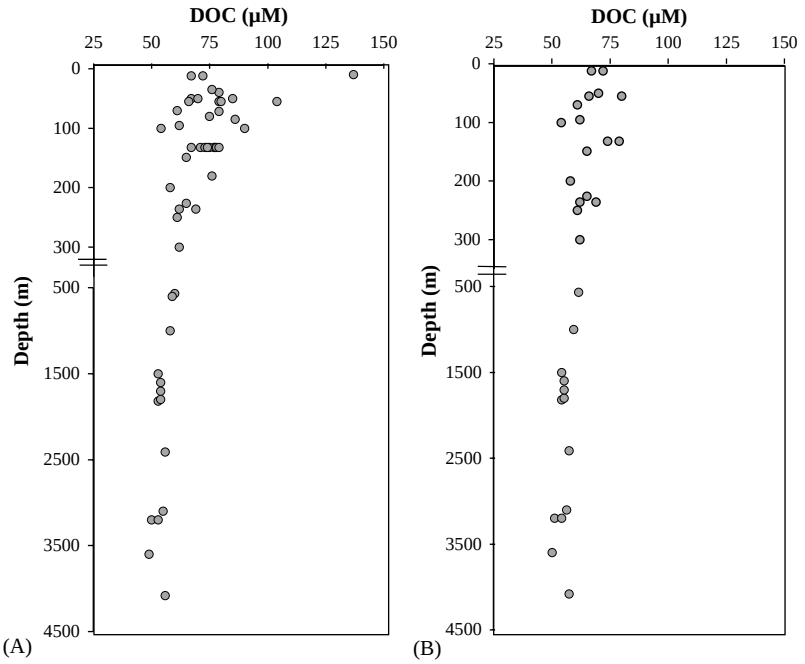


Fig. 2. Distribution of DOC with depth in the Arctic Mediterranean Sea showing all samples (A), and samples with little (<8%) contribution of terrestrial DOC (B).

concentrations decreased with depth (Fig. 2) and increasing salinity (Tables 1 and 2). Surface water DOC concentrations were positively correlated with salinity ($r^2 = 0.882, p < 0.001$) and ranged from 66–137 μM C with higher values in the Arctic Ocean and the East Greenland Current (EGC) relative to the GIN Sea. Elevated DOC concentrations (mean of 97 μM C) were frequently associated with enhanced contributions of terrigenous DOM ($r^2 = 0.764, p < 0.001$; Table 2), and we

believe the variability of DOC in samples from the surface Arctic Ocean was determined largely by river input and to a lesser extent by primary production as reported in earlier studies (e.g. Gordon and Cranfort, 1985; Walsh, 1995). Terrigenous DOC concentrations were estimated in this study from dissolved lignin measurements on the same UDOM samples. The range of surface DOC concentrations observed in this study agrees well with the range of total organic carbon (TOC) concentrations (64–124 μC) reported from the SCICEX-97 expedition (Guay et al., 1999). Arctic Ocean surface DOC values appear elevated relative to DOC concentrations reported from other surface oceans (Benner, 2002a) because of the large input of terrigenous DOM from rivers. This becomes clearer if we exclude surface samples with elevated (>10%) contributions of terrigenous UDOM, resulting in a lower average DOC concentration of 71 (66–80) μM C (Table 2, Fig. 2B). The strong influence of river input on DOC concentrations was also evident at intermediate depths (60–600 m), with average DOC values of 76 and 65 μM C in samples with high (>10%) and low (<8%) contributions of terrigeneous DOC, respectively (Table 2).

Deep-water DOC values (>1000 m) ranged from 49 to 58 μM C and showed no difference between GIN Sea and Arctic Ocean deep waters (Table 1, Fig. 2). These values agree with recently published average deep-water values for the Greenland Sea (55 μM C; Børsheim, 2000) and for the Arctic Ocean (52–56 μM C; Bussmann and Kattner, 2000). They are somewhat lower than total organic carbon (TOC) values reported for the central Arctic by Anderson et al. (1994), but are consistent with their general conclusion that Arctic Ocean deep waters have elevated levels of DOC compared to deep waters of other ocean basins (Hansell and Carlson, 1998). A more detailed survey of the distribution of DOC in the AMS confirmed a range between 46 and 52 μM DOC for deep waters (Amon, in press; Amon et al., in press) and suggests DOM downwelling as the likely source of elevated DOC values in the deep AMS.

The ultrafiltration process recovered between 50% and 70% of the DOC in the Kara Sea and between 18% and 37% of oceanic DOC (Table 1). The difference between recoveries of riverine and marine DOC is mostly a result of the greater abundance of high-molecular-weight DOM in the Ob and Yenisei rivers. The recoveries found in Arctic and GIN Sea samples are typical for marine waters (Benner et al., 1997). Carbon mass balances indicated that DOC recovered in the concentrate and the permeate averaged $98.5 \pm 6.5\%$ (82–117%), of the initial DOC, showing that carbon contamination or losses were minor during the ultrafiltration process.

3.2. Distribution of neutral sugar concentration

The concentration of neutral sugars in UDOM was much higher in the estuarine samples (912–1822 nM) relative to oceanic UDOM samples (31–409 nM), and higher in surface samples (75–409 nM) relative to deep-water samples (31–67 nM; Table 2, Fig. 3A). The depth distribution of neutral sugars in UDOM (Fig. 3A) was characterized by a sharp decrease in the upper 150 m below which the concentration remained fairly constant. Among marine surface samples elevated concentrations of total neutral sugars were associated with presumably fresh phytoplankton-derived UDOM in a few surface ($\leqslant$ 55 m) samples and to a lesser extent in samples with elevated contributions of terrigenous UDOM (Table 2). The reactive nature of neutral sugars even at temperatures close to 0°C (Amon et al., 2001), combined with the heterogenous input of neutral sugars during infrequent phytoplankton blooms and the variable distribution of freshwater, resulted in weak correlations between neutral sugar concentrations and other single parameters like salinity ($r^2 = 0.058$) or DOC concentrations ($r^2 = 0.061$). Exceptionally high concentrations of neutral sugars (558 nM) were detected in the sea ice sample (Table 1), which contained very fresh and labile DOM (Amon et al., 2001). Unlike DOC concentrations, highest mean concentrations of neutral sugars (194 nM) were observed in "marine" surface waters (Table 2). The only study of hydrolyzable neutral sugar concentrations in the Arctic Ocean reported a range between 34 and 2856 nM for unfractionated water samples (Rich et al., 1997). A recent study of dissolved combined

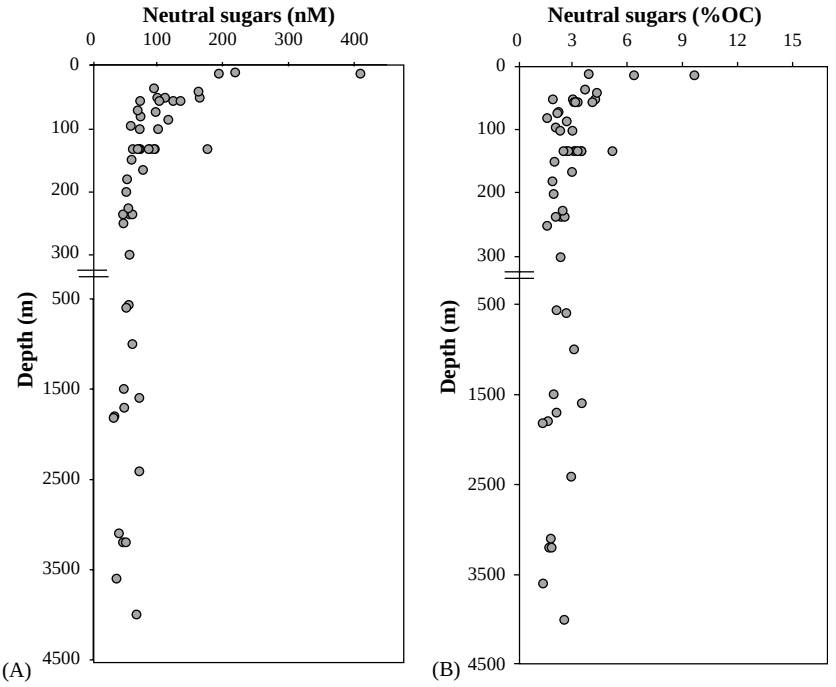


Fig. 3. Distribution of neutral sugar concentrations (A), and neutral sugar yields (B) with depth. The figure represents a summary of all data rather than a single station. Neutral sugar yield is presented as the percentage of organic carbon (% OC) identified as neutral sugar.

neutral sugars in total DOM in the Ross Sea and the Polar Front Zone reported concentrations between 300 and 3000 nM (Kirchman et al., 2001). Compared to UDOM samples from other regions of the ocean (McCarthy et al., 1996; Skoog and Benner, 1997), Arctic Ocean and GIN Sea neutral sugar concentrations appear to be in a similar range.

The neutral sugar yield (% DOC as neutral sugar) was not very different in UDOM samples from the river estuaries and the ocean (1–10%; Table 2), but estuarine samples fell within a narrower range (1.7–3.5%). The Ob had consistently higher yields than the Yenisei (Table 1). Highest yields (3–10%; Table 2) were observed in UDOM samples collected from surface waters ($\leqslant 55$ m) with little terrestrial contribution ($<8\%$; Table 2). The most pronounced trend in neutral sugar yields was the rapid decrease with depth in the upper 150 m (Fig. 3B), indicating the preferential removal of neutral sugars from the DOM pool. Neutral sugar yield has been suggested as a good indicator of the freshness and lability of DOM (Skoog and Benner, 1997; Amon et al., 2001; Benner, 2002a, b). In this data set, neutral sugar yield shows a strong positive relationship to neutral sugar concentration (nM; $r^2 = 0.885$; $p < 0.001$) and a weak relationship to salinity ($r^2 = 0.005$; $p > 0.5$) and DOC concentration ($r^2 = 0.061$; $p > 0.0.1$). The relationship between neutral sugar concentrations and neutral sugar yield is only slightly stronger ($r^2 = 0.937$) if we omit the terrestrially influenced surface samples. The weak relationship between neutral sugar yields and salinity indicates that terrigenous DOM had a minor effect on the neutral sugar yield of Arctic UDOM, suggesting that the neutral sugar yield is a useful indicator of fresh phytoplankton-derived DOM. The range of neutral sugar yields (3–10%; Table 2) in "marine" Arctic Ocean surface UDOM is somewhat lower than values reported for other surface oceans (6–13%; Benner, 2002a).

In a previous study (Amon et al., 2001) we observed a strong relationship between neutral

sugar yield and bulk DOM degradation (Fig. 4A). We can use these results to relate neutral sugar yield to the amount of utilizable or labile DOC under conditions typical for the Arctic Ocean (Fig. 4B). Here we define labile DOC as the DOC that was degraded within 10 days leaving behind about 78 μM DOC (Fig. 4A). The difference between the 78 μM DOC line (Fig. 4A) and the DOC concentration at the different time points during the experiment give us the relative amount of labile DOC (0–30%). The relationship between neutral sugar yield and percent labile DOC (Fig. 4B) is best represented ($r^2 = 0.867$) by the following exponential equation:

$$\text{NS yield } (\%\text{OC}) = 3.32\, e^{0.0389\,(\%\text{DOC}_{\text{lab}})}. \quad (1)$$

The intercept in Fig. 4B represents the neutral sugar yield (3.32%) at 0% labile DOC. This yield is much higher than what was observed in deep-water UDOM of the Arctic Mediterranean Sea indicating the abundance of semi-labile DOC which is degraded on somewhat longer time scales (months to years). The abundance of semi-labile UDOM in the AMS interior is consistent with relatively high DOC concentrations.

Taking into account that the neutral sugar yield of surface UDOM is about twice as high as for bulk DOM (Benner, 2002a) we can use Eq. (1) to roughly estimate the amount of labile DOC in Arctic and other oceanic surface waters from measured values of neutral sugar yield. Arctic surface samples (<55 m) had an average of 2.2% labile DOC (Fig. 4C). The estimated amount of labile DOC in surface waters of the Atlantic and Pacific (10%) and the Ross Sea (6%) appears higher (Fig. 4C). The low concentration and yield of neutral sugars in Arctic Ocean surface waters support the notion that heterotrophic activity is high relative to primary production in this system (Wheeler et al., 1996; Rich et al., 1997; Sherr et al., 1997). To what extent the neutral sugar yield can be used to estimate the pool size of semi-labile DOC in the ocean needs to be experimentally confirmed and compared to in situ measurements.

The average neutral sugar concentration in the deep AMS was 48 nM (Table 2). Related to the average neutral sugar concentration of Arctic Ocean "marine" surface UDOM (194 nM) we can calculate that on average 146 nM or 75% of neutral sugars are of labile or semi-labile nature. The general pattern of neutral sugar concentrations and yields in the Arctic Ocean confirms that their distribution is mainly determined by diagenetic processes.

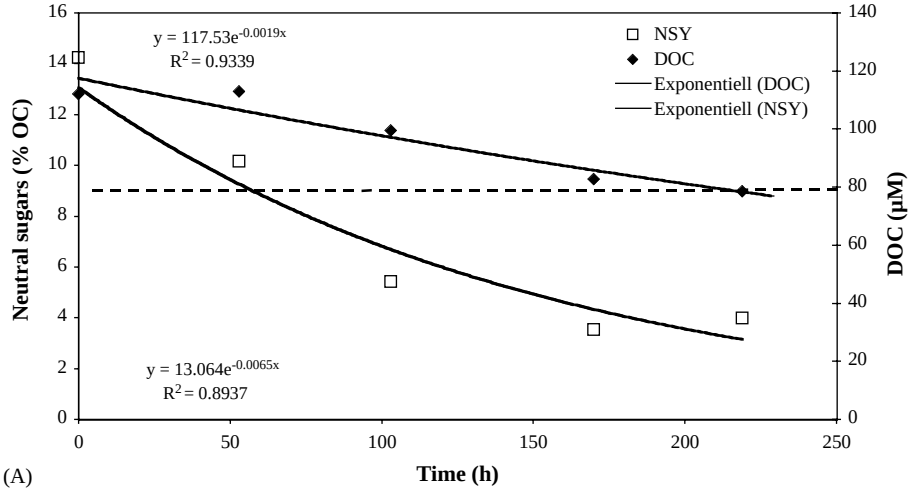
3.3. Neutral sugar composition of arctic UDOM

The composition of neutral sugars in UDOM from the different Arctic Basins and the GIN Sea was compared for geographical and water mass specific patterns, but no significant differences were observed. UDOM from the two river estuaries in the Kara Sea showed rather similar neutral sugar compositions relative to marine samples (Fig. 5). The neutral sugar compositions of the two river estuaries were very similar (Fig. 5A and B) with similar mole percentages (mol%) of the seven sugars characterized. The main differences, based on *t*-statistics, between the neutral sugar composition in river UDOM and marine UDOM was the higher mol% rhamnose ($t > t_{0.05}; p < 0.001$) and the lower mol% fucose ($t > t_{0.05}; p < 0.001$) in river UDOM (Fig. 5). This pattern was also observed when the sugar composition of other rivers was compared to marine DOM (Hedges et al., 1994; Benner and Opsahl,

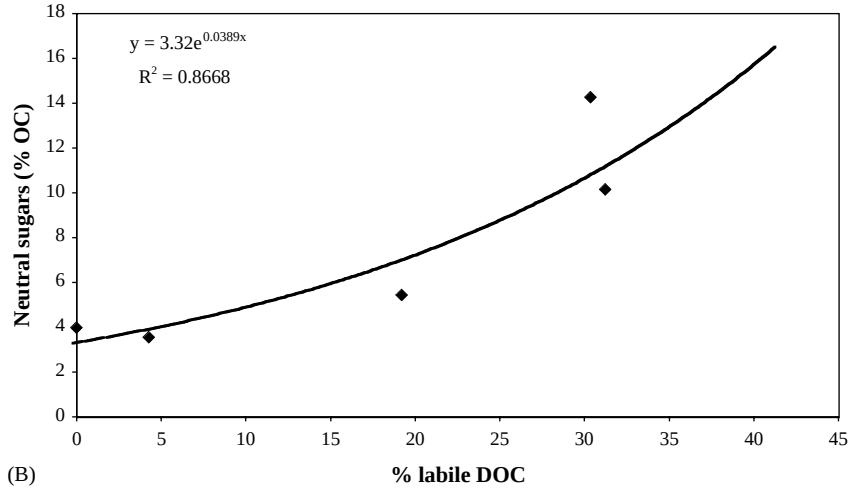
Fig. 4. (A) DOC concentrations and neutral sugar yields (% OC) during a 10 day decomposition experiment with fresh DOM from ice algae. Curves represent the exponential fit to the data. The broken line marks the DOC concentration (78 μM) at the end of the decomposition experiment. (B) The relationship between neutral sugar yield (% OC) and the percent labile DOC. Percent labile DOC was calculated as follows:

$$\%\text{DOC}_{\text{lab}} = \frac{[\text{DOC}] - 78}{[\text{DOC}]} \times 100.$$

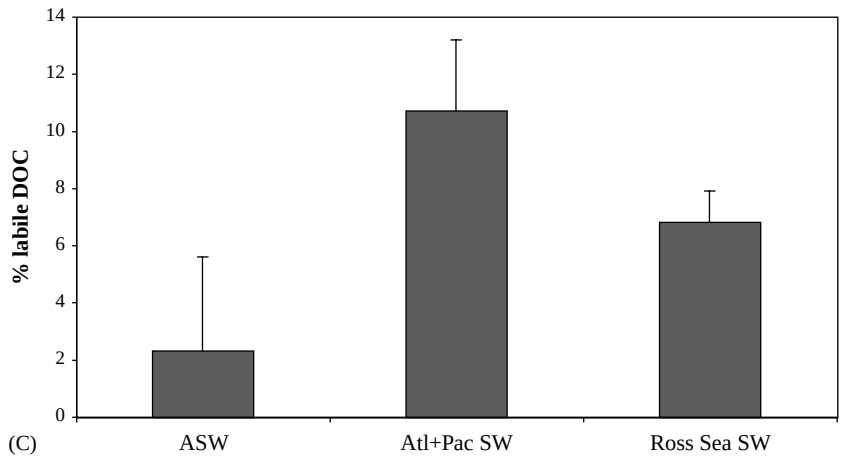
(C) Average percent labile DOC in surface water from the Arctic Mediteranean Sea compared to the Atlantic (McCarthy et al., 1996), Pacific (Skoog and Benner, 1997) and the Southern Ocean–Ross Sea (Kirchman et al., 2001); Error bars represent the standard deviation.


y = 117.53e-0.0019x
R2 = 0.9339
y = 13.064e-0.0065x
R2 = 0.8937
NSY
DOC
Exponentiell (DOC)
Exponentiell (NSY)
Neutral sugars (% OC)
DOC (µM)
Time (h)

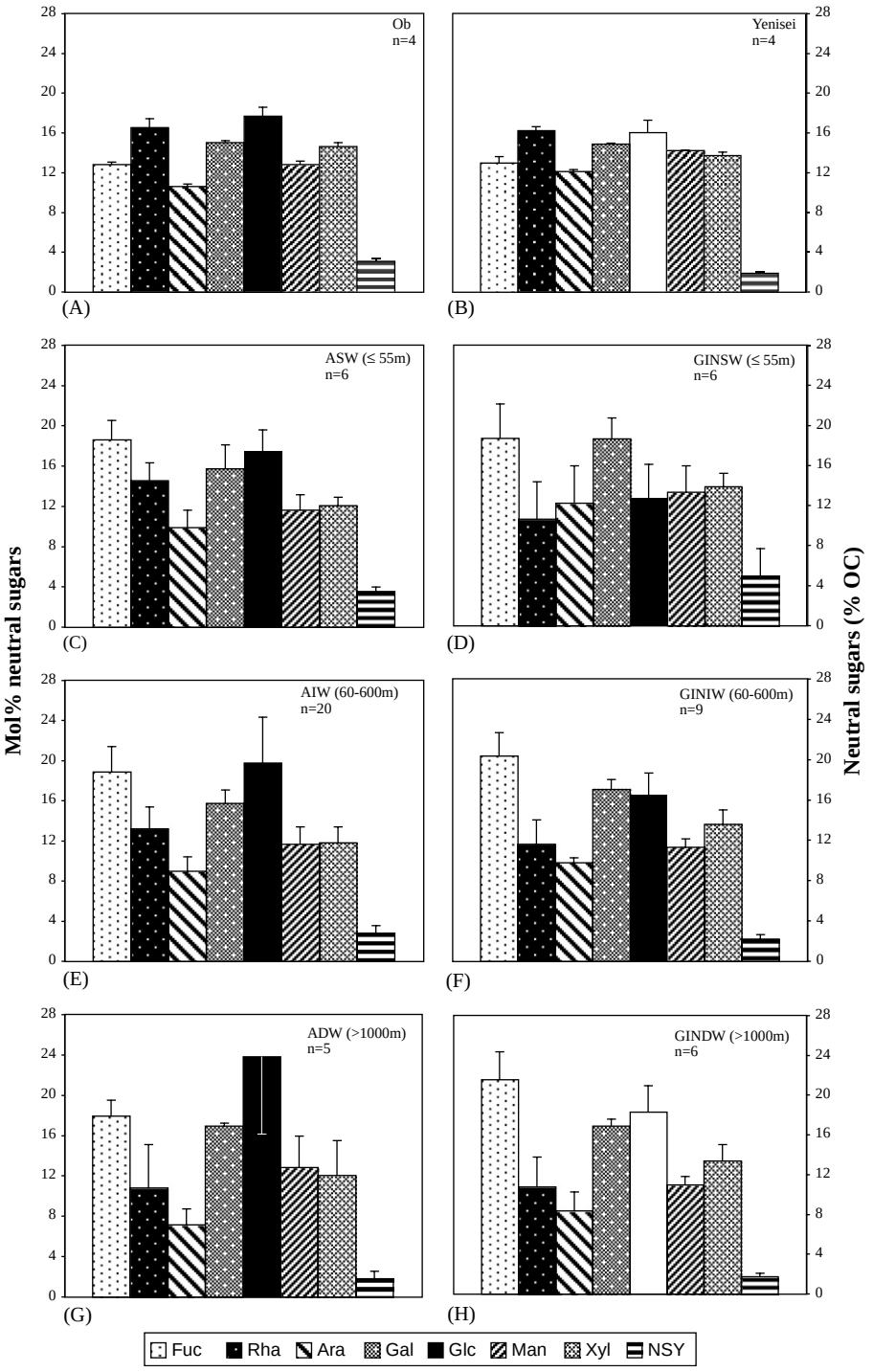
(A)


y = 3.32e0.0389x
R2 = 0.8668
Neutral sugars (% OC)
% labile DOC

(B)


% labile DOC
ASW
Atl+Pac SW
Ross Sea SW

(C)


Ob
n=4
Yenisei
n=4
ASW (≤ 55m)
n=6
GINSW (≤ 55m)
n=6
AIW (60-600m)
n=20
GINIW (60-600m)
n=9
ADW (>1000m)
n=5
GINDW (>1000m)
n=6
(A)
(B)
(C)
(D)
(E)
(F)
(G)
(H)
Mol% neutral sugars
Neutral sugars (% OC)
Fuc
Rha
Ara
Gal
Glc
Man
Xyl
NSY

2001). The average neutral sugar compositions of UDOM samples collected from the central Arctic Ocean surface ($\leqslant 55$ m) were compared to those of GIN Sea surface waters (Fig. 5C and D) and their respective intermediate (60–600 m) and deep-water ($\geqslant 1000$ m) counterparts (Fig. 5 E–H). Statistical comparisons (*t*-test) of the means showed that Arctic surface water UDOM (Fig. 5C) was slightly enriched in mol% rhamnose ($t > t_{0.05}; p < 0.001$) and mol% glucose ($t > t_{0.05}; p < 0.001$), and depleted in mol% galactose ($t > t_{0.05}; p < 0.001$) relative to GIN Sea surface water UDOM (Fig. 5D). Differences in the molecular composition of UDOM were related mainly to depth (Fig. 5C–H) with an increase of mol% glucose ($t > t_{0.05}$; $p < 0.005$) in both regions.

Rich et al. (1997) reported hydrolysable neutral sugar compositions of total DOM in the Arctic Ocean that were dominated by glucose (39 mol%), similar to the bulk composition we observed in selected samples from the Arctic Ocean (data not shown). The dominance of glucose in bulk DOM was reported from several oceanic regions, including the Oregon coast (44–48 mol%), the Sargasso Sea (about 35%; Borch and Kirchman, 1997), the equatorial Pacific (21–60 mol%; Skoog and Benner, 1997), and different locations in the Southern Ocean (35–37 mol%; Kirchman et al., 2001). A number of recent studies (McCarthy et al., 1996; Skoog and Benner, 1997; Aluwihare et al., 1997; Benner and Opsahl, 2001) contain information on the neutral sugar composition of marine UDOM. Surface UDOM samples from different regions of the world ocean including the North Pacific, equatorial Pacific, Sargasso Sea, Gulf of Mexico, Mid-Atlantic Bight, and the North Sea all have similar neutral sugar compositions that are indicative of heteropolysaccharides. In most of the deep-water samples (McCarthy et al., 1996; Skoog and Benner, 1997), glucose is relatively more abundant than in surface samples ($t > t_{0.05}$; $p < 0.05$). The observed similarity of the neutral sugar composition among UDOM samples with different origins (terrestrial and marine) and from different locations (oceanic regions and water masses) is intriguing and suggests degradation processes as the determining factor for the neutral sugar composition of DOM in different aquatic systems.

Freshwater inflow to the Arctic Ocean via rivers supplies a relatively large amount of terrigenous DOM (Köhler et al., in press). The fraction of terrigenous organic matter in Arctic Ocean and GIN Sea UDOM samples is highly variable, ranging from 1% to 38% (Table 2; Opsahl et al., 1999). We used the relative contribution of terrigenous DOM (% TDOC) to separate UDOM samples into groups with high (> 10%) and low (<8%) contributions of terrigenous UDOM (Table 2, Fig. 6). This comparison clearly shows the similarities of neutral sugar composition in UDOM from different sources (terrestrial versus marine) and indicates that neutral sugar composition is not useful for distinguishing terrestrial and marine sources of DOM in the Arctic Ocean.

Freshly produced UDOM from different marine phytoplankton with global importance including sea ice algae is characterized by very high neutral sugar yields (20–40%) and variable neutral sugar compositions (Fig. 7; Biersmith and Benner, 1998; Aluwihare and Repeta, 1999; Hama and Yanagi, 2001). This indicates that neutral sugar compositions of freshly produced material could be used to identify DOM from specific phytoplankton groups.

3.4. The influence of diagenesis on the neutral sugar composition of Arctic Ocean DOM

Amon et al. (2001) demonstrated the influence of bacterial degradation on the molecular composition of fresh dissolved organic matter from an Arctic sea ice sample. Bacteria rapidly (1 week)

Fig. 5. Average neutral sugar composition (mol%), and neutral sugar yield (% OC) of UDOM from the Ob River (A), the Yenisei River (B), Arctic Ocean surface water (ASW; C), Greenland, Island, Norwegian Sea (GIN Sea) surface water (D), Arctic Ocean intermediate water (AIW; E), GIN Sea intermediate water (GINIW; F), Arctic Ocean deep water (ADW; G), and GIN Sea deep water (GINDW; H). Error bars represent the standard deviation of *n* samples. Fuc, fucose; Rha, rhamnose; Ara, arabinose; Gal, galactose; Glc, glucose; Man, mannose; Xyl, xylose; NSY, neutral sugar yield (% OC).

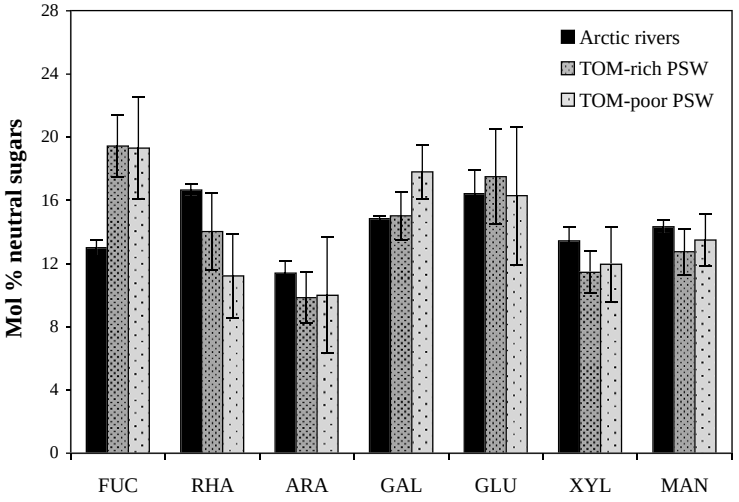


Fig. 6. Average neutral sugar composition (mol%) of UDOM from Ob and Yenisei (Arctic rivers), UDOM ($n=12$) from polar surface water (PSW) rich in terrestrial organic matter (TOM), and UDOM ($n=12$) from PSW poor in TOM. The distinction between TOM-rich and TOM-poor is explained in the text. Error bars represent the standard deviation.

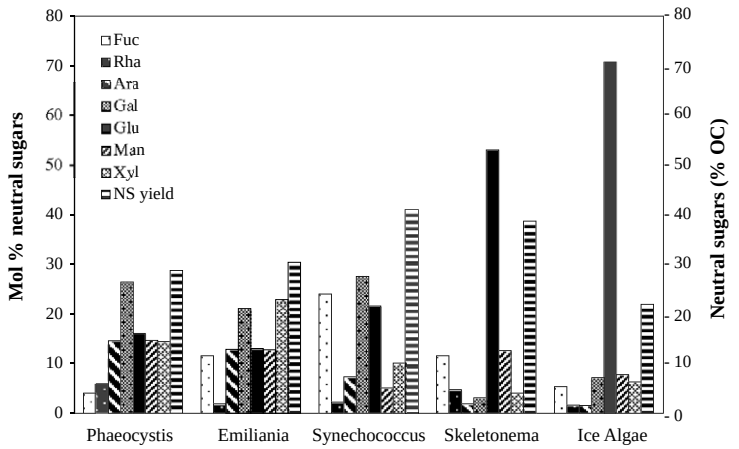


Fig. 7. Neutral sugar composition (mol%) and neutral sugar yield (%) of UDOM harvested from fresh algae cultures, and from a sea ice sample. Data for the culture UDOM were taken from Biersmith and Benner (1998).

utilized about 80% of the total hydrolysable neutral sugars. During decomposition the neutral sugar yield dropped from ~14% to ~4% (Fig. 4A). Neutral sugar composition was also affected by decomposition. The dominance of glucose, not unusual for fresh DOM (Fig. 7; Ittekkot et al., 1981; Benner and Opsahl, 2001; Hama and Yanagi, 2001), declined while the mol% deoxysugars (fucose and rhamnose) increased (Fig. 8). A similar shift in neutral sugar composition was observed during the microbial degradation of DOM from cultured algae and mesocosm studies (Aluwihare et al., 1997; Aluwihare and Repeta, 1999; Meon and Kirchman, 2001; Hama and Yanagi, 2001).

The dominant neutral sugar varies among cultured species and probably with physiological state. The most abundant neutral sugars in fresh UDOM appear to be galactose and glucose (Fig. 7), but other individual sugars have also

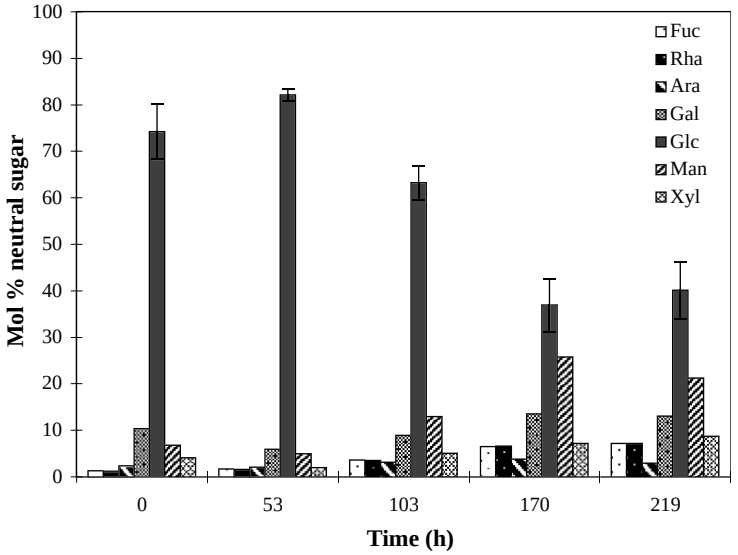


Fig. 8. Changes in the neutral sugar composition during decomposition of fresh, algal-derived DOM. Error bars represent the standard error of two replicates.

been shown to dominate (Aluwihare et al., 1997). The UDOM samples presented in this study have much lower neutral sugar yields and fairly uniform neutral sugar compositions, suggesting they have undergone considerable degradation. To demonstrate the influence of organic matter decomposition on the neutral sugar composition of UDOM, we grouped marine UDOM samples according to diagenetic state. We used the neutral sugar yield to separate fresh and labile UDOM with high neutral sugar yields (>4%) from older and degraded UDOM with low neutral sugar yields (<2.5%; Table 2). By subtracting the mol% of individual neutral sugars of fresh UDOM from their degraded counterparts we obtained the general diagenetic changes that occur in the neutral sugar composition during diagenesis of marine UDOM (Fig. 9). This analysis indicates an enrichment of glucose, fucose and rhamnose, and a depletion of arabinose, galactose and mannose as diagenesis progresses (Fig. 9A). Following the same calculation, this general trend was confirmed with neutral sugar data of UDOM from other oceanic regions including the equatorial and North Pacific, the Sargasso Sea, and the Gulf of Mexico (Fig. 9B; McCarthy et al., 1996; Skoog and Benner, 1997). Assuming that UDOM samples with low neutral sugar yield are representative of deep-water DOM (Fig. 3B, Skoog and Benner, 1997) with an average age of several thousand years (Williams and Druffel, 1987), the observed diagenetic trend applies to much longer time scales than short-term decomposition experiments (Amon et al., 2001; Hama and Yanagi, 2001). Some of the diagenetic trends observed during short-term decomposition (Fig. 8) are similar to the long-term diagenetic trend (e.g. increase of mol% deoxysugars), however, the increase in the mol% glucose was not apparent in the short-term experiment. Interestingly, glucose appears to be the dominant neutral sugar in highly degraded and biorefractory DOM as well as in fresh and labile DOM from certain phytoplankton sources (Fig. 7; Hama and Yanagi, 2001). Glucose is often the dominant neutral sugar in storage polysaccharides, like glucan, which appear to be degraded faster than heteropolysaccharides (Hama and Yanagi, 2001). Homopolysaccharides (storage polysaccharides) are found mainly in fresh phytoplankton- derived DOM. With progressing degradation homopolysaccharides are preferentially utilized leading to a relative enrichment of heteropolysaccharides with a more equimolar neutral sugar composition.

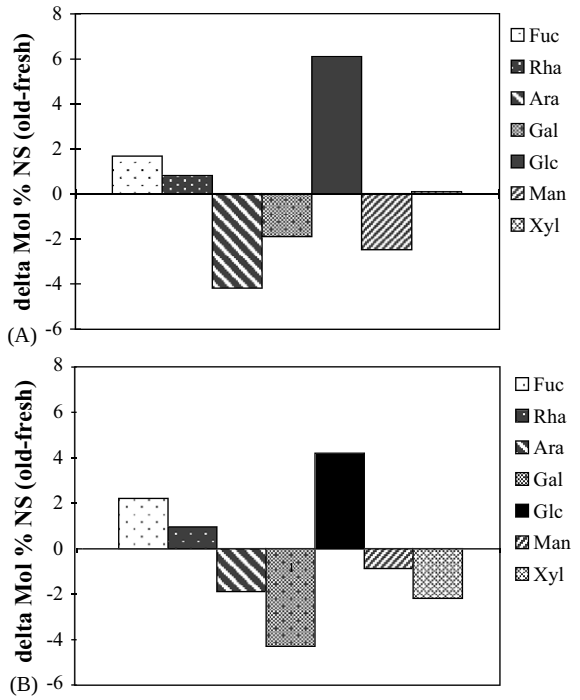


Fig. 9. Diagenetic trends in neutral sugar compositions of natural UDOM as revealed by compositional differences between "fresh" UDOM with a high neutral sugar yield (>4%) and "old" UDOM with a low neutral sugar yield (<2.5%). Panel A shows the data set presented in this study, and panel B represents literature data from McCarthy et al. (1996) and Skoog and Benner (1997).

We used the diagenetic trends presented in Fig. 9 to evaluate patterns of diagenesis based on neutral sugar composition by plotting (Fig. 10) glucose and fucose (enriched) against galactose and arabinose (depleted). UDOM samples from the Arctic Mediterranean Sea (AMS) plot according to their depth distribution with relatively fresh and labile surface samples having the highest contribution of galactose and arabinose and the lowest contribution of glucose and fucose relative to intermediate and deep-water UDOM (Fig. 10). The same depth related trend was observed for the neutral sugar composition of UDOM in the Atlantic and Pacific (Fig. 10; McCarthy et al., 1996; Skoog and Benner, 1997). The variability within each depth level was high making it difficult to see clear differences among ocean basins, however, UDOM from the interior of the AMS appeared less degraded than in the Atlantic and Pacific suggesting that some semi-labile DOM is still present. Hydrolysable combined neutral sugars in the oceans interior represent heteropolysaccharides that are characterized by almost equimolar concentrations of the seven neutral sugars among which fucose, glucose, and galactose appear most abundant.

The equimolar neutral sugar compositions and low neutral sugar yields of Arctic river UDOM indicates that terrigenous UDOM had also undergone considerable degradation before entering the Arctic Ocean. Assuming that the primary source of river DOM are vascular plants in the hinterland, DOM diagenesis likely occurs within the soil-matrix before entering the river and during river transit. A recent study by Hedges et al. (2000) indicates that the composition of riverine organic matter is determined primarily outside the river channel. Compositional similarities are apparent between UDOM from high latitude rivers, Ob and Yenisei, and other major world rivers like the Amazon (Hedges et al., 1994) and the Mississippi (Benner and Opsahl, 2001; Fig. 11). This suggests that similar processes occur across different climate and vegetation zones (polar, temperate, and tropical) leaving behind heteropolysaccharides with nearly equimolar neutral sugar composition.

Diagenetic alterations of neutral sugars in terrigenous and marine particulate organic material (POM) have been investigated in a variety of environments (Cowie and Hedges, 1984; Ittekkot and Arian, 1986; Hedges et al., 1994; Cowie et al., 1995; Hernes et al., 1996; Opsahl and Benner, 2000; Benner and Opsahl, 2001; D'Souza and Bhosle, 2001). These studies consistently identified increases in mol% deoxysugars (fucose and rhamnose) and decreases in mol% glucose as diagenesis progresses. Declining neutral sugar yields with decomposition were observed in studies of lotic and coastal systems (Hedges et al., 1994; Opsahl and Benner, 2000; D'Souza and Bhosle, 2001) but were not obvious in a study of sinking particles in the Pacific Ocean (Hernes et al., 1996). Differences in the neutral sugar composition of organic matter fractions of different diagenetic

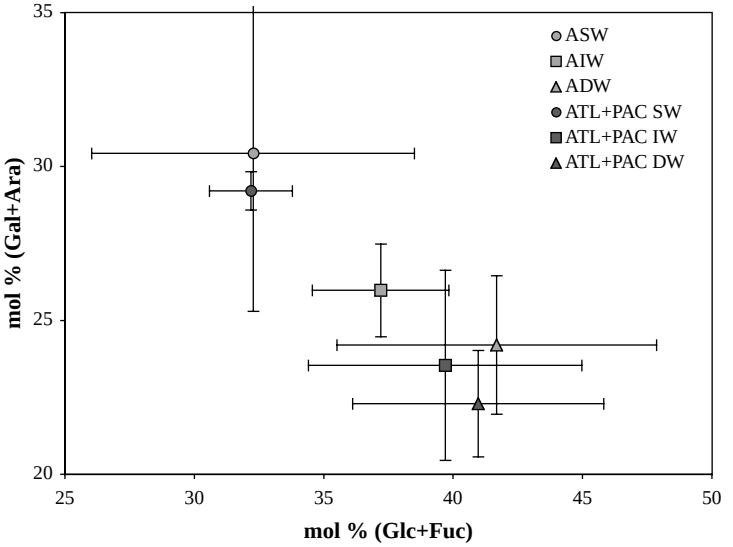


Fig. 10. Property plot showing the diagenetic state of marine UDOM based on the neutral sugar composition (mol% galactose and arabinose versus mol% glucose and fucose). UDOM samples from the Arctic Mediterranean Sea were grouped according to depth (ASW $\leqslant$ 55 m; AIW = 60–600 m; ADW $\geqslant$ 1000 m) and compared to pooled UDOM samples from the Atlantic and Pacific oceans (McCarthy et al., 1996; Skoog and Benner, 1997).

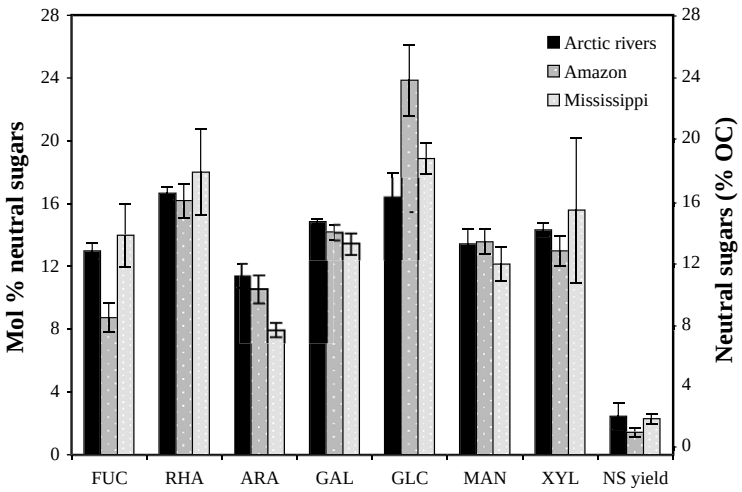


Fig. 11. Average neutral sugar composition and neutral sugar yield of UDOM samples from different major world rivers. Arctic river UDOM represents the average of UDOM samples from Ob and Yenisei. Amazon data were taken from Hedges et al. (1994), and Mississippi data from Benner and Opsahl (2001).

state reflect the variable composition of dominant polysaccharides. The structure and origin of those heteropolysaccharides remains to be discovered and will supply new clues for carbohydrate biogeochemistry.

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