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Distributions of nutrients, dissolved organic carbon and carbohydrates in the western Arctic Ocean

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Abstract

Seawater samples were collected from stations along a transect across the shelf–basin interface in the western Arctic Ocean during September 2002, and analyzed for nutrients, dissolved organic carbon (DOC), and total dissolved carbohydrate (TDCHO) constituents, including monosaccharides (MCHO) and polysaccharides (PCHO). Nutrients (nitrate, ammonium, phosphate and dissolved silica) were depleted at the surface, especially nitrate. Their concentrations increased with increasing depth, with maxima centered at ~125 m depth within the halocline layer, then decreased with increasing depth below the maxima. Both ammonium and phosphate concentrations were elevated in shelf bottom waters, indicating a possible nutrient source from sediments, and in a plume that extended into the upper halocline waters offshore. Concentrations of DOC ranged from 45 to 85 μM and had an inverse correlation with salinity, indicating that mixing is a control on DOC concentrations. Concentrations of TDCHO ranged from 2.5 to 19 μM-C, comprising 13–20% of the bulk DOC. Higher DOC concentrations were found in the upper water column over the shelf along with higher TDCHO concentrations. Within the TDCHO pool, the concentrations of MCHO ranged from 0.4 to 8.6 μM-C, comprising 20–50% of TDCHO, while PCHO concentrations ranged from 0.5 to 13.6 μM-C, comprising 50–80% of the TDCHO. The MCHO/TDCHO ratio was low in the upper 25 m of the water column, followed by a high MCHO/TDCHO ratio between 25 and 100 m, and a low MCHO/TDCHO ratio again below 100 m. The high MCHO/TDCHO ratio within the halocline layer likely resulted from particle decomposition and associated release of MCHO, whereas the low MCHO/TDCHO (or high PCHO/TDCHO) ratio below the halocline layer could have resulted from slow decomposition and additional particulate CHO sources.

Keywords: Nutrients; Dissolved organic carbon; Carbohydrates; Polysaccharides; Western Arctic Ocean

1. Introduction

Dissolved organic carbon (DOC) is the largest OC pool in the ocean and plays a central role in the global carbon cycle (Hedges, 1992; Hansell and Carlson, 2002). Since the high-temperature catalytic oxidation method was introduced, a growing body of literature describes the distribution of DOC and

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its biogeochemical cycles in marine environments, including Arctic regions (Wheeler et al., 1997; Anderson et al., 1998; Opsahl et al., 1999; Amon and Benner, 2003; Dittmar and Kattner, 2003; Guo et al., 2004; Hansell et al., 2004; Shin and Tanaka, 2004; Davis and Benner, 2005; Mathis et al., 2005). However, the distribution, composition, and cycling pathways of DOC in the Arctic Ocean are still poorly understood, largely due to limited data. The composition of DOC is dependent on allochthonous sources (Dittmar and Kattner, 2003) and biological production and consumption (Hansell and Carlson, 1998). Reported DOC concentrations in surface waters of the Arctic Ocean have ranged from 60 to 140 μM (Gordon and Cranford, 1985; Olsson and Anderson, 1997; Wheeler et al., 1997). The total riverine DOC input to the Arctic Ocean is on the order of 25×10^{12} g-C/yr, the highest of all the oceans on a volume basis (Opsahl and Benner, 1997; Dittmar and Kattner, 2003). In addition to terrigenous sources, DOC in the Arctic Ocean is derived from algal blooms (Gosselin et al., 1997), sea ice related processes (Smith et al., 1987; Eicken, 2003), and transport from the Atlantic, mainly in the Atlantic layer (AL), and from the Pacific, especially in the upper water column of the western Arctic (Wheeler et al., 1997; Walsh et al., 1997; Pickart, 2004).

Dissolved organic matter is a key substrate for heterotrophic microorganisms in the ocean (Kähler et al., 1997; Rich et al., 1997), and labile carbohydrates are readily utilized components of the DOC pool (Kirchman et al., 2001). Carbohydrates account for the largest identified fraction of DOC in the ocean, ranging from 3% to 30% of the bulk DOC (Pakulski and Benner, 1994; Benner 2002; Hung et al., 2003). Other characterized organic constituents, such as amino acids, uronic acids, aldehydes and ketones, account for less than 12% of DOC; the rest of DOC is uncharacterized. Carbohydrates, especially acid polysaccharides, are a surface reactive organic component and play an important role in the marine carbon cycle (Alldredge et al., 1993; Engel et al., 2004) and trace element scavenging (Guo et al., 2002; Santschi et al., 2003).

Carbohydrates comprise 10–70% of the OC in plant cells (Romankevich, 1984). Carbohydrates in seawater either originate from direct biogenic input, via release from organisms (Biddanda and Benner, 1997; Hama and Yanagi, 2001), decomposition of organic matter (Hellebust, 1965), and viral lysis (Jumars et al., 1989), or allochthonous sources such as river runoff (Guéguen et al., 2006), sediment resuspension (Arnosti and Holmer, 1999), and lateral advection (Winsor and Chapman, 2004). Carbohydrates are present in all marine environments, but with variable concentrations. For example, concentrations of total carbohydrates in the surface ocean were reported to be 24 μM-C in the Gulf of Mexico (Hung et al., 2003), 7–11 μM-C in the North Atlantic (Burney et al., 1979; Witter and Luther, 2002), 14–20 μM-C in Antarctic waters (Fabiano et al., 1995), 20–30 μM-C in the Pacific (Pakulski and Benner, 1994), and 5–16 μM in the Bering Sea (Guo et al., 2004). However, little is known about the distribution of carbohydrates and their partitioning between monosaccharides (MCHO) and polysaccharides (PCHO) in the western Arctic Ocean, although neutral sugar distributions have been reported (Rich et al., 1997; Amon and Benner, 2003).

In the present study, seawater samples were collected along a transect across the shelf–basin interface in the western Arctic Ocean during September 2002 to examine distributions of nutrients (nitrate, ammonium, phosphate, and dissolved silica), DOC, carbohydrate species, including MCHO and PCHO, and their relationship to hydrographic parameters. An intensive study of the same region was conducted in spring and early summer of 2002 under the aegis of the shelf–basin interaction (SBI) program (Codispoti et al., 2005; Davis and Benner, 2005; Mathis et al., 2005). The present study adds to those findings by presenting data from September, near the time of maximal ice retreat, in a year when sea ice extent was well below the average for the previous two decades (Serreze et al., 2003).

2. Materials and methods

2.1. Study area and sampling

The water column in the western Arctic Ocean is comprised of five major layers (Codispoti et al., 2005). The polar mixed layer (PML), which extends from the surface to between 25 and 50 m depending on season and location, receives most inputs of freshwater from rivers and melting ice. The upper halocline layer (UHL), extending from 50 m to about 200 m, is composed mainly of Pacific origin water that transits through Bering Strait during late spring, summer and fall at an average rate of 0.8 Sv.

(Macdonald et al., 2002; Carmack, 2000) and carries elevated concentrations of nutrients (Codispoti et al., 2005) and is defined by a salinity of approximately 33.1 (Carmack, 2000; Rudels, 2001). The lower halocline layer (LHL) is found beneath the UHL, with salinities ranging from about 34.2 to 34.6 (Jones and Anderson, 1986; Macdonald et al. 2004), and originates mainly from the Atlantic. The AL extends from about 250–850 m and is warmer and more saline than the halocline waters. The Canadian basin deep water (CBDW) is found at depths greater than 850–1000 m, and has properties similar to those of the Atlantic inflow through Fram Strait (Schlosser et al., 1995; Swift et al., 1997; Codispoti et al. 2005).

The central deep basin in the Arctic Ocean, ca. 70% of total area, is covered by sea ice throughout the year, while the shelf seas are seasonally ice-free during summer. The Arctic sea ice minimum extent in summer has been reduced by ~2.8%/decade for the last two decades (Cavalieri et al., 1997). In the summer of 2002, an anomalous Arctic ice melt and retreat occurred, with record low ice extent ca. 14% less than the median for 1979–2000 (Serreze et al., 2003). Similar unusually low ice extent was observed in subsequent years (National Oceanic and Atmospheric Administration, 2006). The amplified warming may alter the biogeochemical cycle in the Arctic Ocean, which remains poorly understood.

Water sampling was conducted in September 2002 during the R/V Mirai cruise (MR02-K05) and the sampling locations are shown in Fig. 1 and Table 1. Our sampling was conducted from the shelf to near the ice-edge in a region usually covered by sea ice in summer, but ice-free during this historic record ice melt and retreat event. In addition to a break/slope station (BRW06), a transect with eight stations across the Chukchi shelf/basin interface was sampled.

Seawater samples were collected using 12 L Niskin bottles mounted on a CTD-rosette. The vertical profiles of temperature and salinity were directly obtained from the CTD sensors, and concentrations of nutrients (N, P, and Si), DO and Chl-*a* were measured on board by Marine Works Japan on behalf of Japan Marine Science and Technology Center (JAMSTEC).

Samples for DOC and carbohydrates were obtained by filtration of water samples through GF/F glass fiber filters (precombusted for 5 h at 500 °C). Samples for DOC analysis were collected into 24 ml glass vials (pre-combusted for 5 h at 550 °C), and then two drops of concentrated HCl were immediately added. Samples were kept in a refrigerator (2–4 °C) until analysis. Samples for carbohydrate analysis were collected into 50 ml acid-cleaned polyethylene bottles (pre-cleaned with 2 N HCl and thoroughly rinsed with Milli-Q water), and immediately frozen at −20 °C until analysis.

2.2. Measurements of nutrients, dissolved oxygen and Chlorophyll-a

Concentrations of nutrients, including nitrate (NO_3^-), nitrite (NO_2^-), ammonium (NH_4^+), phosphate (PO_4^{3-}), and dissolved silica ($Si(OH)_4$) were measured on board with an auto-analyzer (TRACSS-800 continuous flow analytical 4-channel system) using standard methods of Grasshoff et al. (1983). Reproducibility was 0.06–1.3% in terms of the coefficient of variation. Dissolved oxygen (DO) was determined by the Winkler method based on Dickson (1994). Concentrations of Chl-*a* were determined on board using a Turner fluorometer (10-AU-005).

2.3. Determination of dissolved organic carbon

DOC was determined by a high-temperature catalytic oxidation method using a Shimadzu TOC-V analyzer (Guo et al., 1994). Briefly, acidified seawater samples were purged with pure air for 5 min to eliminate inorganic carbon, and then 150 μl were directly injected into the vertical furnace, which contained a standard platinum catalyst at a temperature of 720 °C. Oxidation of the DOC was followed by non-dispersive infrared detection of the generated carbon dioxide. Only the instrument blank was considered as the DOC blank in the calculation of DOC concentrations (Guo et al., 1995). During the experiments, the instrument blank was about 3~6 μM-C. The ceramic covering on top of the standard platinum catalyst in the combustion tube was changed every 2 days during the experimental period, and less than 10 samples were analyzed between injections of Milli-Q water and the working standard solution. With these precautions, control samples had a coefficient of variation of $<5\%$, and the precision, estimated from the standard deviation of replicate injections of seawater, was less than 2% of the mean.

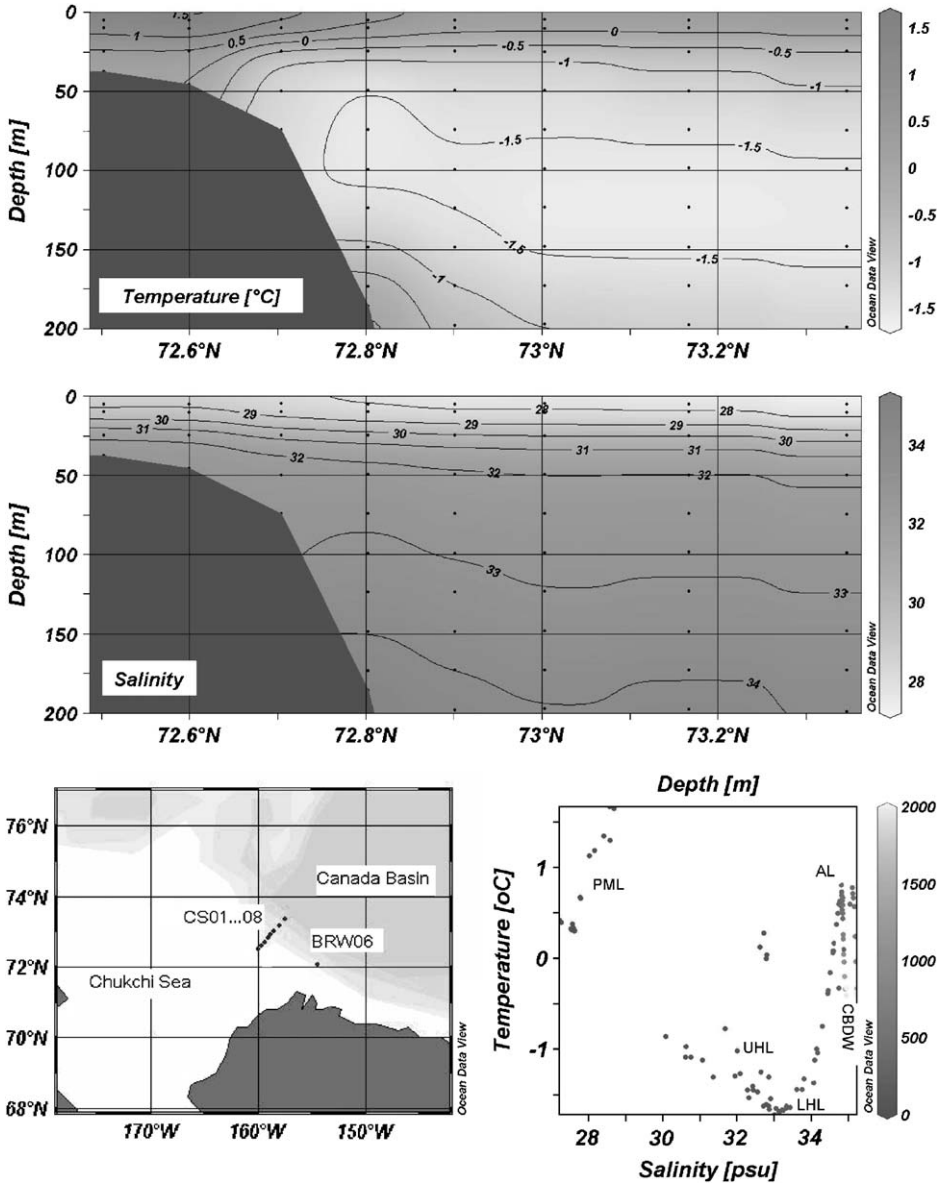

Fig. 1. Sampling locations, temperature–salinity diagram, and distribution of temperature (°C), and salinity along a transect from the Chukchi Shelf to the Canadian Basin in the western Arctic Ocean.

2.4. Determination of carbohydrates

Total dissolved carbohydrate (TDCHO) concentrations, including mono-saccharides (MCHO) and polysaccharides (PCHO), were determined according to a method given by Hung et al. (2001) modified from Myklestad et al. (1997). Briefly, the samples for TDCHO measurements were hydrolyzed with 1 N HCl inside flame-sealed ampules in an oven at 150 °C for one hour, and then the TDCHO concentration (in terms of μM-C) was measured by oxidizing the free reduced sugars with 2,4,6-tripyridyl-*s*-triazine (TPTZ), followed by spectrophotometric analysis of a colored product of reduced Fe^{2+} and TPTZ. The concentration of MCHO was directly measured without hydrolysis, and the concentration of PCHO was obtained by the difference between TDCHO and MCHO concentrations. The precision of this method was ~10%, as estimated from the coefficient of variation (Hung et al., 2001).

Table 1
Sampling location, date and water depth at each station

Station	Date (m/d/y)	Long (°E)	Lat (°N)	Depth (m)
CS-01	9/8/2002	159.998	72.503	40
CS-02	9/9/2002	159.699	72.600	75
CS-03	9/9/2002	159.398	72.704	75
CS-04	9/9/2002	159.100	72.803	190
CS-05	9/9/2002	158.798	72.901	400
CS-06	9/9/2002	158.493	73.003	1300
CS-07	9/9/2002	158.005	73.167	2420
CS-08	9/9/2002	157.475	73.346	3050
BRW-06	9/7/2002	154.506	72.068	1200

3. Results and discussion

3.1. Hydrographic features

The surface water temperature decreased from $>1.5\,^{\circ}C$ over the shelf to near $0\,^{\circ}C$ over the basin (Fig. 1). Surface water salinity was also higher over the shelf compared with the basin area, indicating the influence of melting sea ice, consistent with the extreme recorded sea-ice melting and retreat event in the summer of 2002 (Serreze et al., 2003).

According to the temperature-salinity diagram (Fig. 1), four to five water masses in the study area could be identified, similar to those described in previous studies (Aagaard et al., 1981; Schlosser et al., 1995; Swift et al., 1997; Codispoti et al., 2005): (1) surface water, extending from the surface to ~30–50 m, with salinities of 28–31 and temperatures of 0–1.5 °C, (2) cold and salty water from ~50 to 200 m, comprising the UHL, with characteristic salinities of 32.5–34 and temperatures of −1.0 to −1.7 °C, (3) warmer and more saline water just below 200 m, producing only a slight inflection on the T–S diagram that corresponds to the LHL, (4) the AL, with salinities of 34.8–35 and temperatures of 0.3–0.7 °C, and (5) CBDW, below 1000 m depth, with salinities >34.8 and temperatures <0 °C. The UHL and LHL shoaled by about 40 m near the shelf break; downward sloping isopycnals were also observed there by Pickart et al. (2005) and were attributed to the eastward shelf break jet.

3.2. Distributions of dissolved oxygen and nutrients

The concentration of DO showed a strong vertical gradient, with higher values (300–70 μmol/kg) in the surface mixed layer and lower values (250–300 μmol/kg) in the halocline layers (Fig. 2). The concentration of DO also showed a gradient along the shelf–basin transect (Fig. 2). DO levels found in the upper 50 m were lower over the shelf (275–325 μmol/kg) than farther offshore (325–375 μmol/kg), and especially low DO levels (275–300 μmol/kg) were found in bottom waters over the shelf (Fig. 2), likely due to organic matter decomposition within the sediments or at the sediment–water interface. Oxygen concentrations throughout the upper 200 m were less than those reported by Hill and Cota (2005) for the nearby East Hanna Shoal transect, probably reflecting decreased primary productivity in surface waters and continued net consumption of oxygen below about 30 m depth, which was observed between May and July as well (Hill and Cota, 2005). However, lower oxygen could have resulted from advection of lower oxygen water into the area. In August 2002, Falkner et al. (2005) observed oxygen concentrations as low as 200 μmol/kg in the Chukchi Borderlands area just to the north and west of the area we sampled in September.

Accompanying the lower DO level, a strongly elevated ammonium concentration (0.5–3.5 μmol/kg) was found in the water column overlying shelf sediments (Fig. 2), due to remineralization of organic matter near the sediment–water interface. The plume of maximal ammonium concentration extended from the shelf bottom water into the halocline layer off the shelf break, showing transport from the shelf offshore. The lateral transport from shelf to basin in the halocline layer can occur in saline waters produced by brine rejection during ice formation over shelves (Aagaard and Carmack, 1989; Jones et al., 1991). The ammonium concentrations in the plume had a minimum at the position of the inferred shelf break jet, increased within the halocline layer offshore between 72.9°N and 73.1°N, and then decreased again farther offshore (Fig. 2). This pattern could have arisen from temporal or spatial variability in the jet, or further ammonium additions due to remineralization of sinking particulate matter offshore.

Concentrations of NO_3^-, PO_4^{3-}, and $Si(OH)_4$ showed similar distribution patterns, increasing rapidly with depth from the surface (NO_3^-: below detection limit; PO_4^{3-}: 0.5; $Si(OH)_4$: 5 μmol/kg) to the center of the halocline layer (NO_3^-: 14–15; PO_4^{3-}: 1.6–1.8; $Si(OH)_4$: 35–40 μmol/kg), then decreasing with depth below the nutrient maxima (Fig. 3). Nitrate concentrations, however, were relatively

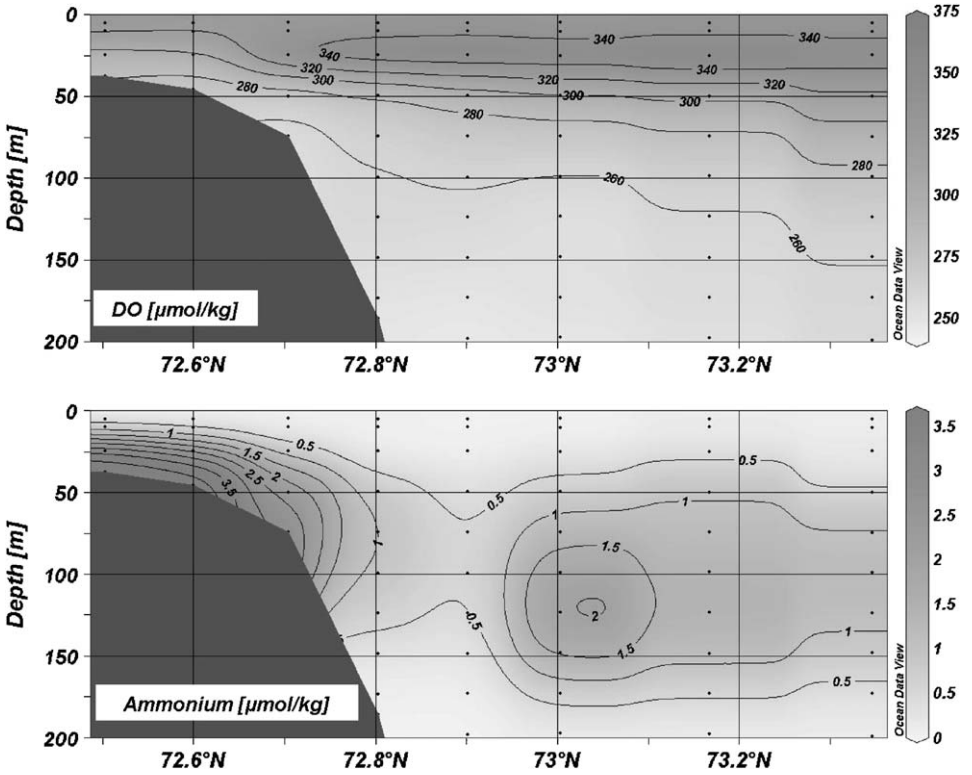

Fig. 2. Section distributions of dissolved oxygen (DO) and ammonium along a transect across the shelf/basin interface in the western Arctic Ocean.

higher in the LHL compared with those of phosphate and silicate. The phosphate and silicate maxima were in the same location as the offshore ammonium maximum and also were located at the depth of the core of the UHL. All of these nutrient distributions showed the effect of the jet at the shelf break, also, with the isolines sloping upward toward the shelf at depths between 150 and 200 m. While NO_3^- was completely depleted at the surface, PO_4^{3-} and $Si(OH)_4$ concentrations were still nonzero. This pattern is characteristic of the PML, which is relatively depleted in nitrate and total dissolved inorganic nitrogen within the SBI study region, due to the influence of Pacific-derived waters that have a similar pattern of nitrate depletion relative to phosphate and silicate (Codispoti et al., 2005).

As noted earlier, the ammonium distribution showed a strong source from the shelf and shelf-break sediments (Fig. 2). PO_4^{3-} also showed somewhat elevated concentrations in the shelf break bottom waters, but not over the shelf. In fact, concentrations of both NO_3^- and $Si(OH)_4$ are lower over the shelf at depths less than about 50 m than at similar depths offshore (Fig. 3). In the case of NO_3^- sediment denitrification could contribute to this pattern (Devol et al., 1997), but since the relative depletion of dissolved silica is similar, enhanced nutrient consumption by algae near the bottom over the shelf is another explanation, especially given elevated Chl-*a* concentrations between 20 m depth and the bottom over the shelf (Fig. 4). Photosynthetically active algae on the sediment surface, mainly diatoms that appeared to have settled after the water column bloom, were found at similar depths on the Bering Sea middle shelf (Alexander et al., 1996). In addition, lower nutrients and warmer temperatures in shelf waters probably also result from an eastward current flow that transports water derived from the Bering Sea shelf (Weingartner et al. 2005).

All of the nutrient distributions were similar to those reported in Codispoti et al. (2005) for the data that were plotted for West Hanna Shoal, East Hanna Shoal, and Barrow Canyon transects, with the exception that our September NO_3^- and $Si(OH)_4$ concentrations were somewhat lower in surface

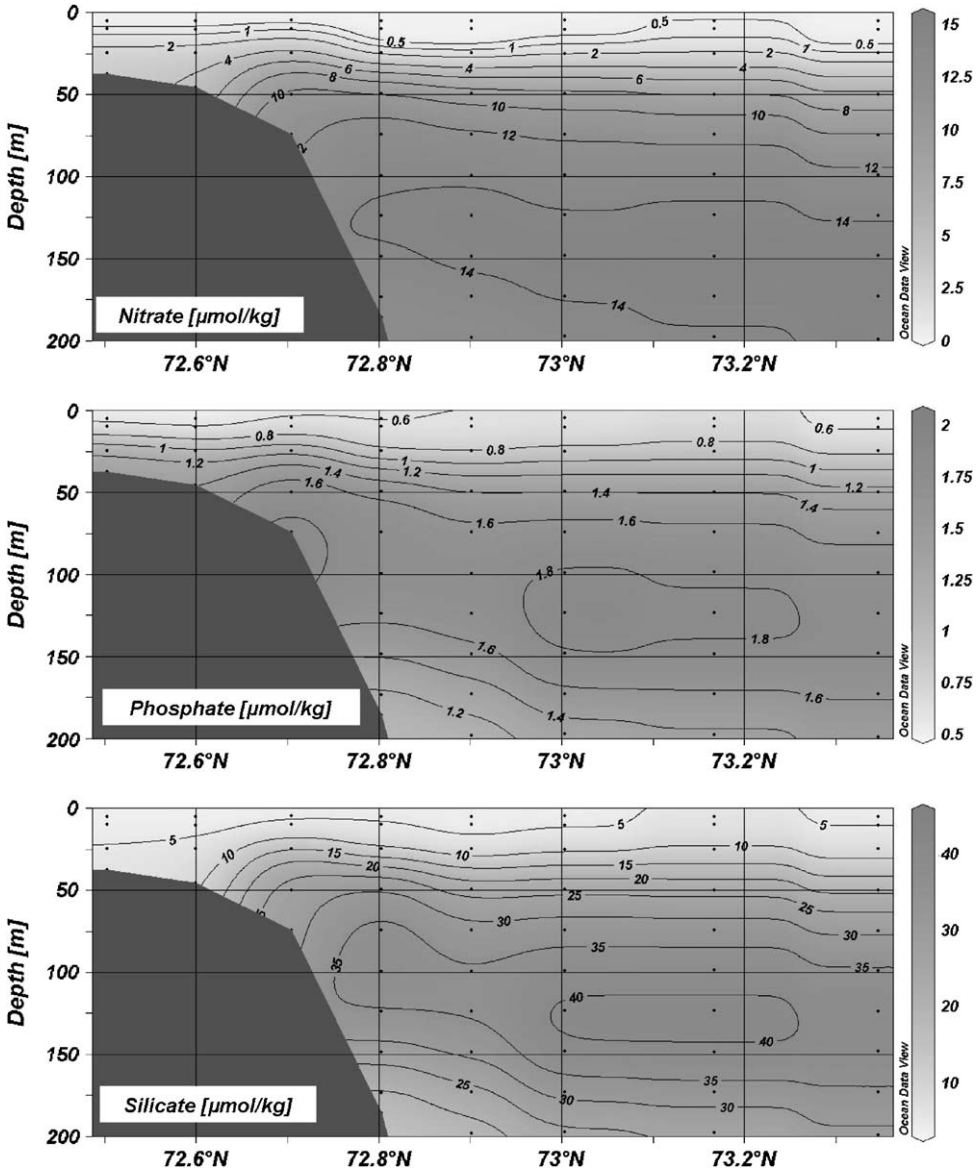

Fig. 3. Distributions of nitrate, phosphate and silicate along a transect across the shelf–basin interface in the western Arctic Ocean.

waters. In particular, plots of NO_3^- vs. salinity, NO_3^- vs. PO_4^{3-}, and $Si(OH)_4$ vs. PO_4^{3-} showed that our data fell centrally within the distributions shown by Codispoti et al. (2005) for summer. For $Si(OH)_4$ our September transect found concentrations depleted below 10 μmol/kg over the shelf to a depth of nearly 50 m, and for NO_3^- shelf concentrations were below 6 μmol/kg above 50 m depth. Offshore the 10 μmol/kg $Si(OH)_4$ isoline was found close to 25 m depth, and the NO_3^- concentrations at 25 m were 1–2 μmol/kg. These levels indicate continuing nutrient consumption after the July August SBI sampling, although the comparisons are not exact because the SBI transects presented were not in exactly the same location as our transect.

3.3. Distributions of Chlorophyll-a and DOC

A subsurface Chl-*a* maximum was centered at ~25 m depth along the shelf–basin transect, with the highest values at shelf stations (0.8–1.2 μg/L), decreasing gradually to 0.2–0.8 μg/L at basin

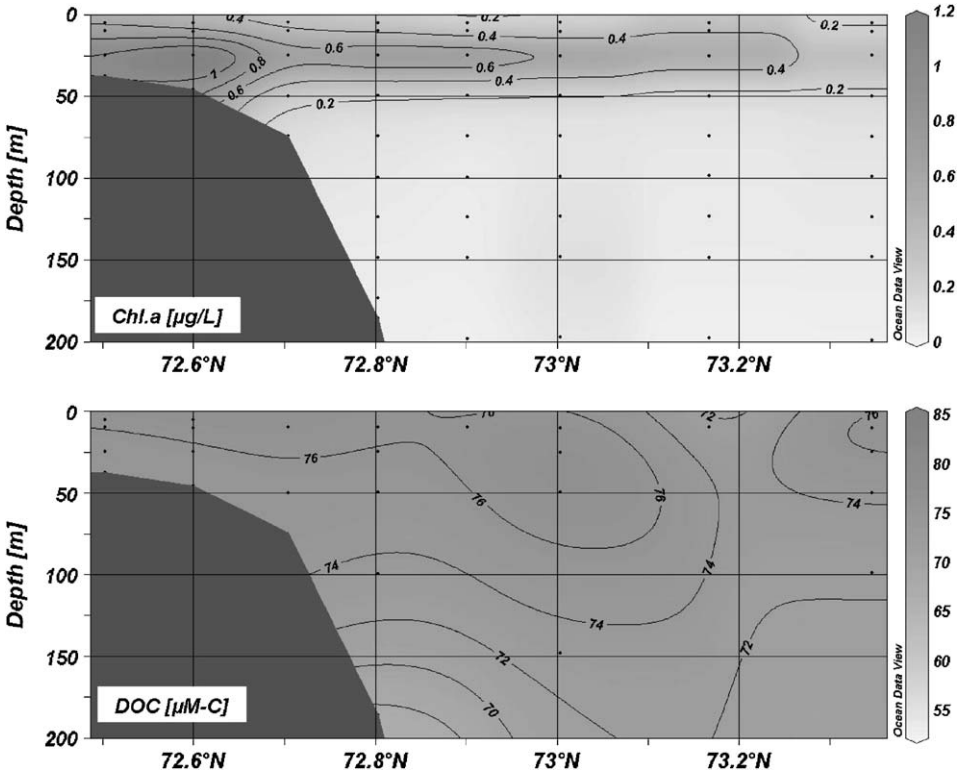

Fig. 4. Distributions of chlorophyll a (Chl-*a*, upper panel) and dissolved organic carbon (DOC, lower panel) along a transect across the shelf–basin interface in the western Arctic Ocean.

stations. The upper boundary of this maximum corresponded closely to the 0.5 µmol/kg nitrate isoline, except over the shelf where ammonium was an additional source of nitrogen; the availability of ammonium probably contributed to the enhanced Chl-*a* maximum over the shelf, also.

At a slope/basin station (BRW06) away from this transect, the vertical profile of Chl-*a* showed an elevated value of 4.0 µg/L at 25 m (see Table 2), higher than values at stations along the section (Fig. 4). The Chl-*a* maximum in the study area was relatively low in comparison with values reported for the ice-edge bloom in the Bering Sea (14 µg/L, Niebauer, et al., 1995), but similar to those reported in shelf waters of the southeastern Bering Sea (0.1–2.6 µg/L, Guo et al., 2004).

Concentrations of DOC ranged from 45 to 85 µM-C in the study area (Fig. 4), with the highest concentrations in the upper water column between 0 and 100 m, decreasing gradually towards 200 m. The vertical distribution of DOC at the station BRW06 also showed a decrease in concentration from 70 µM-C in the surface layer to ~50 µM in the AL (Table 2). Early summer DOC concentrations in the upper 50 m along the West Hanna Shoal transect were slightly less than those we observed, 67.5–70 (Mathis et al., 2005) vs. 72–76 µM-C in early September. Surface water salinity during our observation period was lower, which was consistent with the observations of Mathis et al. (2005) that DOC concentrations were generally higher in less-saline waters, due to the influence of fluvial inputs of DOC. However, concentrations of DOC in the UHL were also about 5 µM-C greater in September than those they observed earlier in the summer, but UHL salinity was unchanged. Both our September shelf surface water and UHL DOC concentrations were very close to the means reported for 2002 summer samples in the SBI area by Davis and Benner (2005). Comparison of all of these measurements confirms the observation of Davis and Benner (2005) that seasonal variations of DOC are minor.

River discharge is important in forming the surface mixed layer in the western Arctic Ocean and also brings a large amount of DOC into the

Table 2
Concentrations of carbohydrates and dissolved organic carbon in the western Arctic Ocean

Station	Depth (m)	Chl-*a* (μg/L)	MCHO (μM-C)	PCHO (μM-C)	TCHO (μM-C)	DOC (μM-C)
CS-01	5	0.45	—	—	12.6	77
CS-01	10	0.69	5.5	10.7	16.2	76
CS-01	25	1.18	4.4	13.6	18.1	73
CS-01	38	0.87	5.7	13.2	18.9	71
CS-02	5	0.36	2.9	8.6	11.6	81
CS-02	10	0.42	7.9	8.6	16.4	79
CS-02	25	1.97	5.9	3.4	9.3	76
CS-02	46	0.56	4.0	0.5	4.5	74
CS-03	10	0.34	5.5	10.3	15.8	77
CS-03	50	0.18	2.2	12.0	14.2	77
CS-04	10	0.26	4.5	8.6	13.0	77
CS-04	25	1.09	8.6	3.4	12.0	77
CS-04	50	0.12	2.9	9.8	12.8	74
CS-04	99	0.07	3.7	6.1	9.9	74
CS-04	186	0.03	—	—	8.1	64
CS-05	10	0.19	1.6	10.5	12.0	74
CS-06	10	0.20	2.0	10.5	12.4	75
CS-06	25	0.92	5.5	8.6	14.1	82
CS-06	50	0.13	5.3	4.3	9.6	77
CS-06	148	0.13	4.7	6.1	10.9	72
CS-07	10	0.45	6.9	8.2	15.1	69
CS-08	10	0.18	6.0	7.9	13.9	72
CS-08	25	0.48	3.7	8.9	12.7	85
CS-08	50	0.17	1.5	5.6	7.0	70
CS-08	99	0.07	0.2	5.9	6.1	71
CS-08	297	—	0.0	1.3	1.3	46
BRW-06	9.4	0.95	4.7	10.2	14.9	65
BRW-06	25	4.22	8.0	6.7	14.7	67
BRW-06	50	0.28	5.8	4.9	10.8	58
BRW-06	98	0.10	5.4	5.1	10.5	53
BRW-06	150	0.06	2.5	5.3	7.9	48
BRW-06	197	0.02	1.4	6.1	7.5	45
BRW-06	247	—	2.1	6.1	8.2	44
BRW-06	496	—	1.7	7.2	8.9	45
BRW-06	743	—	2.0	9.3	11.4	47
BRW-06	988	—	2.4	10.4	12.8	52
BRW-06	1214	—	2.7	12.4	15.1	49

DOC = dissolved organic carbon; MCHO = monosaccharide; PCHO = polysaccharide; TCHO = total carbohydrate; —, no data.

surface mixed layer due to high DOC concentrations in Arctic rivers (Dittmar and Kattner, 2003). Indeed, the concentration of DOC was significantly negatively correlated with salinity ($P<0.01$) in several studies of arctic shelf-slope waters, suggesting a conservative mixing of terrigenous DOC (Guay et al., 1999; Shin and Tanaka, 2004; Guéguen et al., 2005) and an overall physical mixing control on DOC distributions. Hansell et al. (2004) reported that terrigenous DOC is degraded within the Beaufort Gyre with a half-life of 7.1 ± 3.0 years, but that time scale of decomposition is long relative to those of surface water and UHL mixing processes in our study area. In addition to freshwater inputs, phytoplankton production in the shelf and the ice edge algal bloom seemed to contribute to the DOC pool locally (Fig. 4), although Mathis et al. (2005) found that sea ice meltwater seemed to only dilute DOC concentrations.

3.4. Distributions of carbohydrate species

Concentrations of TDCHO ranged from 1.3 to 18.9 μM-C, with an average of 11 μM-C. Within the TDCHO, average concentrations of MCHO and PCHO were 3.7 and 7.5 μM-C, respectively. Concentrations of MCHO ranged from 0.4 to 8.6 μM-C and PCHO from 0.5–13.6 μM-C (Fig. 5). Similar to DOC distributions, concentrations of carbohydrate species were higher in the surface mixed layer and lower below 100 m; in fact, the TDCHO decrease could account for about half of the DOC decrease with depth over the upper 200 m. At the farthest offshore station along the transect, and at the slope Station BRW06, TDCHO concentrations decreased more with depth than they did closer to the shelf. The TDCHO decrease was due to decreased MCHO; PCHO varied little in the upper 200 m, and actually increased with depth in the AL at the slope station.

Though DOC and carbohydrates are both produced by biological processes, there was no significant correlation between Chl-*a* and DOC, TDCHO, MCHO, or PCHO (not shown), indicating that phytoplankton biomass was not the main factor controlling the concentration of DOC and carbohydrates in the water column. Instead, phytoplankton production coupled with microbial and grazing activities often control DOC and carbohydrate concentrations in seawater (Strom et al., 1997; Hopkinson et al., 2002; Guo et al., 2004). However, TDCHO, MCHO and PCHO were negatively

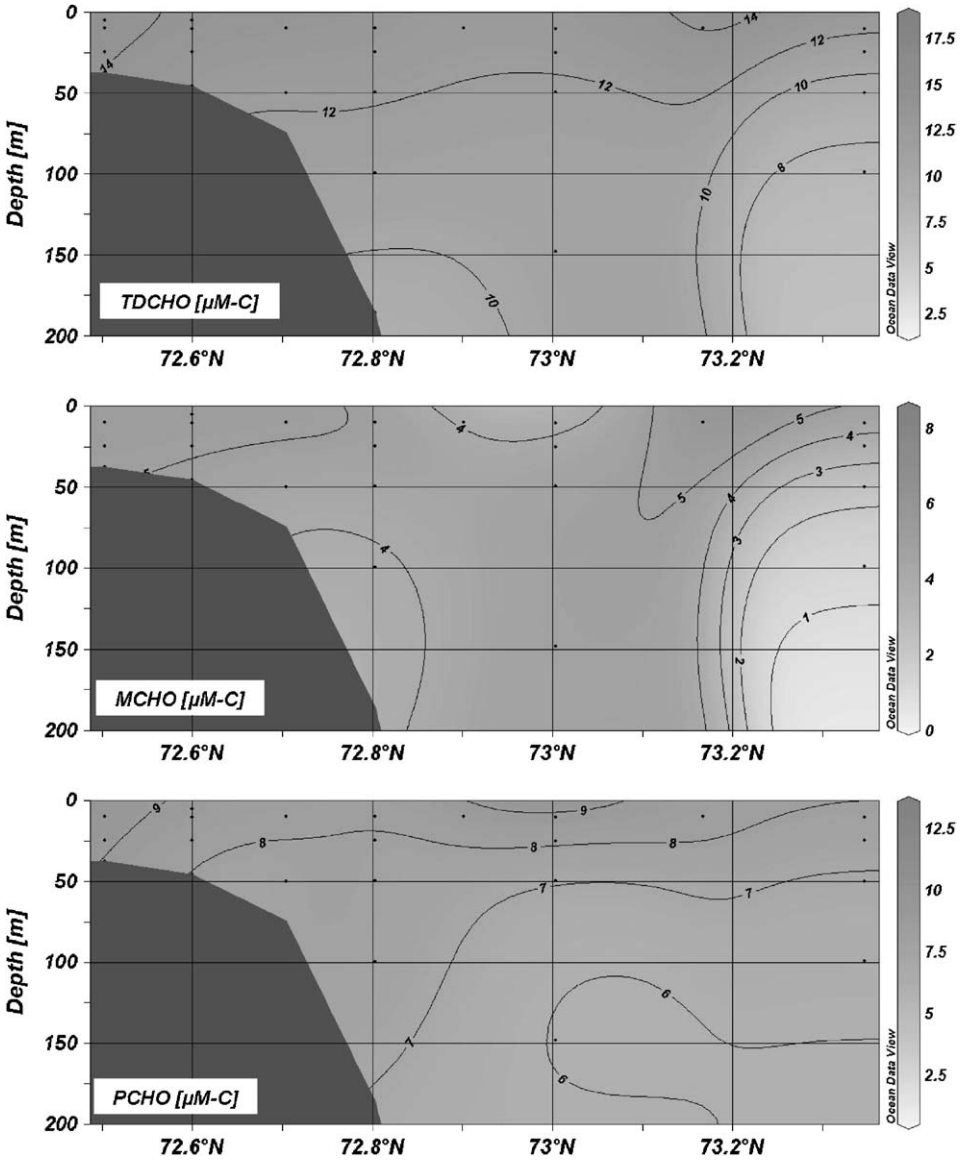

Fig. 5. Distributions of total dissolved carbohydrates (TDCHO, upper panel), monosaccharides (MCHO, middle panel), and polysaccharides (PCHO, lower panel), along a transect from the Chukchi Sea to the Canadian Basin (all in µM-C).

correlated with salinity ($P<0.01$, 0.01 and 0.05, respectively), indicating that sources including freshwater inputs and ice algae could be important for carbohydrates in the western Arctic Ocean (Krembs et al., 2002; Melnikov et al., 2002).

Concentrations of TDCHO, MCHO and PCHO at station BRW06 decreased from the surface layer (10–15 µM-C for TDCHO; 5–8 µM-C for MCHO; and 5–10 µM-C for PCHO, respectively) to 200 m (TDCHO: 8–10 µM-C; MCHO: 2–5 µM-C; PCHO: 5–6 µM-C) (Fig. 6), the decrease occurring in UHL waters. Below 200 m, in the AL, both TDCHO and PCHO increased with increasing depth (TDCHO: from 8–15 µM-C; PCHO: from 5–12 µM-C). DOC concentrations increased by a similar amount over the same depth range, i.e., the DOC concentration increase could be largely attributed to the increase in PCHO. No difference, or a small decrease, in DOC between the UHL and AL was observed by others working in this area in 2002 (Davis and Benner, 2005; Mathis et al., 2005). Comparing the data sets it appears that dissolved organic matter concentrations were unusually low in the BRW06 UHL samples (as opposed to AL concentrations

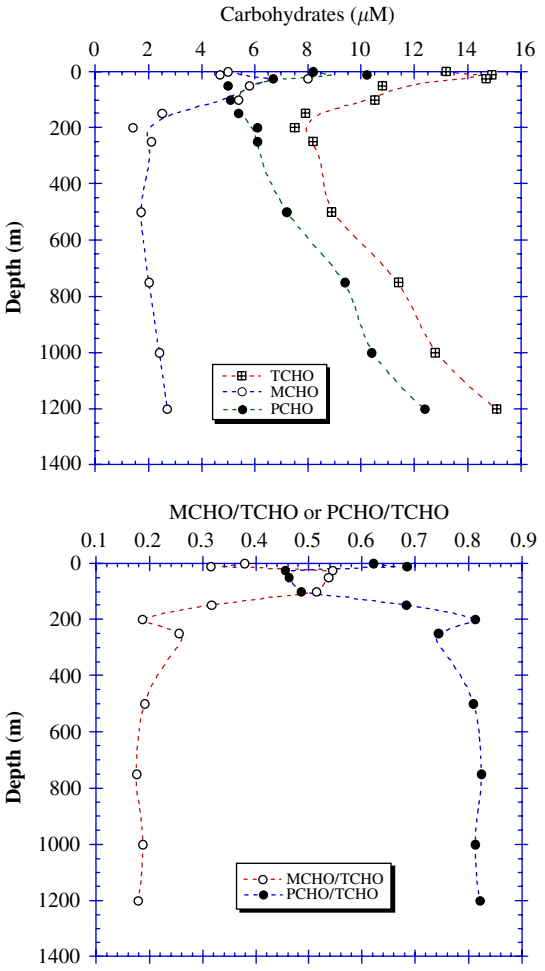

Fig. 6. Vertical profiles of total carbohydrates (TDCHO), monosaccharides (MCHO) and polysaccharides (PCHO) (all in μM-C), and ratios of MCHO/TDCHO and PCHO/TDCHO at the station BRW06 (MCHO: monosaccharides; PCHO: polysaccharides; TDCHO: total dissolved carbohydrates).

being elevated), suggesting biological consumption, which is also consistent with the lower oxygen concentrations in September samples.

The distribution of carbohydrates between MCHO and PCHO changed with water depth. For example, the ratio of MCHO to TDCHO at station BRW06 first increased from ~0.3 in the surface water to >0.5 in the surface mixed layer and then decreased again to ~0.2 below 100 m, while the ratio of PCHO to TDCHO first decreased from ~0.65 at the surface to <0.5 in the surface mixed layer, and then increased to 0.8 below 100 m (Fig. 6). Below 400 m, both MCHO/TDCHO and PCHO/TDCHO ratios remain fairly constant, with PCHO being the predominant carbohydrate species. Carbohydrates generally have a higher PCHO/TDCHO ratio in the upper water column but a lower PCHO/TDCHO ratio below the euphotic zone in tropical and subtropical ocean regions (Pakulski and Benner, 1994). Engel et al. (2004) proposed that aggregation of PCHO into particles could result in a higher proportion of MCHO in the water column. In the western Arctic, PCHO comprised most carbohydrate in the upper 10–25 m, with a PCHO/TDCHO ratio of 0.62–0.68 (Fig. 6), consistent with those reported for other oceanic environments (Pakulski and Benner, 1994; Hung et al., 2003). Within the halocline layer, MCHO and PCHO were almost equally important, with slightly higher MCHO. Below 100 m, PCHO became the predominant form again (Fig. 6), which is distinctly different from tropical and subtropical oceanic environments. The fact that the MCHO/TDCHO ratio was higher than the PCHO/TDCHO ratio within the halocline layer indicated the net effect of decomposition processes, producing a significant fraction of MCHO or breaking down a significant fraction of PCHO (Figs. 5 and 6), consistent with the oxygen minimum and nutrient maximum, and decreased oxygen (relative to summer) in the halocline. As with the nutrient and oxygen properties of the halocline waters, carbohydrate distributions could be mainly established by processes occurring over the shelf. Lower ratios of MCHO/TDCHO in the deeper water column were likely the result of low rates of heterotrophic decomposition.

The percentages of MCHO and PCHO in the bulk DOC varied from 4–12% and 8–22%, respectively (Table 2). A higher percentage of MCHO in DOC was found in the surface mixed layer, and decreased from ~12% at ~100 m to ~5% in the halocline layer, with a relatively constant value below 200 m in the water column. Our carbohydrate percentages in the bulk DOC were similar to those reported for surface waters in the Gulf of Mexico, Atlantic and Pacific Ocean (10–20%, Pakulski and Benner, 1994, Hung et al., 2001), but with a higher MCHO/TDCHO ratio in the upper water column of the western Arctic Ocean. The vertical variation of the PCHO/DOC ratio was somewhat different from that of MCHO/DOC. While the ratio of MCHO/DOC changed little in the water column below 200 m, the ratio of PCHO/DOC increased with increasing water depth, from ~10% at 200 m to 22% in bottom waters (Table 2, Fig. 6). Hence, the increase in the

percentage of carbohydrates in the bulk DOC in the water column below 200 m was mainly due to the contribution of PCHO. The increase of both MCHO and PCHO concentrations with increasing water depth could simply result from slow decomposition due to low temperature and signatures inherited from northern North Atlantic water masses. We lack data on spatial variation within the basin to determine whether there is either significant addition or removal of carbohydrates in the AL and CBDW, but nutrient and oxygen distributions suggest the composition of these water masses is little altered within the Arctic Basin (Codispoti et al., 2005).

4. Conclusions

In most ways this September, 2002, sampling yielded results similar to those obtained during the more extensive SBI studies in spring and early summer. The water column in the study area remained strongly stratified in early September; as was true throughout the spring and summer stratification resulted from lowered surface water salinity due to freshwater inputs from river discharge and sea ice melting. Concentrations of nutrients were depleted at the surface, to a slightly greater extent than earlier in the summer, and maxima occurred in the halocline. Both phosphate and ammonium also had elevated concentrations in the shelf bottom water, suggesting a strong source from sediments, and a plume of elevated concentrations extended into the upper part of the UHL. Oxygen concentrations were lower throughout the upper 200 m than they were earlier in summer, particularly near the bottom over the shelf.

DOC concentrations were similar to those measured during the SBI cruises earlier in the summer, confirming that seasonal variations are small (Davis and Benner, 2005). Concentrations of DOC and carbohydrates were higher in the upper 100 m of the water column, especially over the shelf and near the ice edge, suggesting that algal blooms and melting ice could be an important source of DOC and carbohydrates locally, resulting in higher ratios of PCHO/TDCHO in the surface water. However, considering all surface water samples, DOC did not correlate with Chl-*a* concentrations, but did correlate negatively with salinity, suggesting that, in addition to biomass, terrestrial inputs, grazing and microbial activities are also important in the supply of DOC in the water column. Because of the strong density gradient and therefore low vertical mixing, organic matter could be trapped in the halocline and decomposed, resulting in a higher MCHO proportion in the halocline layer, or the low mixing could simply preserve water mass characteristics established over the shelf. Lower DOC, TDCHO and oxygen in the halocline layer, accompanied by high nutrient concentrations, reflect the cumulative effects of organic matter decomposition since the water mass formed. Both the TDCHO concentration and PCHO/DOC ratio decreased from the surface to the halocline layer and then increased with increasing water depth, suggesting little decomposition of carbohydrates in deeper water. The relative distributions of DOC, MCHO and PCHO were useful as indicators of biological and physical processes controlling organic matter distribution in the water column.

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