Limnol. Oceanogr., 52(6), 2007, 2434–2444
© 2007, by the American Society of Limnology and Oceanography, Inc.

Quantitative estimates of labile and semi-labile dissolved organic carbon in the western Arctic Ocean: A molecular approach

Jenny Davis and Ronald Benner[1]
University of South Carolina, Marine Science Program, Columbia, South Carolina 29208

Abstract

A novel molecular approach based on carbon-normalized yields of combined amino acids was developed to quantify concentrations of labile (L), semi-labile (S), and refractory (R) dissolved organic carbon (DOC) in shelf and basin waters of the Western Arctic Ocean. Concentrations of L-DOC were seasonally and spatially variable (0.1–14.2 μmol L^{-1}). In contrast, concentrations of S-DOC were much less variable (20.2 $\pm$ 0.68 μmol L^{-1} SE). Average concentrations of L-DOC in shelf waters increased from 0.7 μmol L^{-1} to 2.4 μmol L^{-1} between the spring and summer of 2002 and from 1.4 μmol L^{-1} to 3.9 μmol L^{-1} between the spring and summer of 2004. Primary productivity increased 2–3-fold between spring and summer, indicating a strong linkage between plankton and L-DOC production. Patterns of L-DOC abundance in surface waters are suggestive of multiple mechanisms of L-DOC production, including direct release from phytoplankton and release during grazing. Concentrations of L-DOC were not correlated with those of total DOC. Elevated concentrations of L-DOC in halocline waters (40–200-m depth) of the Canada Basin indicated rapid transport of shelf-produced DOC into the basin. Chemical and physical properties of basin waters with elevated L-DOC concentrations indicated a sediment-derived source of basin L-DOC. The approach presented here for quantifying the labile and semi-labile fractions of DOC is a potentially powerful tool for understanding processes controlling the distribution, production, and utilization of dissolved organic matter.

Favorable light conditions and high nutrient concentrations during the summer result in exceptionally high rates of primary productivity in the Chukchi Sea of the Western Arctic Ocean (Springer and McRoy 1993; Hill and Cota 2005). Off-shelf transport of plankton-derived organic matter from this region has been suggested as a primary driver of metabolism in the adjacent, highly oligotrophic Canada Basin (Walsh et al. 1989). The Chukchi Sea is characterized by strong benthic-pelagic coupling (Grebmeier 1993; Springer and McRoy 1993). Vertical export of particulate organic carbon (POC) from the highly productive water column supports an extremely rich benthic community, which is heavily utilized by benthic-feeding marine mammals. The high rates of particle flux required to sustain such a food web, in combination with the low concentrations of POC measured in the Canada Basin (Wheeler et al. 1997), imply that a significant shelf-to-basin connection would be based largely on dissolved rather than particulate carbon.

Water column production results in seasonal inputs of fresh plankton-derived dissolved organic carbon ([DOC] Davis and Benner 2005), whereas benthic remineralization of sinking organic matter results in substantial DOC release from the sediments (Cooper et al. 2005). Both processes exhibit a large degree of spatial and temporal variability, and consequently large seasonal and spatial variations occur in DOC concentration and reactivity (Davis and Benner 2005). The key to understanding the significance of transported DOC as a substrate for basin metabolism therefore lies in defining its lability.

The potential value of dissolved organic matter (DOM) as a substrate for microbial heterotrophs is generally described in terms of bioavailability. Three categories of DOM availability are defined (labile, semi-labile, and refractory) based on general timescales of biological utilization (Kirchman et al. 1993, Carlson and Ducklow 1995). By this definition, labile DOM is utilized on timescales of hours to weeks. Semi-labile DOM is utilized on timescales of months to years, and refractory DOM is utilized on timescales of centuries to millennia. Depth distributions of DOC can be used to quantify refractory DOM by assuming deep-ocean DOM is used on very long timescales. The old average radiocarbon age of deep-water DOC (Williams and Druffel 1987; Druffel et al. 1992) and its resistance to biological utilization (Barber 1968) are consistent with its definition as refractory DOC. Subtraction of deep-water DOC from surface DOC concentrations yields the combined concentration of labile and semi-labile DOC (Carlson 2002). Microbial bioassay experiments are then necessary to distinguish the labile and semi-labile fractions. It is impractical to conduct bioassay experiments at every sampling station, so the abundance and distribution of the labile fraction is seldom known. This approach has been used to produce quantitative estimates of the semi-labile and labile reservoirs in well-stratified open ocean systems (Carlson and Ducklow 1995; Carlson et al. 2000) but is less applicable in dynamic shelf systems like the Chukchi Sea, which can vary on small spatial scales.

[1] Corresponding author (Benner@biol.sc.edu).

Acknowledgments

We thank the captain, crew, and scientists of the USCGC *Healy* for assistance with sample collection and are grateful to the service group for providing hydrographic and nutrient data. Bob Campbell and Stephan Plourde provided plankton net tow material. Karl Kaiser provided technical support and valuable comments. This manuscript benefited from comments by Elizabeth Canuel and two anonymous reviewers.

This study was supported by National Science Foundation grant OPP-0125301.

This research was conducted as part of the Shelf-Basin Interactions (SBI) program.

Carbon-normalized yields of major biomolecules, such as amino acids and neutral sugars, have been used as qualitative indicators of the diagenetic state and biological availability of natural organic matter (Skoog and Benner 1997; Amon et al. 2001; Benner 2003). Freshly-produced marine DOM is enriched in these compounds, thus elevated concentrations of amino acids and neutral sugars are indicative of labile material. Using a similar approach, McCallister et al. (2006) showed the relationship between polyunsaturated fatty acids and total fatty acids is a useful indicator of DOM reactivity. Molecular indicators of DOM bioavailability are useful for defining spatial and temporal trends of DOM production and consumption (Amon and Benner 2003; Davis and Benner 2005), but this approach has been limited to qualitative assessments of bioavailability.

In the present study we used bioassay experiments and water column distributions of amino acids and DOC to define average carbon-normalized amino acid yields for the labile and semi-labile fractions of Arctic DOM. These data were used in a novel approach to quantitatively calculate the labile (L), semi-labile (S), and refractory (R) components of DOM. Several interesting patterns emerged when this approach was applied to survey data from the Western Arctic Ocean. A strong seasonal increase in the abundance of L-DOC is readily apparent. The distribution of L-DOC does not correlate with total DOC concentrations, a finding which underscores the utility of conceptually dividing DOM into its L, S, and R components. High concentrations of L-DOC in basin waters indicate that shelf-produced organic matter is rapidly transported into the basin. The ability to quantitatively divide DOM into lability-based categories is a powerful tool that will significantly further our understanding of DOM dynamics and the processes that control its distribution.

Materials and methods

Survey sampling—Samples were collected during cruises aboard the USCGC *Healy* in the spring (05 May–15 June) and summer (17 July–26 August) of 2002 and in the spring (15 May–23 June) and summer (18 July–26 August) of 2004. Sampling stations were spread across the Chukchi shelf and several shelf-to-basin transects that targeted known areas of basin ventilation, specifically, the Herald Valley and Barrow Canyon regions. The environments sampled here represent a wide range of trophic states, from highly productive to extremely oligotrophic. Water samples were collected in Niskin bottles mounted on a rosette with a conductivity-temperature-depth (CTD) sensor, chlorophyll, and chromophoric DOM fluorometers. Water samples collected from depths <300 m were filtered (GF/F), whereas samples collected from >300 m were not filtered because of low particle concentrations. All samples were stored frozen until analysis in the home laboratory. In all, 289 water-column samples were collected and analyzed for DOC and dissolved amino acid (DAA) concentrations.

Analyses—DOC and total dissolved nitrogen were analyzed by high-temperature oxidation using a Shimadzu TOC-V with inline chemiluminescent nitrogen detector (Shimadzu TN-1). Instrument blanks (2.5 μmol L^{-1} C, $\pm$0.5 SE) were determined by injection of Milli-Q water and subtracted from measured sample concentrations. Deep Sargasso Sea reference water (47 μmol L^{-1} C, $\pm$0.5 SE) was injected every 6–8 samples to ensure stable operating conditions. Total hydrolysable amino acids were determined with an Agilent high-performance liquid chromatography system equipped with a Licrosphere RP18 (end capped) 4 $\times$ 250 mm column with 5-μm particles. Dissolved samples were hydrolyzed in the vapor phase with 6 mol L^{-1} HCl at 150°C for 32.5 min. After hydrolysis samples were neutralized and then separated as o-phthaldialdehyde derivatives following the method of Lindroth and Mopper (1979) with minor modifications (Kaiser and Benner 2005). The approach used here does not distinguish between free and combined forms of amino acids; all reported concentrations are for total hydrolysable amino acids. Inorganic nutrient measurements were conducted aboard ship by the service team via standard autoanalyzer methods. Statistical tests were performed using JMP version 5.0.1a software (SAS Institute).

Bioassay experiments—Microbial bioassay experiments were conducted to characterize the labile component of Arctic plankton DOM and its amino acid yield. Shipboard experiments were conducted in the dark at ambient surface-water temperatures (−1°C) in 1-liter polypropylene bottles using surface waters collected via a thru-hull pumping system from a depth of about 3 m. Incubation containers were filled with seawater mixed at a 1 : 10 dilution (nine parts 0.2-μm filtered water : one part Whatman GF/C glass fiber (pore size 1.2 μm) filtered water to provide a microbial inoculum) and then amended with 1.75 mL of fresh plankton DOM. The added DOM was isolated by filtration (Whatman glass fiber GF/F) of plankton (mainly diatoms) collected with a 50-μm mesh net during a vertical plankton tow in a diatom bloom. The plankton-derived DOM was added to surface waters collected from two different locations, and each of these experiments was conducted in duplicate. Subsamples were collected at various times during the course of each experiment and analyzed for DOC and DAA concentrations.

Quantifying labile, semi labile, and refractory DOM—As depicted in Fig. 1, the fraction of DOC as amino acid (AA% DOC) decreases as decomposition progresses (Amon et al. 2001; Yamashita and Tanoue 2003). Amino acid yields can therefore be used to define the L, S, and R components of DOM. Using this approach, the R fraction of DOM is defined by the average amino acid yield in deep water (>1,000 m). The deep-water concentrations of DOC and DAA were subtracted from surface water (<200 m) samples leaving the DOC and DAA concentrations in the combined L + S fractions of DOM. The combined L + S DOM was separated into labile and semi-labile components, by solving the simultaneous equations:

$$(L + S)_y = (L_f \times L_y) + (S_f \times S_y) \quad (1)$$

$$L_f + S_f = 1 \quad (2)$$

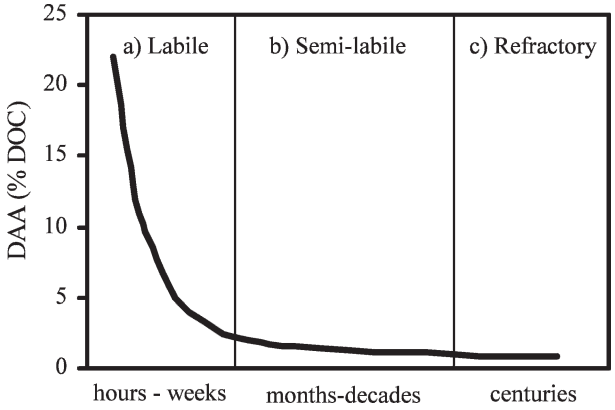

Fig. 1. Conceptual figure showing the relationship between the three major fractions of DOM based on biological reactivity and the amino acid carbon yields associated with each component. (a) Labile, (b) Semi-labile, and (c) Refractory.

where $(L + S)_y$ is the carbon-normalized yield of amino acids in labile + semi-labile DOM; L_y and S_y are amino acid yields of labile and semi-labile DOM, respectively; and L_f and S_f are the fractions of the total L + S reservoir that are labile and semi-labile.

The amino acid yield of labile Arctic DOM (L_y) was determined from analyses of the fresh plankton DOM used in the two bioassay experiments described above. Semi-labile DOM has a continuum of reactivies that span the range between labile and refractory DOM (Fig. 1). The long turnover times by which this material is defined preclude the use of bioassay experiments to determine the average amino acid yield of semi-labile DOM. Because of these long turnover times, the "average" material in the S-DOM reservoir should fall toward the older end of the continuum. The amino acid yield chosen to represent the semi-labile component of DOM (S_y) was the lowest value within the range.

Results

Bioassay experiments—The bioassay experiments demonstrated the highly labile nature of Arctic plankton DOM (Fig. 2). DOC concentrations decreased by 40% or more during the experiments, and DAA concentrations decreased by more than 90%. The carbon-normalized amino acid yield dropped precipitously from an average value of 21% DOC at the beginning of the experiments to an average value of 1.6% DOC after 14 days. The DAA yields at the end of the experiments were much greater than that of deep-water DOC (average yield 0.7% DOC), but the rate of DAA removal had slowed dramatically. Inorganic nutrients were in abundant supply throughout the incubations, indicating that nutrient limitation was not a factor in DOC utilization (Fig. 2). Based on these experiments we defined the "labile" fraction of DOC as that material that is utilized within 14 days. This fraction is characterized by a range of amino acid carbon yields from 1.6–21% DOC.

Calculation of L-, S-, and R-DOC—The approach and calculations used in this study for dividing DOC into its L, S, and R components are dependent upon the amino acid yields chosen to represent these components. Each of these components represents a continuum of reactivities and a range of amino acid yields (Fig. 1), thus it is important to select representative amino acid yields for each component. The value we chose to represent L-DOC (21% DOC), is the amino acid yield measured in freshly-produced DOM from Arctic plankton. As a result, L_y is representative of the most labile DOC in this system, and calculated concentrations of L-DOC based on this yield are likely conservative. The refractory component, by definition, is the deep-water concentrations of DOC and DAA, thus the average deep-water concentrations (DOC = 49.9 μmol L^{-1}, DAA = 85.5 nmol L^{-1}) were chosen to represent R-DOC. Deep-water concentrations were determined from the average concentrations of both constituents in Arctic deep-water samples (>1,000 m) collected during four cruises in 2002 and 2004 (Table 1). Deep-water amino acid yields ranged between 0.43% DOC and 1.09% DOC. The average deep-water amino acid yield was 0.7% DOC.

Defining representative yields for the R and L end members is relatively straightforward, but choosing an appropriate yield for the S fraction is more challenging. Semi-labile DOM is used on timescales of months to decades, and it is not possible to determine the appropriate value experimentally. The range of yields for S-DOC is defined by the minimum DAA yield for L-DOC (1.6% DOC) and the highest yield measured for R-DOC (1.09% DOC). The value chosen here to represent S-DOC (1.1% DOC) is at the lower end of the range. This choice of S_y value has minimal effect on calculated S-DOC concentrations, as is illustrated in the following example. The concentrations of S-DOM calculated using DAA yields of 1.1% DOC (the value we chose) and 1.6% DOC (the yield of the most reactive fraction of S-DOM), are shown in Fig. 3. In most cases the difference between concentrations of S-DOC in the same sample calculated with the two values was less than 1 μmol L^{-1}. Thus, the choice of S_y has minimal effect on calculated L-DOC concentrations as well.

Survey data—DOC concentrations ranged from 120 μmol L^{-1} in surface waters to 46 μmol L^{-1} at 2,000 m. Surface water (<200 m) concentrations were spatially variable (Fig. 4) but averaged between 70 μmol L^{-1} and 73 μmol L^{-1} for all cruises. Dissolved amino acids ranged from 156 nmol L^{-1} to 949 nmol L^{-1} in surface waters and from 66 nmol L^{-1} to 113 nmol L^{-1} in deep water. Surface DAA concentrations were much more variable than DOC concentrations (Fig. 4) and showed a strong seasonal signal with average concentrations increasing from 221 nmol L^{-1} in spring 2002 to 336 nmol L^{-1} in summer 2002 and from 213 nmol L^{-1} in spring 2004 to 374 nmol L^{-1} in summer 2004. Elevated summer concentrations of DAA resulted in elevated carbon-normalized amino acid yields in the summer with average yields of labile + semi-labile DOC $(L + S)_y$ of 1.5% DOC in spring 2002 and 2.8% DOC in summer 2002. Corresponding values for spring and summer 2004 were 2.1% DOC and 4.7% DOC, respectively.

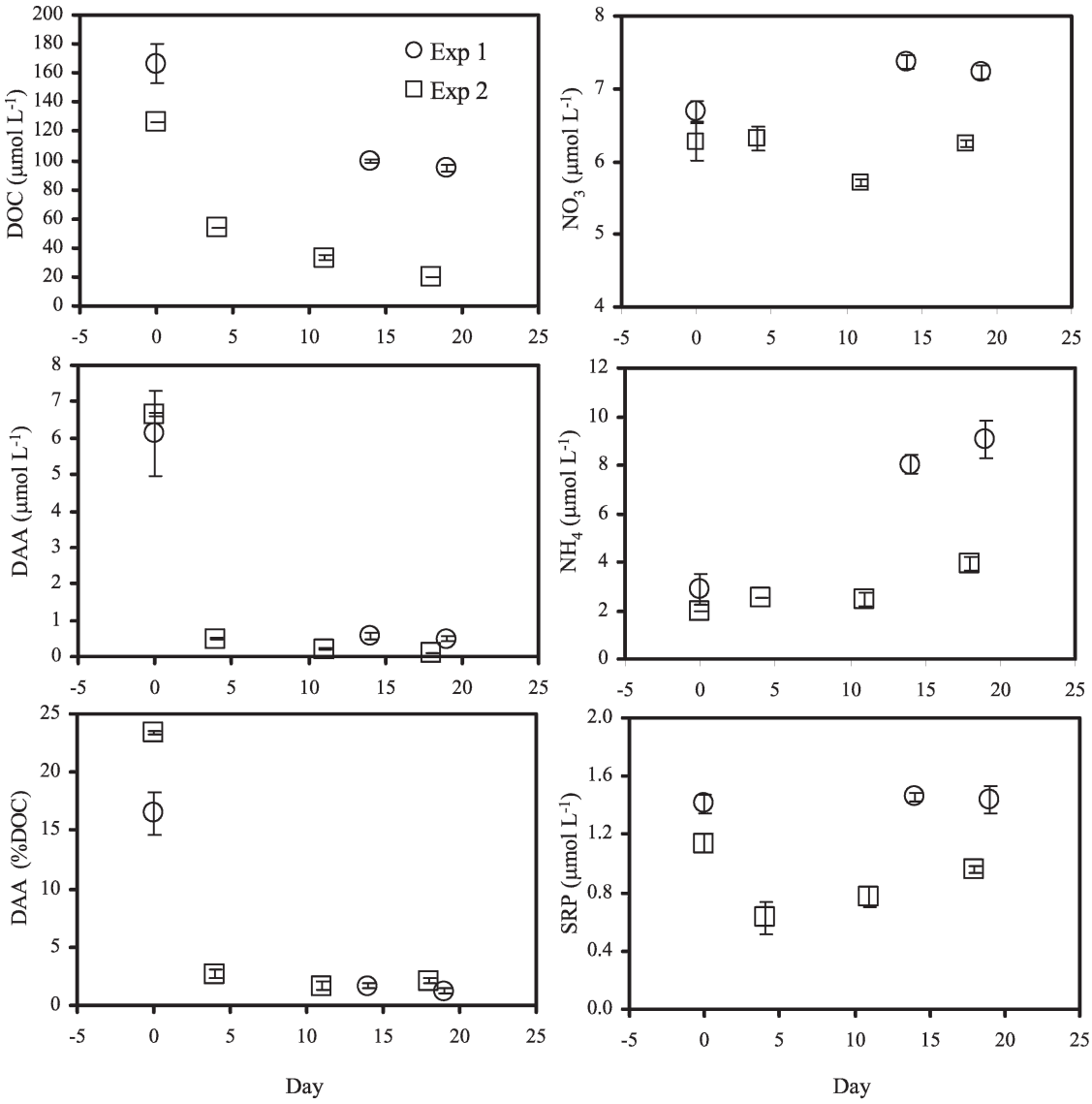

Fig. 2. Changes in DOC, DAA, amino acid yield (% DOC), NO_3, NH_4, and soluble reactive phosphorous (SRP) during decomposition of fresh Arctic plankton DOM.

Seasonal depth distributions of L-DOC and S-DOC are presented in Fig. 5. In the spring of 2002, concentrations of L-DOC were <2 μmol L^{-1} throughout the upper 200 m. Based on spring 2002 distributions, we used 2 μmol L^{-1} as a reference point for defining "elevated" concentrations of L-DOC. In the summer of 2002, concentrations of L-DOC exceeded 2 μmol L^{-1} in most samples from depths <50 m (average 2.96 $\pm$ 2.44), with concentrations as high as 12 μmol L^{-1} (Fig. 5). In 2004, concentrations of L-DOC were elevated in both seasons, relative to 2002, with values as high as 6 μmol L^{-1} in spring and 14 μmol L^{-1} in summer. Seasonal depth distributions mirrored those detected in 2002, with little change in concentration with depth in the spring and a general trend of decreasing concentrations with depth in summer (Fig. 5). In all seasons, S-DOC was more abundant than L-DOC, with concentrations reaching >40 μmol L^{-1} in some surface stations in 2004 (Table 2; Fig. 5). One noticeable difference among sampling periods was the elevated concentrations of L-DOC at depth in 2004, with concentrations up to 6–8 μmol L^{-1} at depths of 140 m (Fig. 5). These samples will be discussed separately.

Table 1. Seasonal averages of DOC and DAA for all samples from >1,000-m depth. Values in parentheses are standard errors. Refractory DOC and DAA are defined as the average concentrations over all seasons.

Season	DOC (μmol L^{-1})	*n*	DAA (nmol L^{-1})	*n*
Spring 2002	48.8 ($\pm$0.81)	15	76.0 ($\pm$3.3)	8
Summer 2002	50.6 ($\pm$0.77)	17	83.4 ($\pm$2.8)	8
Spring 2004	50.6	2	84.3	2
Summer 2004	50.5 ($\pm$1.6)	10	108.0 ($\pm$5.5)	4
Refractory	49.9 ($\pm$0.5)	44	85.5 ($\pm$3.5)	22

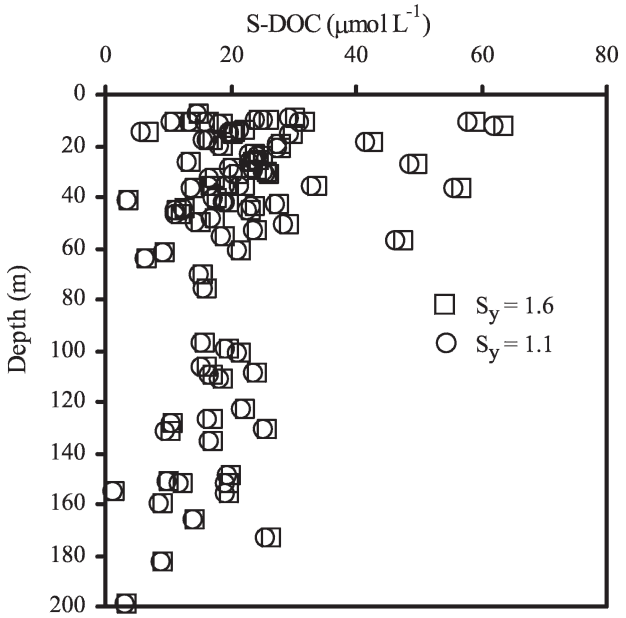

Fig. 3. Concentrations of semi-labile DOC in summer 2004 calculated using values of 1.1 and 1.6 as representative amino acid yields of S-DOC.

Calculated surface-water (<200 m) concentrations of S-DOC averaged 21.6 μmol L^{-1} ($\pm$0.68 SE) across all sampling seasons and did not change significantly on a seasonal or annual basis (Table 2). In contrast, average surface-water concentrations of L-DOC ranged from 0.7 μmol L^{-1} to 3.9 μmol L^{-1}, and analysis of variance followed by Tukey's means comparisons detected significant differences in the concentrations of L-DOC among the four seasons ($F_{3,189} = 20.95$, $p < 0.05$). L-DOC exhibited both seasonal and annual trends with significantly greater concentrations in summer than spring of both years (2002, $p < 0.05$; 2004, $p < 0.001$), and significantly greater concentrations in summer of 2004 than in summer of 2002 ($p < 0.01$). In 2002, the average concentration of L-DOC was 3.4$\times$ greater in summer than in spring. In 2004, the average concentration of L-DOC increased by a factor of 2.8 between seasons. Averages of L-, S-, and R-DOC by sampling season indicate that 1–5% of bulk Arctic DOC is labile and 26–30% is semi-labile. The majority of DOC (~70%) in all seasons was refractory.

No significant relationships were detected among calculated concentrations of labile and semi-labile DOC and chlorophyll fluorescence, dissolved oxygen, total dissolved nitrogen, or ultraviolet absorption at 350 nm (an indicator

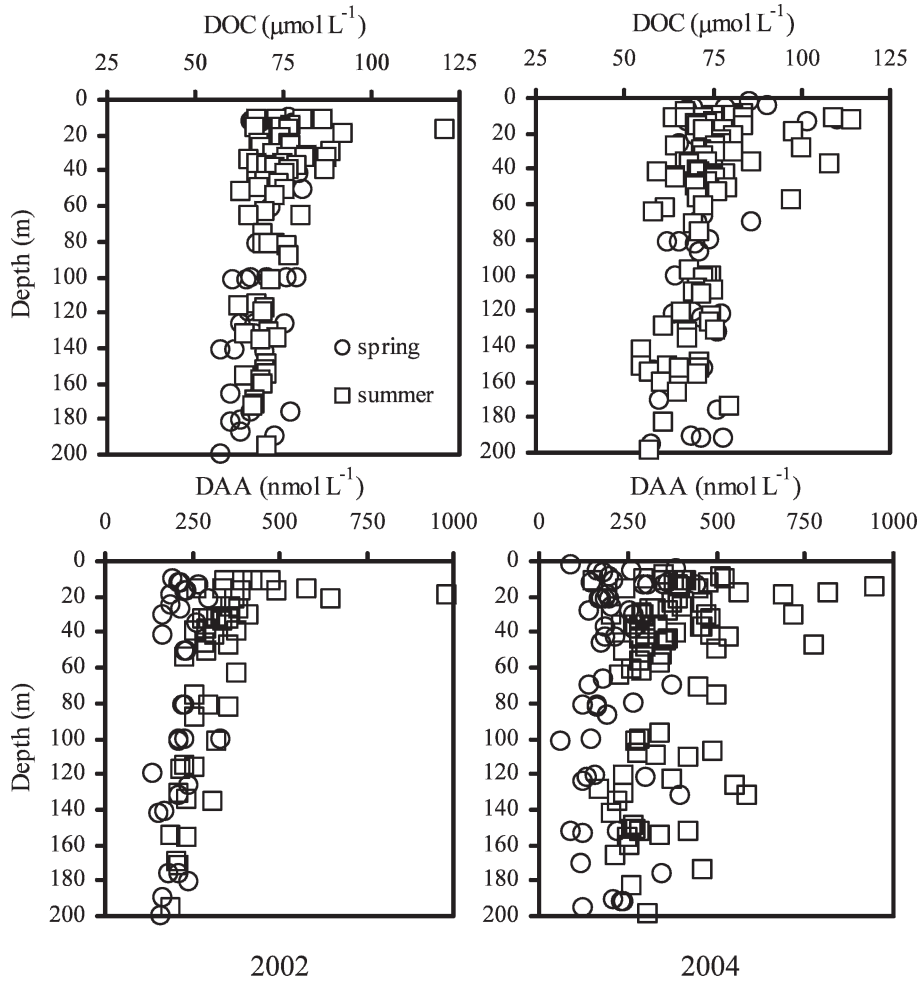

Fig. 4. Depth distributions of DOC and total hydrolyzable DAA by season and year.

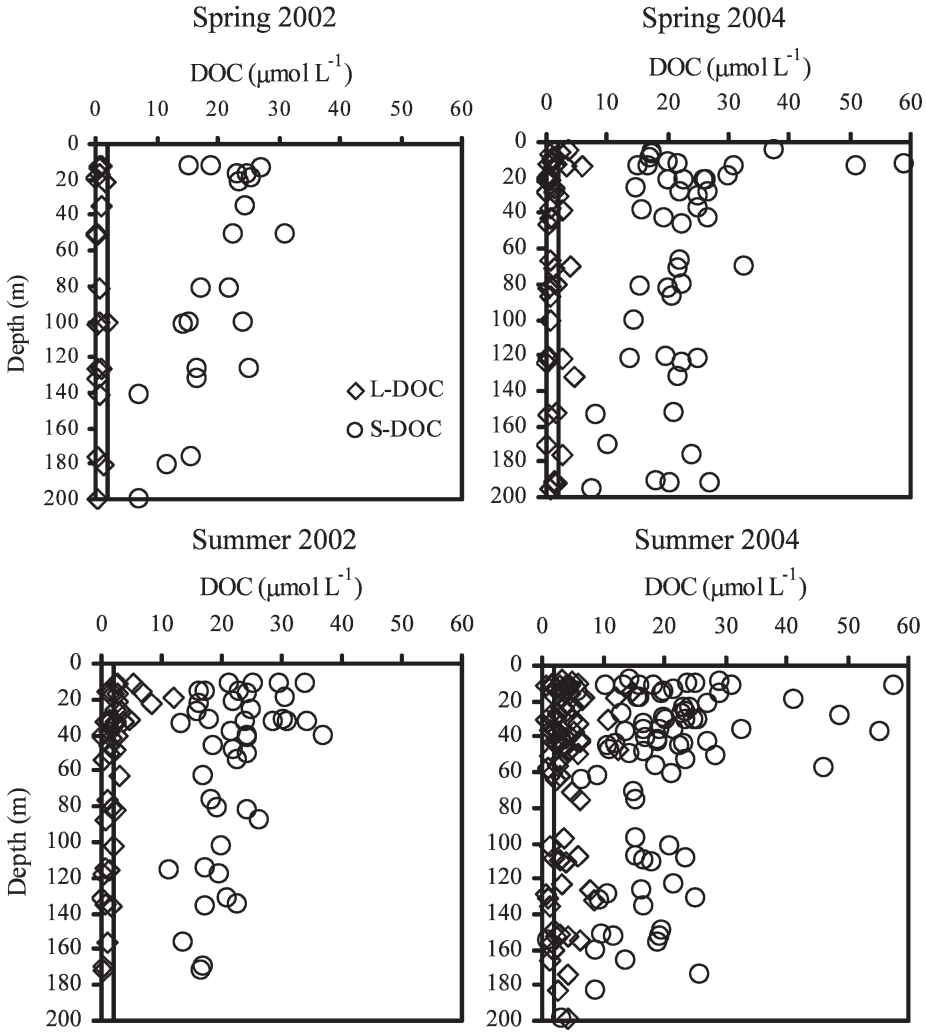

Fig. 5. Calculated concentrations of labile and semi-labile DOC in the upper 200 m by season. Elevated L-DOC concentrations (>2 μmol L^{-1}) are indicated by vertical line.

of terrigenous sources; data not shown). The lack of a strong correlation between chlorophyll fluorescence and L-DOC could indicate that grazing is a more important source of L-DOC than direct release from phytoplankton. There was a strong correlation between DOC and S-DOC concentrations in the upper 200 m ($r > 0.96$; $p < 0.0001$ in all seasons) but not between DOC and L-DOC (Fig. 6). A spatial analysis of DOC, L-DOC, and S-DOC concentrations and chlorophyll fluorescence in a shelf-to-basin transect through Barrow Canyon is presented in Fig. 7.

Table 2. Seasonal average concentrations (and standard errors) of labile (L) and semi-labile (S) DOC in the upper 200 m.

Season	L-DOC (μmol L^{-1})	S-DOC (μmol L^{-1})	*n*
Spring 2002	0.7 (±0.1)	19.8 (±1.3)	23
Summer 2002	2.4 (±0.3)	23.3 (±1.3)	46
Spring 2004	1.4 (±0.2)	22.4 (±1.3)	47
Summer 2004	3.9 (0.3)	20.5 (±1.2)	84

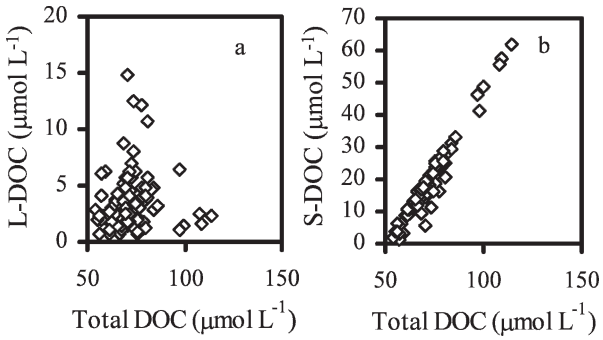

Fig. 6. Comparisons between (a) labile DOC and total DOC and (b) semi-labile DOC and total DOC. Concentrations of semi-labile and labile DOC were calculated based on amino-acid carbon yields. Total DOC values are measured concentrations of bulk DOC in each sample. Data presented here are all surface-water (<200 m) samples from summer 2004.

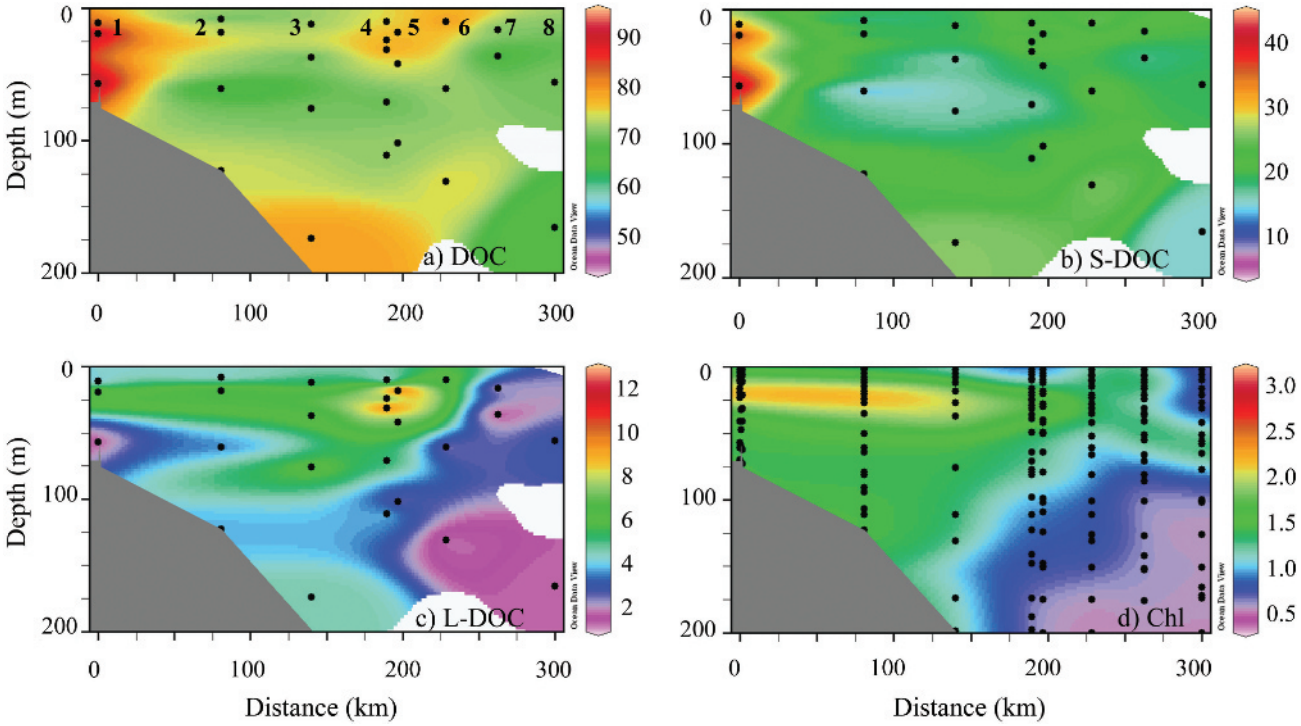

Fig. 7. Summer 2004 distributions of (a) DOC, (b) S-DOC, (c) L-DOC (μmol L^{-1}), and (d) chlorophyll fluorescence (Chl) in the Barrow Canyon transect. Station numbers are indicated on panel a.

In general, L-DOC in Barrow Canyon is concentrated in the depth zone of maximum productivity (15–40 m) and is higher near the shelf and in surface waters of the deep basin. S-DOC is elevated in the shallow upper shelf waters at the head of Barrow Canyon and, with the exception of this high point, is fairly evenly distributed throughout the water column.

Discussion

The marine DOM reservoir is a heterogeneous mixture of biomolecules with varying reactivities. Attempts to characterize the lability of this reservoir have been confounded by its complex composition and by natural temporal and spatial variability in DOM production. The approach presented here provides a novel means of looking inside the ''black box'' of DOM. Total hydrolysable amino acids are a major component of freshly-produced DOM and ideal molecules for tracking changes in DOM reactivity because they are readily utilized during organic matter diagenesis. Other major classes of biomolecules, such as neutral sugars, would also be useful using this approach, but we chose amino acids because these molecules are sources of available nitrogen as well as carbon. The approach of using C-normalized yields of amino acids for quantitatively calculating R-, S-, and L-DOC concentrations enables a degree of spatial and temporal resolution and sensitivity that was not possible with previous bioassay approaches. The only requirements of the approach presented here are knowledge of the concentrations of refractory DOC and DAA and the amino acid yield in a fresh sample of the dominant organic matter source material. Once these parameters are established, this approach can be applied to any samples for which DOC and DAA concentrations are measured.

Numerous environmental factors influence the biological utilization of DOM. Temperature (Pomeroy et al. 1991), nutrient availability (Zweifel et al. 1993), and bacterial abundance and community composition (Elifantz et al. 2007) have all been shown to influence the rates and extent of DOM utilization. Many bioassay approaches for characterizing L-DOC directly measure the rate and extent of DOC consumption during a given time period, whereas the molecular approach described herein provides a measure of the amount of L-DOC in a water sample. The molecular L-DOC measurement is based on the inherent bioavailability of DAA, and unlike the bioassay approach it does not directly measure rates of DOC utilization. Thus, the molecular approach can be used to identify L-DOC in water masses in which microbial populations are not actively utilizing L-DOC due to unfavorable environmental conditions, whereas the bioassay approach is blind to L-DOC under these conditions. This difference makes the molecular approach particularly useful for understanding the physical transport and distribution of L-DOC in aquatic environments.

Seasonality of Arctic DOM—Surface-water concentrations of DOC and DAA were highly spatially variable. The extremely heterogeneous nature of this system is underscored by the fact that during summer in the Chukchi Sea, amino acid concentrations varied by a factor of four among sampling stations. There was a general trend of greater DAA and DOC concentrations over the Chukchi Shelf

than in the basin surface waters, particularly in the summer. Primary productivity exhibited similar spatial trends (Hill and Cota 2005; Kirchman et al. unpubl. data). Seasonal comparisons of the average concentrations of DOC and DAA indicate a substantial increase in DAA between spring and summer without a corresponding increase in DOC. A similar pattern was observed in the Ross Sea, where Kirchman et al. (2001) noted a 10-fold seasonal increase in neutral sugars but only a 20% increase in DOC, and in the Arctic where concentrations of DOC and dissolved neutral sugars were not correlated (Rich et al. 1997). The lack of change in bulk DOC concentrations despite substantial increases in reactive components of DOM is likely a function of the high background of refractory DOC and the rapid utilization of labile components. Increased concentrations of DAA in the Chukchi Sea during summer have previously been shown to be the result of fresh marine production (Davis and Benner 2005).

Average surface-water (<200 m) concentrations of L-DOC exhibited a strong seasonality that corresponded to changes in primary productivity (Hill and Cota 2005; Kirchman et al. unpubl. data). This pattern was not apparent in S-DOC concentrations. In the winter, when daylight hours are limited and the entire Chukchi Shelf is ice-covered, primary productivity is negligible. In late spring, increased day length and receding ice cover result in dramatic increases in primary productivity. In 2002 and 2004, average primary productivity more than doubled from spring to summer (Hill and Cota 2005). In both years, the average concentration of L-DOC in surface waters also more than doubled between spring and summer (Table 2). The magnitude of increase was much greater in 2004 than in 2002, which reflects differences in productivity. Overall, primary productivity was 3× greater in 2004 than 2002 (Kirchman et al. unpubl. data). The average percentage of surface DOC that was identified as L-DOC increased from 0.9% to 2.9% between spring and summer of 2002 and between 1.8% and 5.9% between spring and summer of 2004, indicating a much larger portion of DOC was available for rapid utilization in the summer. There were no significant differences in mean surface-water concentrations of S-DOC between seasons or years. This lack of change in the average concentration of semi-labile material suggests that the majority of DOC in this reservoir has long turnover times (Fig. 1).

The absence of a seasonal signal in the average values of S-DOC and the strong relationship between DOC and S-DOC (Fig. 6) would seem to suggest that, as a whole, this component of DOC is not very reactive. It is important to remember, however, that the range of turnover times results in an accumulation of old material within the S-DOC pool. Consequently, the turnover of the relatively small but more rapidly removed fraction of S-DOC is difficult to detect. Primary productivity in the study region, in addition to being highly seasonal, is spatially variable. In 2002, rates of summer production as high as 2.9 g C m^{-2} d^{-1} were measured at some shelf stations, whereas the average rate in basin surface waters was 0.32 g C m^{-2} d^{-1} (Hill and Cota 2005). If the analysis of seasonal changes in S-DOC is limited to samples from the highly productive Chukchi Shelf region where the inputs of fresh DOM should be greatest, a trend of increased summertime S-DOC concentrations is apparent, with shelf-averaged concentrations increasing from 21 μmol L^{-1} to 26 μmol L^{-1} between spring and summer 2002, and from 27 μmol L^{-1} to 34 μmol L^{-1} between spring and summer 2004. Thus, the Arctic S-DOC reservoir is more dynamic than it would appear based on surface-water seasonal averages.

Estimated turnover times of S-DOC for other systems range widely. In the Ross Sea, all of the DOC that exists in excess of deep-water concentrations was consumed within 6 months (Carlson et al. 2000), whereas in the Sargasso Sea ~80% of semi-labile DOC turned over on timescales of >1 yr (Carlson et al. 1998; Hansell and Carlson 1998). In both cases, similar approaches were used for estimating S-DOC stocks. It is unclear why there should be such a large range of turnover times for S-DOC, but Kirchman et al. (2001) suggested that this may be a factor of molecular composition. The measured carbon-normalized yields of neutral sugars in Ross Sea semi-labile DOM approached 50%, whereas in the Arctic only about 10% of semi-labile DOC is characterized as neutral sugars (Rich et al. 1997).

Abundance and spatial distribution of L-DOC—One of the primary advantages of the molecular approach for describing DOC reactivity is the ability to quantify L- and S-DOC in discrete samples. The lack of a significant relationship between concentrations of DOC and L-DOC (Fig. 6) illustrates the utility of this approach. The application of this approach to the Western Arctic indicated a surprising degree of spatial heterogeneity in L-DOC concentrations. Summer concentrations of L-DOC in the shallow Chukchi Sea ranged between 1 μmol L^{-1} and 12 μmol L^{-1}, and the percent of total DOC that could be identified as L-DOC reached 13% at some shelf stations. In general, L-DOC concentrations were greater in shelf waters than in basin surface waters, but this trend was not statistically significant due to the large degree of variability in concentrations. Both primary and bacterial productivity were also found to be highly variable between sampling stations (Kirchman et al. unpubl. data). Thus the heterogeneous distribution of L-DOC is a consequence of the heterogeneous nature of DOC production and consumption and the rapid utilization of this most reactive component of DOC.

One of the dominant pathways by which northward flowing water from the Chukchi Sea enters the Canada Basin is through Barrow Canyon (Weingartner et al. 2005). This pathway is of increased importance in the summer (Roach et al. 1995), thus we use the summer 2004 distribution of DOC in Barrow Canyon (Fig. 7) to highlight several trends in L-DOC distribution. Concentrations of DOC were highest (up to 97 μmol L^{-1}) over the shallow upper slope at Station (Sta.) 1 and generally decreased with depth and distance into the basin. High rates of primary production (>3 g C m^{-2} d^{-1}) were measured at the head of Barrow Canyon in both spring and summer 2004 (Hill unpubl. data), and analysis of long-

term chlorophyll *a* data for this region indicate high levels of water column production to be the norm (Dunton et al. 2005). Elevated DOC concentrations were also observed in a deep sample (174 m) at Sta. 3 (80 μmol L^{-1}) and in surface waters at Sta. 4, 5, and 6 (76–80 μmol L^{-1}).

Concentrations of L-DOC were greater in near-shelf surface waters (4–7 μmol L^{-1}) than basin surface waters (1–2.5 μmol L^{-1}; Fig. 6). Although concentrations of L-DOC and chlorophyll fluorescence were not linearly correlated, the highest concentrations of L-DOC did occur in the zone of maximum chlorophyll fluorescence (15–40 m). Both parameters decreased with depth in basin waters, and both were substantially lower in basin surface waters (Sta. 7 and 8) than at stations closer to the shelf. The highest measured concentration of L-DOC in Barrow Canyon (12 μmol L^{-1}; Sta. 4 and 5) did not co-occur spatially with the greatest chlorophyll fluorescence, indicating a temporal disconnect between production and consumption processes. The plume-like distribution of L-DOC at 10–50 m, which appears to extend much farther into basin surface waters than the elevated chlorophyll fluorescence, indicates the transport of shelf-produced L-DOC into basin surface waters (Fig. 7). Similar L-DOC distribution patterns were observed in the other shelf-to-basin transects sampled here. The most striking feature of DOC in Barrow Canyon is the lack of correspondence in the distributions of L-, S-, and bulk DOC (Fig. 7). High concentrations of DOC are not indicative of labile DOC in this system.

Off-shelf transport of labile DOC—In the summer of 2004, several subsurface samples (>50 m) in the Canada Basin contained elevated concentrations of L-DOC (>2 μmol L^{-1}). Concentrations as high as 8 μmol L^{-1} were measured at depths of 140 m, and several of these samples were collected well into the basin, raising questions about the source of this material. Rates of primary productivity are negligible at these depths so an in situ source is highly unlikely. The salinity and temperature characteristics of these waters (Table 3) indicate that they are from the halocline, a permanent feature at ~50–225 m in this part of the Arctic Ocean. The halocline forms a strong barrier to mixing, thus downward mixing of surface-produced L-DOC is an unlikely source. The upper halocline in the Canada Basin is formed from Pacific waters that have passed through the Bering Straight and across the Chukchi Shelf. The upper halocline is characterized by salinities between 32 and 33.5 and near freezing temperatures (Shimada et al. 2005). Previous investigators have speculated that halocline ventilation is an important mechanism for moving shelf-produced organic matter into the Canada Basin (Walsh 1995; Walsh et al. 1997).

Sea-ice formation in shelf waters during the winter is thought to be the primary means of halocline ventilation (Aagaard et al. 1981). As the seawater freezes, salt rejection results in the formation of dense brines that sink to the bottom. Lateral advection of these brines from the Chukchi Sea into the Canada Basin is thought to be the primary source of the Canada Basin upper halocline. The chemical characteristics of sinking brines are modified by interactions with the active benthic communities of the Chukchi Shelf. The effects of this modification are evident in elevated concentrations of inorganic nutrients, which result from benthic remineralization of sinking particulate matter (Jones and Anderson 1986; Cooper et al. 2005). Recent evidence indicates that benthic remineralization of particulate matter also results in the release of substantial amounts of DOC. Cooper et al. (2005) measured DOC release rates of up to 0.3 mmol m^{-2} d^{-1} in highly-productive shelf sediments. Previous studies have shown that remineralization of sedimenting algal blooms can result in significant dissolved organic nitrogen (DON) release (Hansen and Blackburn 1992). We measured elevated concentrations of L-DOC (up to 4 μmol L^{-1}) in several near-bottom samples with halocline temperature and salinity characteristics. These samples were collected from outer shelf/slope stations at depths of up to 173 m, making an in situ water column source of elevated L-DOC extremely unlikely. Thus, DOC release from sediments provides a plausible source of L-DOC to dense bottom waters that form the halocline.

Table 3. Summer 2004 samples from Canada Basin halocline with elevated L-DOC (>2 μmol L^{-1}).

Depth (m)	Temperature (°C)	Salinity	L-DOC (μmol L^{-1})	Silicate (μmol L^{-1})
42	−1.645	32.355	2.5	34.8
42	−1.428	32.479	6.0	25.6
50	−0.997	32.227	5.5	17.4
62	−1.724	32.827	2.7	46.9
64	−1.524	32.877	2.2	31.6
71	−1.694	32.866	4.7	42.6
76	−1.493	32.438	6.0	37.5
97	−1.452	32.508	3.4	25.1
107	−1.514	33.274	5.5	32.8
110	−1.522	33.165	2.9	31.8
111	−1.088	33.730	3.9	28.8
123	−1.727	32.955	3.3	42.1
127	−1.480	32.459	7.6	28.8
132	−1.520	32.858	8.3	32.7
152	−1.678	32.783	2.4	38.8
152	−1.472	33.328	4.1	37.3
173	−1.526	33.165	4.0	19.5

A prominent feature of Canada Basin upper halocline waters is a silicate maximum (up to 45 μmol L^{-1}), which occurs at a salinity of ~33.1 (Jones and Anderson 1986; Jones et al. 1991). Elevated silicate concentrations serve as a reliable tracer of Pacific water in the Canada Basin because silicate concentrations in the underlying Atlantic waters are <12 μmol L^{-1} (Jones and Anderson 1986). All of the subsurface samples with high L-DOC occurred in upper halocline waters with elevated silicate (>20 μmol L^{-1}) (Table 3). The high silicate concentrations in these samples indicate that the water masses were previously in contact with Chukchi Shelf sediments, and thus we infer that the most likely source of the elevated L-DOC concentrations in these samples is release from sediments. Sediment release of L-DOC into dense bottom waters and the subsequent advection of these waters into the Canada Basin represent a lateral form of benthic-pelagic coupling.

The detection of shelf-produced L-DOC in basin waters suggests rapid transport of this material off the shelf because L-DOC is normally used within 1–2 weeks of production under favorable environmental conditions. Kadko and Muench (2005) detected high concentrations of the short-lived, sediment-derived isotope ^{224}Ra at the Canada Basin Arctic Ice Experiment (ICEX) station at depths of 50–150 m. They estimated a minimum transport rate of 40 cm s^{-1}, based on the mean-life (5.25 days) of ^{224}Ra and the nearest possible shelf source (Barrow Canyon, 200 km away from ICEX). The mechanisms responsible for such rapid transit remain unclear but our observations of elevated concentrations of L-DOC at several locations in basin waters are consistent with such transport events and further indicate they may not be uncommon. Not all halocline samples contained elevated concentrations of L-DOC, indicating the distribution was very heterogeneous, as would be expected if the transport were the result of sporadic, high-flow events such as eddies. Mesoscale eddies are prevalent features in the Canada Basin (Manley and Hunkins 1985). It is speculated that many of these eddies originate on the outer Chukchi Shelf near point Barrow and therefore may be an important mechanism for moving Chukchi Sea waters into the Canada Basin (Manley and Hunkins 1985; Muench et al. 2000). Eddy transport of high L-DOC water from shelf to basin is consistent with the sporadic distributions of basin L-DOC.

References

Aagaard, K., L. K. Coachman, and E. Carmack. 1981. On the halocline of the Arctic Ocean. Deep-Sea Res. **28:** 529–545.

Amon, R. M. W., and R. Benner. 2003. Combined neutral sugars as indicators of the diagenetic state of dissolved organic matter in the Arctic Ocean. Deep-Sea Res. I **50:** 151–169.

———, H. P. Fitznar, and R. Benner. 2001. Linkages among the bioreactivity, chemical composition, and diagenetic state of marine dissolved organic matter. Limnol. Oceanogr. **46:** 287–297.

Barber, R. T. 1968. Dissolved organic carbon from deep water resists microbial oxidation. Nature **220:** 274–275.

Benner, R. 2002. Chemical composition and reactivity, p. 59–90. *In* D. A. Hansell and C. A. Carlson [eds.], Biogeochemistry of marine dissolved organic matter. Academic Press.

———. 2003. Molecular indicators of the bioavailability of dissolved organic matter, p. 121–137. *In* S. Findlay and R. Sinsbaugh [eds.], Aquatic ecosystems: Interactivity of dissolved organic matter. Elsevier.

Carlson, C. A. 2002. Production and removal processes, p. 91–151. *In* D. A. Hansell and C. A. Carlson [eds.], Biogeochemistry of marine dissolved organic matter. Academic Press.

———, and H. W. Ducklow. 1995. Dissolved organic carbon in the upper ocean of the central Equatorial Pacific, 1992: Daily and fine-scale vertical variations. Deep-Sea Res. II **42:** 639–656.

———, ———, D. A. Hansell, and W. O. Smith. 1998. Organic carbon partitioning during spring phytoplankton blooms in the Ross Sea polynya and Sargasso Sea. Limnol. Oceanogr. **43:** 375–386.

———, D. A. Hansell, E. T. Peltzer, and W. O. Smith, Jr. 2000. Stocks and dynamics of dissolved and particulate organic matter in the southern Ross Sea, Antarctica. Deep-Sea Res. II **47:** 3201–3225.

Cooper, L. W., and others. 2005. Linkages among runoff, dissolved organic carbon, and the stable oxygen isotope composition of seawater and other water mass indicators in the Arctic Ocean. J. Geophys. Res. **110**: G02013, doi:10.1029/2005JG000031.

Davis, J., and R. Benner. 2005. Seasonal trends in the abundance, composition and bioavailability of particulate and dissolved organic matter in the Chukchi/Beaufort Seas and western Canada Basin. Deep-Sea Res. II **52:** 3396–3410.

Druffel, E. R. M., R. M. Williams, J. E. Bauer, and J. R. Ertel. 1992. Cycling of dissolved and particulate organic matter in the open ocean J. Geophys. Res. **97:** 15639–15659.

Dunton, K. H., J. L. Goodall, S. V. Schonberg, J. M. Grebmeier, and D. R. Madiment. 2005. Multi-decadal synthesis of benthic-pelagic coupling in the western arctic: Role of cross-shelf advective processes. Deep-Sea Res. II **52:** 3462–3477.

Grebmeier, J. M. 1993. Studies on pelagic-benthic coupling extended onto the Soviet continental shelf in the northern Bering and Chukchi seas. Cont. Shelf Res. **13:** 653–668.

Hansell, D. A., and C. A. Carlson. 1998. Net community production of dissolved organic carbon. Global Biogeochem. Cycles. **12:** 443–453.

Hansen, L. S., and T. H. Blackburn. 1992. Effect of algal bloom deposition on sediment respiration and fluxes. Mar. Biol. **112:** 147–152.

Hill, V., and G. Cota. 2005. Spatial patterns of primary production on the shelf, slope and basin of the Western Arctic. Deep-Sea Res. II **52:** 3324–3343.

Jones, E. P., and L. G. Anderson. 1986. On the origin of the chemical properties of the Arctic Ocean halocline. J. Geophys. Res. **91:** 10759–10767.

Kadko, D., and R. Muench. 2005. Evaluation of shelf-basin interaction in the western Arctic by use of short-lived radium isotopes: The importance of mesoscale processes. Deep-Sea Res. II **52:** 3227–3244.

Kaiser, K., and R. Benner. 2005. Hydrolysis induced racemization of amino acids. Limnol. Oceanogr. Meth. **3:** 318–325.

Kirchman, D. L., C. Lancelot, M. Fasham, L. Legendre, G. Radach, and M. Scott. 1993. Dissolved organic matter in biogeochemical models of the ocean, p. 209–225. *In* G. T. Evans and M. J. R. Fasham [eds.], Towards a model of ocean biogeochemical processes. Springer-Verlag.

———, B. Meon, H. W. Ducklow, C. A. Carlson, D. A. Hansell, and G. Steward. 2001. Glucose fluxes and concentrations of dissolved combined neutral sugars (polysaccharides) in the Ross Sea and polar front zone, Antarctica. Deep-Sea Res. II **48:** 4179–4197.

Lindroth, P., and K. Mopper. 1979. High performance liquid chromatographic determination of subpicomole amounts of amino acids by precolumn fluorescence deriatization with *o*-phthaldialdehyde. Anal. Chem. **51:** 1667–1674.

Manley, T. O., and K. Hunkins. 1985. Mesoscale eddies of the Arctic Ocean. J. Geophys. Res. **90:** 4911–4930.

McCallister, S. L., J. E. Bauer, and E. A. Canuel. 2006. Bioreactivity of estuarine dissolved organic matter: A combined geochemical and microbiological approach. Limnol. Oceanogr. **51:** 94–100.

Muench, R. D., J. T. Gunn, T. E. Whitledge, P. Schlosser, and W. Smethie, Jr. 2000. An Arctic Ocean cold core eddy. J. Geophys. Res. **105:** 23997–24006.

Pomeroy, L. R., W. J. Wiebe, D. Deibel, R. J. Thompson, G. R. Rowe, and J. D. Pakulski. 1991. Bacterial response to temperature and substrate concentrations during the Newfoundland spring bloom. Mar. Ecol. Prog. Ser. **75:** 143–159.

Rich, J., M. Gosselin, E. Sherr, B. Sherr, and D. L. Kirchman. 1997. High bacterial production, uptake and concentrations of dissolved organic matter in the Central Arctic Ocean. Deep-Sea Res. II **44:** 1645–1663.

Roach, A. T., K. Aagaard, C. H. Pease, S. A. Salo, T. Weingartner, V. Pavlov, and M. Kulakov. 1995. Direct measurements of transport and water properties through Bering Straight. J. Geophys. Res. **100:** 18443–18458.

Shimada, K., M. Itoh, S. Nishino, F. McLaughlin, and E. Carmack. 2005. Halocline structure in the Canada Basin of the Arctic Ocean. Geophys. Res. Lett. **32**: L03605, doi:10.1029/2004GL021358.

Skoog, A., and R. Benner. 1997. Aldoses in various size fractions of marine organic matter: Implications for carbon cycling. Limnol. Oceanogr. **42:** 1803–1813.

Springer, A. M., and C. P. McRoy. 1993. The paradox of pelagic food webs in the northern Bering Sea-III. Cont. Shelf Res. **13:** 575–599.

Walsh, J. J., D. A. Dieterle, F. E. Muller-Karger, K. Aagard, A. T. Roach, T. E. Whitledge, and D. A. Stockwell. 1997. CO2 cycling in the coastal ocean. II. Seasonal organic loading to the Canadian Basin from source waters south of Bering Straight. Cont. Shelf Res. **17:** 1–36.

———, and others. 1989. Carbon and nitrogen cycling within the Bering/Chukchi Seas: Source regions of organic matter affecting AOU demands of the Arctic Ocean. Prog. Oceanogr. **22:** 279–361.

Weingartner, T., K. Aagarard, R. Woodgate, S. Danielson, Y. Sasaki, and D. Cavalieri. 2005. Circulation on the north central Chukchi Sea shelf. Deep-Sea Res. II **52:** 3150–3174.

Wheeler, P. A., J. M. Watkins, and R. L. Hansing. 1997. Nutrients, organic carbon and organic nitrogen in the upper water column of the Arctic Ocean: implications for the sources of dissolved organic carbon. Deep-Sea Res. II **44:** 1571–1592.

Williams, P. M., and E. R. M. Druffel. 1987. Radiocarbon in dissolved organic matter in the central North Pacific Ocean. Nature **330:** 246–248.

Yamashita, Y., and E. Tanoue. 2003. Distribution and alteration of amino acids in bulk DOM along a transect from bay to oceanic waters. Mar. Chem. **82:** 145–160.

Zweifel, U. L., B. Norman, and Å. Hagström. 1993. Consumption of dissolved organic carbon by marine bacteria and demand for inorganic nutrients. Mar. Ecol. Prog. Ser. **101:** 23–32.

Received: 12 January 2007
Accepted: 20 May 2007
Amended: 15 June 2007