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Dissolved organic matter composition and bioavailability reflect ecosystem productivity in the Western Arctic Ocean

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Abstract

Dissolved organic carbon (DOC) and total dissolved amino acids (TDAA) were measured in high (Chukchi Sea) and low (Beaufort Sea) productivity regions of the Western Arctic Ocean to investigate the composition and bioavailability of dissolved organic matter (DOM). Concentrations and DOC-normalized yields of TDAA in Chukchi surface waters were relatively high, indicating an accumulation of bioavailable DOM. High yields of TDAA were also observed in the upper halocline of slope and basin waters, indicating off-shelf transport of bioavailable DOM from the Chukchi Sea. In contrast, concentrations and yields of TDAA in Beaufort surface waters were relatively low, indicting DOM was of limited bioavailability. Yields of TDAA in the upper halocline of slope and basin waters were also low, suggesting the Beaufort is not a major source of bioavailable DOM to slope and basin waters. In shelf waters of both systems, elevated concentrations and yields of TDAA were often observed in waters with higher chlorophyll concentrations and productivity. Surface concentrations of DOC were similar ($p > 0.05$) in the two systems despite the contrasting productivity, but concentrations and yields of TDAA were significantly higher ($p < 0.0001$) in the Chukchi than in the Beaufort. Unlike bulk DOC, TDAA concentrations and yields reflect ecosystem productivity in the Western Arctic. The occurrence of elevated bioavailable DOM concentrations in the Chukchi implies an uncoupling between the biological production and utilization of DOM and has important implications for sustaining heterotrophic microbial growth and diversity in oligotrophic waters of the Central Arctic basins.

1 Introduction

Two contrasting systems, the Chukchi and Beaufort Seas, occur adjacent to each other in the Western Arctic Ocean. The Chukchi Sea is a large (620×10^3 km^2) and shallow (~ 80 m avg.) inflow shelf area that receives nutrient-rich Pacific waters via Bering Strait, which support a very productive ecosystem (Jakobsson et al., 2004;

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Sakshaug, 2004; Grebmeier et al., 2006). In comparison, the Beaufort Sea is a narrow and small (178×10^3 km^2) river-influenced interior shelf that is relatively deep (~ 124 m avg.; Jakobsson et al., 2004). The major nutrient sources to the Beaufort shelf are the Mackenzie River and upwelling (Macdonald et al., 1987). Primary productivity is limited in regions of the Beaufort shelf due to the high water turbidity and stratification caused by coastal erosion and river runoff (Carmack and Wassmann, 2006).

The distinct shelf typology and nutrient supply lead to the contrasting productivity between the Chukchi and Beaufort Seas. Primary productivity in the Chukchi Sea parallels nutrient concentrations and increases from 30–90 g C m^{-2} yr^{-1} in the northeast to 720 g C m^{-2} yr^{-1} in the southwest (Walsh et al., 1989; Springer and McRoy, 1993; Cota et al., 1996; Hill and Cota, 2005). Areas associated with seasonal upwelling, such as Barrow Canyon, are typically more productive (e.g., 8 g C m^{-2} d^{-1}) than adjacent waters (Hill and Cota, 2005). In contrast, primary productivity in the Beaufort Sea is relatively low (10–70 g C m^{-2} yr^{-1}) due to lower nutrient availability and reflects the strong influence from the Mackenzie River (Carmack et al., 2004; Sakshaug, 2004; Lavoie et al., 2009). Shelf waters are less productive within the river plume (e.g., < 10 g C m^{-2} yr^{-1}) as a result of limited light penetration and become more productive outside the plume (30–70 g C m^{-1} yr^{-1}) (Sakshaug, 2004; Carmack and Wassmann, 2006) Relatively high primary production is observed in the eastern Beaufort Sea where the Cape Bathurst polynya forms during May–June at the entrance to the Amundsen Gulf. These open waters extend the phytoplankton growth season, resulting in elevated primary production (Arrigo and van Dijken, 2004; Brugel et al., 2009).

Off-shelf transport of organic matter from productive shelf waters is thought to be an important carbon source for heterotrophic metabolism in the interior Arctic basins (Walsh et al., 1989; Davis and Benner, 2005, 2007; Mathis et al., 2007). The disparity between a large demand of organic carbon in the basins and low concentrations of particulate organic carbon (POC) suggests the shelf–basin connection likely relies on dissolved organic carbon (DOC) (Wheeler et al., 1997). The extent of this reliance, however, is largely determined by the concentrations and bioavailability of dissolved organic

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matter (DOM), which are likely to vary spatially and temporally along with ecosystem productivity. Exploring the role of DOM in the shelf-basin connection therefore requires the assessment of DOM bioavailability under varying productivity regimes.

Amino acids, the building blocks of peptides and proteins, are major biochemical components of all organisms, and they are abundant in plankton-derived DOM. They are typically bioreactive and susceptible to microbial degradation, making them good indicators of the bioavailability of DOM in aquatic systems (Amon et al., 2001; Benner, 2003; Davis et al., 2009). High concentrations of bioavailable DOM, as indicated by high concentrations and DOC-normalized yields of total dissolved amino acids (TDAA), are observed in the Chukchi Sea (Davis and Benner, 2005, 2007). It is speculated that bioavailable DOM produced in the Chukchi shelf is entrained into the halocline of the Canadian Basin and fuels oxygen utilization there (Walsh et al., 1997; Davis and Benner, 2007). It is unclear whether a similar process is active in the Beaufort Sea due to a paucity of data for this region. In addition, despite the fact that the Chukchi Sea is more productive than the Beaufort Sea, differences in surface-water concentrations of DOC are not apparent (Davis and Benner, 2005; Guéguen et al., 2005; Mathis et al., 2005). It is therefore interesting to consider how the bioavailability of DOM differs between the two regions.

In this study, the concentrations of DOC and TDAA in the Chukchi and Beaufort Seas were compared to investigate the composition and bioavailability of DOM in these adjacent but quite different systems. Bioavailable DOM is broadly defined as all components that are biologically reactive on timescales ranging from days to years, and includes labile and semi-labile DOM. Our results reveal that the contrasting productivity between the Chukchi and Beaufort Seas is reflected in DOM composition and in the fraction of bioavailable DOM.

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2 Materials and methods

2.1 Study sites and sample collection

The Chukchi and Beaufort Seas were surveyed during four summer cruises of three different Arctic projects. In 2002 (17 July–21 August) and 2004 (18 July–26 August), water samples from the Chukchi Sea and the adjacent Canada Basin were collected aboard the research vessel USCGC *Healy*, as part of the Western Arctic Shelf–Basin Interactions (SBI) project (http://www.eol.ucar.edu/projects/sbi/; Fig. 1). In 2008 (19 July–29 July), water samples were collected from the Mackenzie River plume, Beaufort Sea, and Amundsen Gulf on the CCGS *Amundsen*, as part of the Circumpolar Flaw Lead (CFL) program (http://web.mac.com/barber1818/iWeb/IPY-CFL/; Fig. 1). In 2009 (27 July–27 August), waters in the Mackenzie River plume, Beaufort Sea, and Canada Basin were sampled on the CCGS *Amundsen* as part of the Malina (MAL) program (http://malina.obs-vlfr.fr/; Fig. 1). Water samples from the four cruises were collected at various depths using Niskin bottles mounted on a rosette with a conductivity-temperature-depth (CTD) sensor. Samples were filtered through cleaned (450 °C, 4h) GF/F glass fiber filters and stored frozen (−20 °C) in 60 ml high-density polyethylene screw-cap bottles until analyses of DOC, total dissolved nitrogen (TDN), and TDAA were performed in the home laboratory.

The broad spatial scale of sampling sites in this study covers a wide range of environments that vary in primary productivity. The SBI 2002 and 2004 cruises covered relatively productive waters of the Chukchi Sea, which receives nutrient-rich water from the Pacific Ocean, whereas the CFL 2008 and MAL 2009 cruises covered the less productive Southern Beaufort Sea, which is influenced by runoff from the Mackenzie River. In this study, sampling regions were separated into shelf (bottom depth ≤ 100 m, salinity ≥ 27.0), slope (100 m < bottom depth ≤ 1000 m), and basin (bottom depth > 1000 m) areas. In the slope and basin regions, surface water was defined as 0–80 m depth, which includes the chlorophyll maximum layer. The upper halocline in the slope and basin was delimited by depth (80–180 m) and salinity (32.0 ≤ salinity ≤ 33.9; Table 1).

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2.2 Chemical analyses

Aliquots of filtered (Whatman GF/F; 0.7-µm nominal pore-size) water samples were acidified to pH ≈ 2 with 2 mol l^{-1} hydrochloric acid (HCl) for DOC and TDN analyses. DOC and TDN were measured using high temperature combustion and a Shimadzu TOC-V analyzer equipped with an inline chemiluminescence nitrogen detector (Shimadzu TN-1; Davis and Benner, 2005). Milli-Q water (blank) and reference standards (Deep Sargasso Sea water) were injected every 6 th sample to check the accuracy of the measurements.

Aliquots of filtered water samples were hydrolyzed for analysis of TDAA using an agilent High Performance Liquid Chromatography (HPLC) system equipped with a fluorescence detector (excitation: 330 nm; emission: 450 nm). Water samples were dried with pure nitrogen gas and hydrolyzed using a vapor phase method with 6 mol l^{-1} HCl at 150 °C for 32.5 min. After neutralization, TDAA were measured as *o*-phthaldialdehyde (OPA) derivatives following the method of Kaiser and Benner (2005). The separation of compounds was performed on a Licrosphere RP18 (4.6 × 150 mm, 5 µm particles) or a Zorbax SB-C18 (4.6 × 150 mm, 3.5 µm particles) column. Eighteen amino acids were included in the analysis: asparagine + aspartic acid (Asx), glutamine + glutamic acid (Glx), serine (Ser), histidine (His), glycine (Gly), threonine (Thr), β-alanine (β-Ala), arginine (Arg), alanine (Ala), γ-aminobutyric acid (γ-Aba), tyrosine (Tyr), valine (Val), phenylalanine (Phe), isoleucine (Ile), leucine (Leu), and lysine (Lys).

DOC-normalized yields of TDAA (% DOC) were calculated as the percentage of DOC measured as amino acids. The degradation index (DI) is a reactivity indicator based on protein amino acid compositions (Dauwe and Middelburg, 1998). In this study, the DI was calculated following the method of Dauwe et al. (1999), as modified by Kaiser and Benner (2009) for application to DOM. The non-protein amino acids (β-Ala and γ-Aba) were not included in the DI calculation.

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2.3 Bioavailable DOM

Three categories of DOM biological lability (labile, semi-labile, and refractory) were defined by Davis and Benner (2007) based on DOC-normalized yields of TDAA. Refractory DOM refers to deep-water DOM (> 1000 m) that has an average TDAA yield of 0.70 % DOC in the Arctic Ocean and is resistant to biological utilization over long timescales (decades to millennia; Davis and Benner, 2007). In our study, bioavailable DOM is defined as the sum of labile and semi-labile fractions of DOM. Accordingly, DOM with yields of TDAA greater than 0.70 % DOC is bioavailable, and increasing yields of TDAA reflect increasing concentrations of bioavailable DOM.

2.4 Statistical analyses

Statistical analyses were performed with SPSS 20.0 (IBM Statistical Package for the Social Sciences Inc.). The significance of correlations between variables was determined using the Spearman's rho test (two-tailed, $\alpha = 0.05$) because the data were not normally distributed. Statistical differences were assessed using the Mann-Whitney U test (two-tailed, $\alpha = 0.05$) because of unequal group sizes and non-normal distribution of the data.

3 Results

3.1 Concentrations and distribution of DOM in the Mackenzie River plume

Small boat surveys of surface waters in the Mackenzie River plume (salinity: 0.15–29.90) were conducted during the CFL 2008 and MAL 2009 cruises (Fig. 1). Concentrations of DOC ranged from 106 to 458 µmol l^{-1}, with the highest value occurring in the Mackenzie River (salinity: 0.15). The concentrations of DOC across the salinity gradient followed a similar conservative mixing trend during the two cruises ($R^2 = 0.9260$, $p < 0.001$, $n = 19$; Fig. 2a). Non-conservative mixing across the salinity gradient was

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observed in concentrations of TDAA, and sources of TDAA were evident at mid salinities (6.5–15.5; Fig. 2b). DOC-normalized yields of TDAA were minimal in the river (0.42 % DOC) and progressively increased with salinity (Fig. 2c). The two highest yields (1.20 and 1.32 % DOC) were observed at mid-salinity locations with elevated TDAA concentrations, indicating a plankton source. Yields of TDAA were generally higher at mid salinities (6.5–15.5) during CFL 2008 than MAL 2009 (Fig. 2c).

3.2 Concentrations and composition of DOM in the Chukchi and Beaufort Seas

DOC concentrations in Chukchi and Beaufort shelf waters ranged from 59 to 146 µmol l^{-1} (avg.: 81 µmol l^{-1}) and showed considerable variability at all depths (Fig. 3a). In comparison, DOC concentrations were lower in slope and basin waters (41–201 µmol l^{-1}; avg.: 67µmol l^{-1}) (Fig. 3a–c; Table 1). Concentration ranges and depth trends of DOC were similar among cruises, with elevated concentrations occurring in near surface waters and decreasing concentrations with depth (Fig. 3b, c).

TDAA concentrations in shelf, slope, and basin waters were more variable than DOC concentrations and ranged from 70 to 983 nmol l^{-1} (avg.: 311 nmol l^{-1}; Fig. 4a–c). TDAA concentrations were substantially higher in the Chukchi Sea (SBI 2002, 2004; avg.: 323 nmol l^{-1}) than in the Beaufort Sea (CFL 2008, MAL 2009; avg.: 186 nmol l^{-1}). Peak concentrations of TDAA in shelf waters were typically found at 10–30 m (Fig. 4a). Concentrations of TDAA generally declined from shelf waters to slope and basin waters (Fig. 4a–c; Table 1). Elevated concentrations of TDAA were found at greater depths (~ 200 m) in slope and basin waters during SBI 2002 and 2004 (Fig. 4b, c). Concentrations of TDAA in slope waters during CFL 2008 (avg.: 185 nmol l^{-1}) were significantly higher than those at similar depths during MAL 2009 (avg.: 161 nmol l^{-1}) ($p < 0.05$; Fig. 4b).

DOC-normalized yields of TDAA were much higher in the Chukchi Sea (0.39–4.23 % DOC, avg.: 1.41 % DOC) compared with the Beaufort Sea (0.47–3.29 % DOC, avg.: 0.84 % DOC) (Fig. 5a–c). Maximal TDAA yields in shelf waters were found at 10–30 m (Fig. 5a). Yields of TDAA in slope and basin waters were particularly high in the upper

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200 m during SBI 2004 and sometimes exceeded those in shelf waters (Fig. 5b, c). Yields of TDAA in slope waters during CFL 2008 (avg.: 0.88 % DOC) were significantly higher than those at similar depths during MAL 2009 (avg.: 0.76 % DOC) ($p < 0.001$; Fig. 5b).

Average amino acid degradation index (DI) values for the four cruises ranged from −1.58 to 1.08 (Table 1). During SBI 2002, 2004, and MAL 2009, DI values decreased from shelf waters to slope-basin surface waters, and with depth (Table 1). An opposite trend was observed during CFL 2008. In general, DI values were lower in the Chukchi Sea (SBI 2002, 2004) than in the Beaufort Sea (CFL 2008, MAL 2009) (Table 1). The variable DI values indicate compositional variations of DOM in the systems. Correlations between DI values and TDAA yields were highly inconsistent (data not shown; SBI 2002: $r = 0.9064$, $p < 0.001$, $n = 43$; SBI 2004: $r = 0.4694$, $p < 0.001$, $n = 81$; CFL 2008: $r = -0.2537$, $p = 0.2945$, $n = 19$; MAL 2009: $r = 0.6838$, $p < 0.001$, $n = 67$), suggesting DI values are less useful indicators of bioavailable DOM in the heterogeneous waters of the Western Arctic (Davis et al., 2009).

3.3 Statistical comparisons of DOM in the Chukchi and Beaufort Seas

3.3.1 Spatial and temporal variations of DOM in the Chukchi and Beaufort Seas

The SBI 2002 and 2004 data were combined to represent the Chukchi Sea region, and the CFL 2008 and MAL 2009 data were combined to represent the Beaufort Sea region. In both regions, average concentrations of DOC and TDAA, and TDAA yields generally decreased from shelf waters to slope-basin surface waters, with a greater gradient occurring in the Beaufort Sea (Fig. 6a–c). One exception was that yields of TDAA in Chukchi shelf and slope-basin surface waters were quite similar (~ 1.6 % DOC; Fig. 6c). Significant differences in DOC concentrations and TDAA yields between shelf waters and slope-basin surface waters were found in the Beaufort Sea ($p < 0.01$) but not in the Chukchi Sea ($p > 0.1$) (Table 2; Fig. 6a, c). Differences in TDAA concentrations were highly significant among shelf waters, slope-basin surface waters, and

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slope-basin upper halocline waters ($p < 0.01$; Table 2; Fig. 6b). DOC and TDAA concentrations and TDAA yields in the upper halocline of both regions were substantially lower than those in shelf waters and slope-basin surface waters (Table 2; Fig. 6a–c).

Interannual variation of DOM concentrations and composition in the Chukchi Sea was examined by comparing data from SBI 2002 with data from SBI 2004. In shelf waters, none of the three parameters were significantly different between 2002 and 2004 ($p > 0.2$; Fig. 7a–c). Differences were significant in slope-basin surface waters, where DOC concentrations were significantly higher in 2002 ($p < 0.05$; Fig. 7a) and concentrations and yields of TDAA were substantially higher in 2004 (concentration: $p = 0.0585$, yield: $p < 0.0001$; Fig. 7b, c). In contrast to DOC ($p = 0.3028$; Fig. 7a), TDAA concentrations and yields in the upper halocline were significantly higher in 2004 than in 2002 ($p < 0.01$; Fig. 7b, c). In 2002, average DOC and TDAA concentrations and TDAA yields decreased from shelf to slope-basin waters (Fig. 7a–c). In 2004, however, elevated concentrations and yields of TDAA were observed in both slope-basin surface and upper halocline waters (Fig. 7b, c), and average yields of TDAA were even higher in slope-basin surface and upper halocline waters than in shelf waters (Fig. 7c).

3.3.2 Comparisons of DOM between the Chukchi and Beaufort Seas

Average DOC concentrations in both shelf waters and slope-basin surface waters were slightly higher in the Beaufort Sea than in the Chukchi Sea (Fig. 6a), but not significantly different (shelf waters: $p > 0.4$; slope-basin surface waters: $p > 0.05$; Table 3). Significantly higher DOC concentrations were observed in upper halocline waters in the Chukchi compared with the Beaufort ($p < 0.0001$; Table 3; Fig. 6a). Concentrations and yields of TDAA in shelf waters were significantly higher (~ 1.5-fold) in the Chukchi than in the Beaufort ($p < 0.0001$; Table 3; Fig. 6b, c). The differences in concentrations and yields of TDAA between the two regions were more pronounced in slope-basin surface and upper halocline waters, with the values in the Chukchi Sea almost double those in the Beaufort Sea ($p < 0.0001$; Table 3; Fig. 6b, c).

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4 Discussion

4.1 Concentrations and bioavailability of DOM in the Chukchi Sea

Surface concentrations of DOC and TDAA in the Chukchi Sea were spatially variable and generally corresponded with variations in primary productivity (Hill and Cota, 2005; Kirchman et al., 2009a). Concentrations of DOC and TDAA decreased by ~ 10 % from shelf to slope-basin surface waters, and primary production also decreased from shelf to basin waters (Kirchman et al., 2009a). DOC-normalized yields of TDAA in surface waters (~ 1.6 % DOC) were more than 2-fold greater than those in refractory DOM (0.70 % DOC; Davis and Benner, 2007) and displayed minor spatial variations in shelf and slope-basin surface waters, indicating a substantial supply of bioavailable DOM in surface waters of the Chukchi Sea. Maximal concentrations and yields of TDAA were observed at depths of 10–30 m where chlorophyll concentrations and primary production were also maximal in summer (Cota et al., 1996; Hill and Cota, 2005). This subsurface maximum was not observed for DOC concentrations. In comparison, concentrations of DOC and TDAA and yields of TDAA were significantly lower in the upper halocline ($p < 0.01$), but TDAA yields (1.38 % DOC) were greater than those of semi-labile and refractory DOM (1.1 and 0.70 % DOC, respectively; Davis and Benner, 2007). This indicates that although there was a substantial drawdown of bioavailable DOM below the euphotic zone, concentrations of bioavailable DOM remained relatively high in these waters.

The seasonal variability of bioavailable DOM in the Chukchi Sea was previously described by Davis and Benner (2007). Here, we further discuss the interannual variations of bioavailable DOM in different Chukchi regions. Concentrations of DOC and TDAA and yields of TDAA in shelf waters were high in the summers of 2002 and 2004 and were not significantly different between the two years ($p > 0.2$), indicating bioavailable DOM in shelf waters was relatively abundant and displayed small interannual variations. Concentrations and yields of TDAA decreased by over 30 % from shelf to slope-basin surface waters in 2002. In contrast, in 2004 concentrations of TDAA in

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slope-basin surface waters remained high and the TDAA yields were even higher than those in shelf waters (1.84 vs. 1.58 % DOC). Summer primary productivity in 2004 (0.62 g C m^{-2} d^{-1}) was ~ 2.5 times higher than that in 2002 (0.24 g C m^{-2} d^{-1}), but the highest production in 2004 occurred in shelf waters rather than in slope-basin waters (Kirchman et al., 2009a). The observations of higher primary production in shelf waters and greater DOM bioavailability in slope-basin surface waters suggest a rapid off-shelf transport of bioavailable DOM in 2004. Concentrations and yields of TDAA in upper halocline waters were significantly higher in 2004 than in 2002 ($p < 0.0001$). In 2004, the average yield of TDAA in upper halocline waters (1.64 % DOC) was very similar to that of shelf waters (1.58 % DOC), thereby suggesting a source of shelf-produced labile DOM (Davis and Benner, 2007). The off-shelf transport of bioavailable DOM, however, was not apparent in 2002. These comparisons exhibit irregular interannual variability of bioavailable DOM in different Chukchi regions, as controlled by both biological and physical processes.

4.2 Concentrations and bioavailability of DOM in the Beaufort Sea

Concentrations of DOC in the Mackenzie River plume ranged from 458 µmol l^{-1} in the river to 106 µmol l^{-1} at a salinity of 29.9 and exhibited fairly conservative mixing across the salinity gradient in 2008 and 2009, as observed previously (Emmerton et al., 2008) and in other Arctic river plumes (Cauwet and Sidorov, 1996; Kattner et al., 1999; Amon, 2004). Conservative mixing indicates minor net changes in DOC concentrations during transport and could be due to the refractory nature of riverine DOC or the rapid balance between sources and sinks of DOC. Desorption from sediments and plankton productivity can be major sources of DOM in river plumes (Macdonald et al., 1998; Benner and Opsahl, 2001; Dagg et al., 2004), whereas flocculation, bio- and photodegradation can be important sinks of DOM (Chin-Leo and Benner, 1992; Uher et al., 2001; Bélanger et al., 2006; Garneau et al., 2006). Concentrations and yields of TDAA in the Mackenzie River plume were more variable across the salinity gradient, with elevated concentrations and yields of TDAA at mid salinities indicating a plankton source

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of bioavailable DOM. However, compared to river plumes at lower latitudes (e.g., the Mississippi River plume; Dagg et al., 2004), primary production, production of bioavailable DOM, and microbial processes in the Mackenzie River plume are relatively low (Retamal et al., 2007; Emmerton et al., 2008; Retamal et al., 2008).

Relatively high concentrations of DOC and TDAA and yields of TDAA were observed in regions of the Beaufort shelf and reflected the influence of the Mackenzie River. Riverine input of nutrients supported limited areas of elevated primary production (Raimbault et al., unpublished) and elevated concentrations and yields of TDAA in shelf waters, but low nutrient concentrations in surface together with stratification of shelf waters during the summer typically resulted in the formation of a chlorophyll and productivity maximum at ~ 30 m (Carmack et al., 2004; Lavoie et al., 2009; Raimbault et al., unpublished). This pattern is reflected in elevated concentrations and yields of TDAA below the surface. DOC and TDAA concentrations and yields of TDAA decreased rapidly (by 9 %, 31 %, and 27 %, respectively) from shelf to slope-basin surface waters, as conditions became more oligotrophic due to the extensive sea ice cover in the summer of 2009. The low levels of primary production were reflected in low concentrations (200 nmol l^{-1}) and yields (0.85 % DOC) of TDAA during this study. Concentrations of DOC and TDAA were lowest in upper halocline waters, and the off-shelf subsidy of bioavailable DOM was not apparent. Yields of TDAA in the upper halocline (0.78 % DOC) were comparable to values in refractory DOM (0.70 % DOC), indicating DOM in these waters is resistant to biodegradation.

Heterogeneous distributions of bioavailable DOM in the Beaufort Sea were apparent from comparisons of the Amundsen Gulf (CFL 2008) and the Southeastern Beaufort Sea (MAL 2009). Concentrations ($p < 0.05$) and yields ($p < 0.001$) of TDAA were significantly higher in the Amundsen Gulf than in the Southeastern Beaufort Sea, but there was no significant difference ($p = 0.4294$) in DOC concentrations between the two regions. These higher TDAA concentrations are likely attributable to higher primary productivity (0.28 g C m^{-2} d^{-1}) in the Amundsen Gulf than in the Southeastern Beaufort region (0.07 g C m^{-2} d^{-1}) at the time of sampling (Sallon et al., 2011; Raimbault et al.,

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unpublished). Although the observed variability of DOM and productivity can also be due to differences in sampling years (2008 vs. 2009), higher primary production in the Cape Bathurst polynya (52–175 g C m^{-2} yr^{-1}) than in the rest of the Beaufort Sea (including the Mackenzie shelf) is a well recognized feature in the Amundsen Gulf (Arrigo and van Dijken, 2004; Brugel et al., 2009; Forest et al., 2011). In addition to the release of bioavailable DOM from plankton, bacterial degradation of particulate organic matter and zooplankton activities provide additional sources of bioavailable DOM in the Amundsen Gulf (Juul-Pedersen et al., 2010; Forest et al., 2011; Kellogg et al., 2011). The elevated concentrations and yields of TDAA in the Amundsen Gulf are consistent with the higher productivity in this region.

Interannual variability of DOM in the Beaufort Sea is difficult to address given our limited data, but areas covering similar salinity ranges in the Mackenzie River plume and some shelf and slope waters were sampled during CFL 2008 and MAL 2009. Comparisons among these regions indicated higher TDAA concentrations and yields in 2008 than in 2009, with negligible differences in DOC concentrations. Strong seasonal forcing governs biological productivity in the Beaufort Sea such that interannual variability in DOM is not unexpected, but we anticipate less temporal variability in the Beaufort than in the Chukchi. Previous field and remote sensing analyses indicate less pronounced interannual variations in phytoplankton biomass and production in the Beaufort Sea as compared with the Chukchi Sea (Arrigo and van Dijken, 2004; Brugel et al., 2009).

4.3 Comparisons of bioavailable DOM between the Chukchi and Beaufort Seas

It is interesting to consider how the contrasting productivity between the Chukchi and Beaufort Seas influences the concentrations and bioavailability of DOM in the two systems. Primary productivity in the Chukchi Sea (e.g., 30–720 g C m^{-2} yr^{-1}; Springer and McRoy, 1993; Cota et al., 1996; Kirchman et al., 2009a) is typically much higher than that in the Beaufort Sea (e.g., 12–28 g C m^{-2} yr^{-1}; Carmack et al., 2004; Brugel et al., 2009; Lavoie et al., 2009). Given the higher primary productivity, higher rates of DOM

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production and consumption through the microbial loop are expected in the Chukchi Sea. However, DOC concentrations in shelf and slope-basin surface waters were not significantly different between the Chukchi and Beaufort Seas, and slightly higher values were even observed in the Beaufort. Higher DOC concentrations in some areas of the Beaufort shelf likely reflected the influence of the Mackenzie River. The difference in primary productivity between the two regions was not reflected in the concentrations of bulk DOC.

In sharp contrast to the similarities in DOC concentrations, TDAA concentrations in Chukchi shelf and slope-basin surface waters were 50–90 % higher ($p < 0.0001$) than those in the Beaufort. The bioavailability of DOM, as indicated by yields of TDAA, was also significantly ($p < 0.0001$) higher (by 90 %) in surface waters of the Chukchi Sea compared with those of the Beaufort Sea. Primary productivity in the Chukchi Sea during the sampling periods ranged from 0.24 to 0.62 g C m^{-2} d^{-1} and resulted in the production of DOM that is rich in amino acids and is of high bioavailability (Davis and Benner, 2005, 2007; Kirchman et al., 2009a). In comparison, primary productivity in nutrient-poor waters of the Beaufort Sea was low (0.03–0.45 g C m^{-2} d^{-1}; Sallon et al., 2011; Raimbault et al., unpublished) and led to lower concentrations of bioavailable DOM. The contrasting productivity of the Chukchi and Beaufort Seas is clearly imprinted in the abundance and distribution of TDAA.

Significantly higher DOC and TDAA concentrations and yields of TDAA were evident in the upper halocline of the Chukchi region in comparison to the Beaufort. High concentrations and yields of TDAA were observed to depths of 200 m in the Chukchi region and appear to be derived from shelf and slope waters in the region (Davis and Benner, 2007). A variety of mechanisms likely contribute to the transport of bioavailable DOM into upper halocline waters, including the injection of dense Pacific winter water and mesoscale eddies that form along the shelf break (Manley and Hunkins, 1985; Mathis et al., 2007; Spall et al., 2008). The release of DOM from particles or during grazing is also a potential source of bioavailable DOM (Cooper et al., 2005; Azam and Malfatti, 2007), particularly in the highly productive Chukchi Sea. In contrast, these indicators

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of bioavailable DOM were not observed in the upper halocline of the Beaufort Sea. Bioavailable DOM is important for sustaining the heterotrophic community in the upper halocline (Wallace et al., 1987; Cota et al., 1996). Concentrations of bioavailable DOM in the upper halocline of the Chukchi region were higher than those in the Beaufort, thereby revealing the important role of the Chukchi Sea in providing bioavailable DOM to low-productivity basins of the Arctic Ocean. This strong shelf–basin interaction was not apparent in the Beaufort Sea.

The observed net accumulation of bioavailable DOM during the summer in the Chukchi Sea and adjacent slope-basin waters indicates an uncoupling between the biological production and utilization of DOM. The direct cause(s) of this uncoupling is unknown, but it suggests DOM remineralization in the microbial loop is depressed. Temperature and concentrations of labile substrates play important roles in regulating bacterial growth and the functioning of the microbial loop (Pomeroy and Deibel, 1986; Kirchman et al., 2009b; Ortega-Retuerta et al., unpublished). Additions of relatively high concentrations of bioavailable substrates to water collected from the Chukchi Sea can result in delayed responses from the microbial community that can persist for days to weeks before utilization occurs (Davis et al., 2009). This slow response to bioavailable substrates could also indicate deficiencies in the metabolic diversity of the microbial community for the added substrates. In any case, the net accumulation of bioavailable DOM in the Chukchi Sea and other productive shelves, such as the Barents Sea, could be critical for sustaining heterotrophic microbial communities and microbial diversity in the highly oligotrophic waters of the Central Arctic basins.

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Table 1. Physicochemical characteristics in shelf, slope and basin waters of the Chukchi and Beaufort Seas*.

Cruise	Depth (m)	Temperature (°C)	Salinity (psu)	DOC (μmol l^{-1})	TDN (μmol l^{-1})	TDAA (nmol l^{-1})	TDAA (% DOC)	DI	*n*
Shelf (0–80 m)									
SBI 2002	24 ± 11	1.29 ± 3.26	31.17 ± 1.41	77 ± 12	8.0 ± 4.5	462 ± 177	1.70 ± 0.66	−0.20 ± 0.80	22
SBI 2004	26 ± 16	4.53 ± 3.37	31.40 ± 0.89	83 ± 17	7.9 ± 4.4	406 ± 107	1.58 ± 0.43	−0.50 ± 0.54	19
CFL 2008	nd	nd	nd	nd	nd	nd	nd	nd	nd
MAL 2009	19 ± 16	1.56 ± 2.48	29.95 ± 1.67	85 ± 20	6.1 ± 1.9	289 ± 138	1.17 ± 0.57	0.45 ± 0.90	18
Slope-basin (surface: 0–80 m)									
SBI 2002	39 ± 16	−1.32 ± 0.41	31.40 ± 1.17	76 ± 6	10.1 ± 5.8	319 ± 61	1.12 ± 0.21	−0.90 ± 0.61	24
SBI 2004	35 ± 17	−0.10 ± 1.77	31.24 ± 1.12	73 ± 5	7.7 ± 4.0	402 ± 165	1.84 ± 0.79	−1.17 ± 1.09	44
CFL 2008	5 ± 1	6.20 ± 1.87	29.01 ± 1.25	74 ± 5	5.1 ± 0.6	225 ± 14	1.00 ± 0.07	0.49 ± 1.13	12
MAL 2009	37 ± 26	0.09 ± 2.17	29.69 ± 3.51	78 ± 25	5.8 ± 2.0	192 ± 47	0.80 ± 0.14	−0.44 ± 0.41	37
Slope-basin (upper halocline: 80–180 m, 32.0–33.9 psu)									
SBI 2002	131 ± 29	−1.53 ± 0.17	33.22 ± 0.41	69 ± 3	18.6 ± 2.1	243 ± 41	0.92 ± 0.17	−1.58 ± 0.42	23
SBI 2004	129 ± 23	−1.50 ± 0.15	33.09 ± 0.35	70 ± 5	17.2 ± 1.4	344 ± 119	1.64 ± 0.66	−1.35 ± 1.43	20
CFL 2008	112 ± 30	−1.39 ± 0.12	33.20 ± 0.33	66 ± 4	16.9 ± 2.8	177 ± 19	0.84 ± 0.06	1.08 ± 1.15	9
MAL 2009	136 ± 26	−1.38 ± 0.06	32.93 ± 0.39	64 ± 3	16.2 ± 1.6	150 ± 18	0.75 ± 0.11	−0.63 ± 0.46	13

* Samples were collected during four summer cruises (July–August). Definitions: shelf–bottom depth ≤ 100 m, salinity ≥ 27.0; slope–bottom depth 100–1000 m; basin–bottom depth > 1000 m.
Surface water in the slope and basin was defined as 0–80 m depth. Upper halocline water in the slope and basin was defined based on depth and salinity (80–180 m, 32.0 ≤ salinity ≤ 33.9). Data are reported as averages ± standard deviations. nd: not determined.

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Table 2. Statistical comparisons of the concentrations of DOC and TDAA, and TDAA yields in the Chukchi and Beaufort Seas (Mann-Whitney U test).

	DOC (μmol l^{-1})	TDAA (nmol l^{-1})	TDAA (% DOC)
Chukchi Sea			
Shelf vs. Slope-basin surface	$p = 0.1408$	$p < 0.01$	$p = 0.3678$
Shelf vs. Slope-basin upper halocline	$p < 0.001$	$p < 0.0001$	$p < 0.01$
Slope-basin (surface vs. upper halocline)	$p < 0.0001$	$p < 0.01$	$p < 0.05$
Beaufort Sea			
Shelf vs. Slope-basin surface	$p < 0.01$	$p < 0.0001$	$p < 0.001$
Shelf vs. Slope-basin upper halocline	$p < 0.0001$	$p < 0.0001$	$p < 0.0001$
Slope-basin (surface vs. upper halocline)	$p < 0.0001$	$p < 0.0001$	$p = 0.0842$

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Table 3. Comparisons of the concentrations of DOC and TDAA, and TDAA yields in the Chukchi and Beaufort Seas* (Mann-Whitney U test).

	DOC (μmol l^{-1})		TDAA (nmol l^{-1})		TDAA (% DOC)	
	Chukchi	Beaufort	Chukchi	Beaufort	Chukchi	Beaufort
Shelf	80 ± 15	85 ± 20	428 ± 140	289 ± 138	1.62 ± 0.53	1.17 ± 0.57
	(p = 0.4338)		(p < 0.0001)		(p < 0.0001)	
Slope-basin (surface)	74 ± 5	77 ± 22	378 ± 147	200 ± 44	1.63 ± 0.74	0.85 ± 0.15
	(p = 0.0570)		(p < 0.0001)		(p < 0.0001)	
Slope-basin (upper halocline)	70 ± 4	65 ± 4	307 ± 109	161 ± 22	1.38 ± 0.64	0.78 ± 0.10
	(p < 0.0001)		(p < 0.0001)		(p < 0.0001)	

* SBI 2002 and 2004 were combined to represent the Chukchi Sea region, whereas CFL 2008 and MAL 2009 were combined to represent the Beaufort Sea region. Data are reported as the average ± standard deviation, with the p-value in the parentheses.

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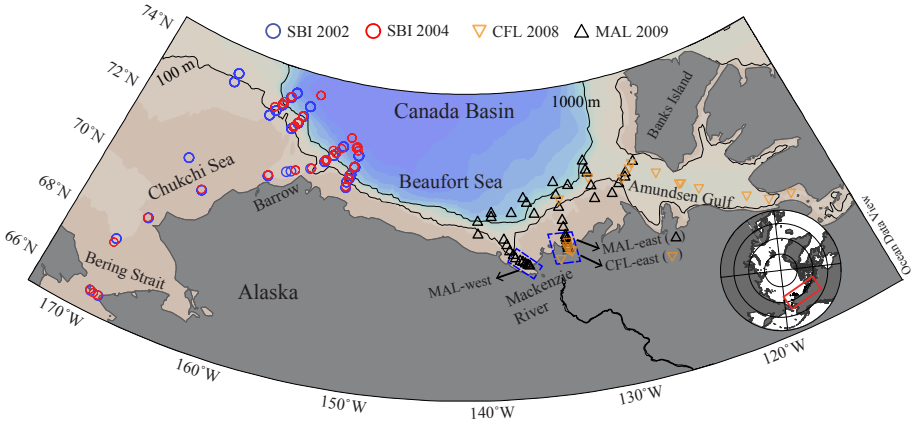

Fig. 1. Locations of sampling stations in the Western Arctic Ocean. Four cruises were conducted during the summer and sampled the shelf, slope, and basin environments of the Chukchi and Beaufort Seas. Blue circles – SBI 2002; red circles – SBI 2004; brown inverse triangles – CFL 2008; black triangles – MAL 2009. The Mackenzie River plume was surveyed during CFL 2008 (CFL-east) and MAL 2009 (MAL-west and MAL-east). The 100 and 1000 m isobaths are shown.

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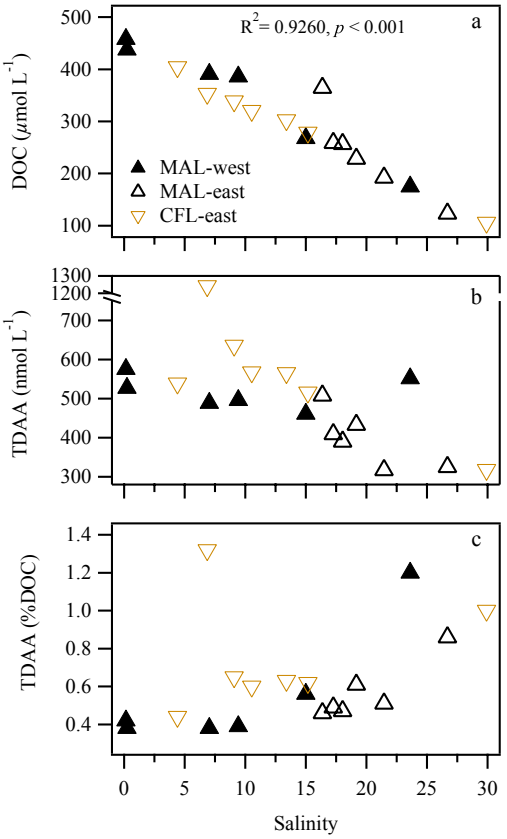

Fig. 2. Mixing patterns of DOM in the Mackenzie River plume. Distributions of **(a)** dissolved organic carbon (DOC), **(b)** total dissolved amino acids (TDAA), and **(c)** yields of TDAA (% DOC) across the salinity gradient.

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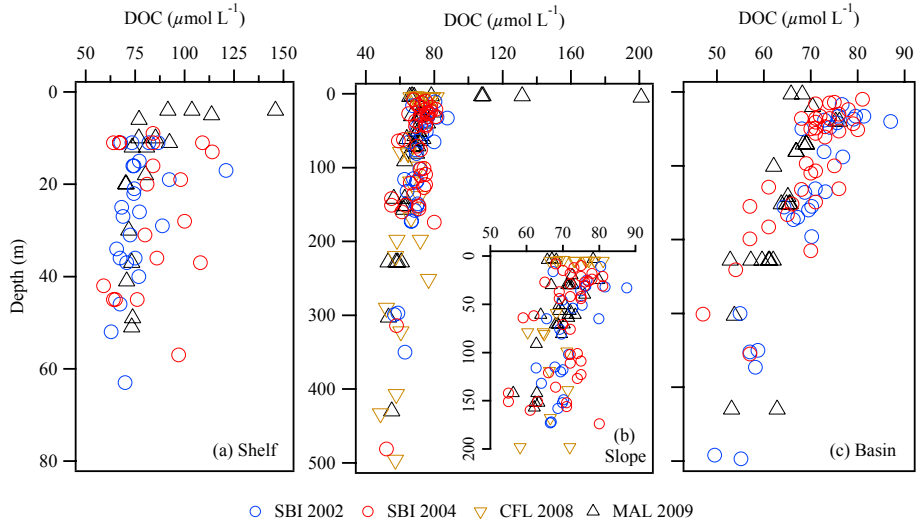

Fig. 3. Concentrations of dissolved organic carbon (DOC) in **(a)** shelf, **(b)** slope, and **(c)** basin waters of the Chukchi Sea (SBI 2002, SBI 2004) and Beaufort Sea (CFL 2008, MAL 2009).

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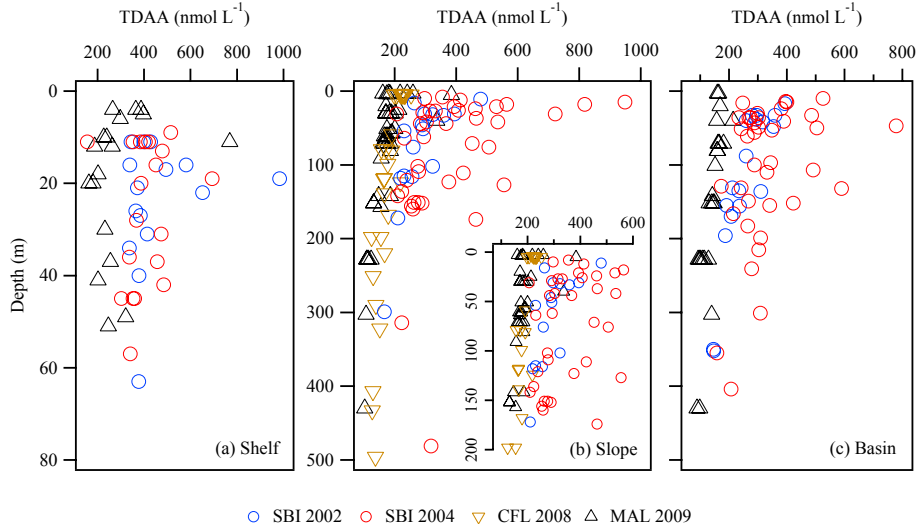

Fig. 4. Concentrations of total dissolved amino acids (TDAA) in **(a)** shelf, **(b)** slope, and **(c)** basin waters of the Chukchi Sea (SBI 2002, SBI 2004) and Beaufort Sea (CFL 2008, MAL 2009).

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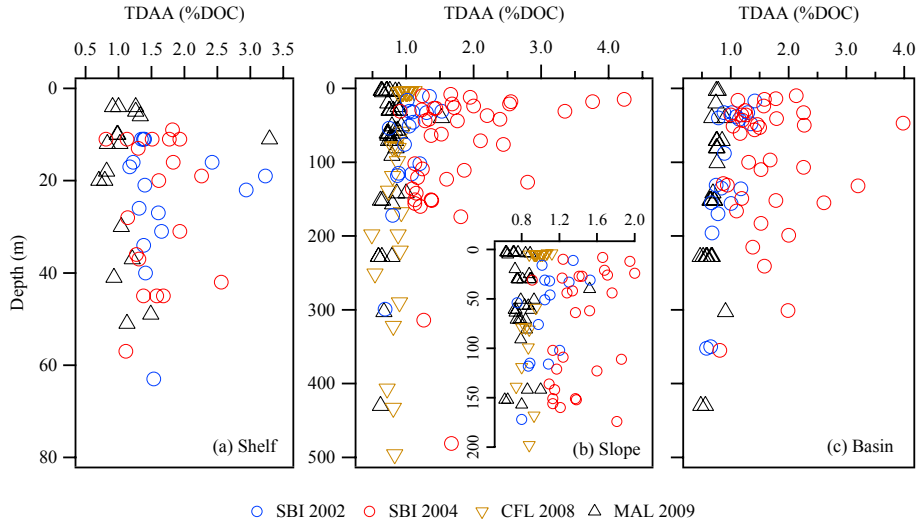

Fig. 5. DOC-normalized yields of total dissolved amino acids in **(a)** shelf, **(b)** slope, and **(c)** basin waters of the Chukchi Sea (SBI 2002, SBI 2004) and Beaufort Sea (CFL 2008, MAL 2009).

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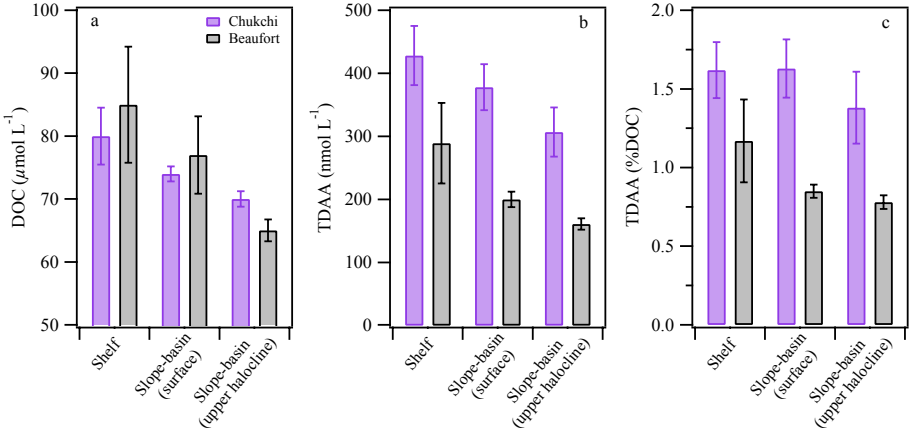

Fig. 6. Spatial variability of average concentrations of **(a)** dissolved organic carbon (DOC) and **(b)** total dissolved amino acids (TDAA), and **(c)** yields of TDAA in shelf, slope, and basin waters of the Chukchi and Beaufort Seas. Error bars represent two times the standard error.

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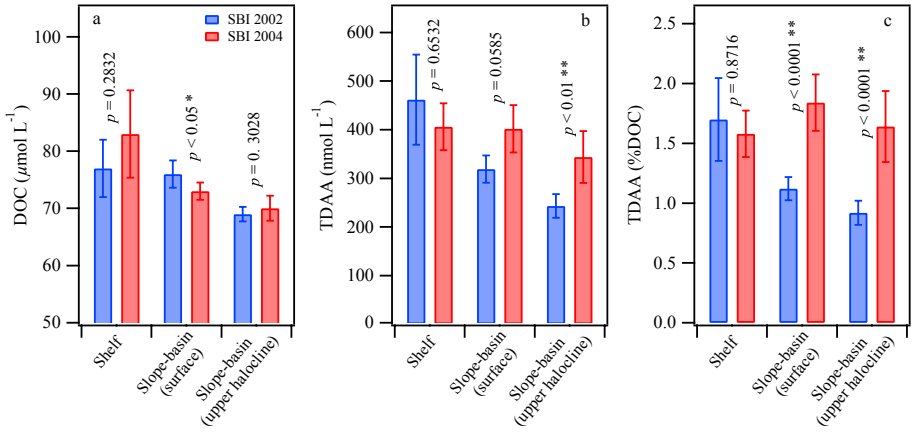

Fig. 7. Temporal comparisons of average concentrations of **(a)** dissolved organic carbon (DOC) and **(b)** total dissolved amino acids (TDAA), and **(c)** yields of TDAA in shelf, slope, and basin waters between SBI 2002 and 2004. Error bars represent two times the standard error. Significant ($p < 0.05$) and highly significant ($p < 0.01$) differences are marked with one or two asterisks, respectively.

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