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Strong hydrographic controls on spatial and seasonal variability of dissolved organic carbon in the Chukchi Sea

Jeremy T. Mathis[a,*], Dennis A. Hansell[a], Nicholas R. Bates[b]

[a]Rosenstiel School of Maine and Atmospheric Science, 4600 Rickenbacker Causeway, Miami, FL 33149-1098, USA
[b]Bermuda Biological Station for Research, Inc., 17 Biological Station Lane, Ferry Reach, Bermuda, GE01, UK

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Abstract

A detailed analysis of dissolved organic carbon (DOC) distribution in the Western Arctic Ocean was performed during the spring and summer of 2002 and the summer of 2003. DOC concentrations were compared between the three cruises and with previously reported Arctic work. Concentrations of DOC were highest in the surface water where they also showed the highest degree of variability spatially, seasonally, and annually. Over the Canada Basin, DOC concentrations in the main water masses were: (1) surface layer (71 ± 4 μM, ranging from 50 to 90 μM); (2) Bering Sea winter water (66 ± 2 μM, ranging from 58 to 75 μM); (3) halocline layer (63 ± 3 μM, ranging from 59 to 68 μM), (4) Atlantic layer (53 ± 2 μM, ranging from 48 to 57 μM), and (5) deep Arctic layer (47 ± 1 μM, ranging from 45 to 50 μM). In the upper 200 m, DOC concentrations were correlated with salinity, with higher DOC concentrations present in less-saline waters. This correlation indicates the strong influence that fluvial input from the Mackenzie and Yukon Rivers had on the DOC system in the upper layer of the Chukchi Sea and Bering Strait. Over the deep basin, there appeared to be a relationship between DOC in the upper 10 m and the degree of sea-ice melt water present. We found that sea-ice melt water dilutes the DOC signal in the surface waters, which is contrary to studies conducted in the central Arctic Ocean.

Keywords: DOC; Arctic Ocean; Chukchi Sea; Carbon

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1. Introduction

One of the goals of the Western Arctic Shelf–Basin interactions (SBI) Program is to gain a greater understanding of the distribution and dynamics of dissolved organic carbon (DOC) in the Western Arctic Ocean; particularly in its variability and transport over the Chukchi Sea shelf, adjacent slope, and basin. The role of DOC in the global carbon cycle is of considerable interest because the marine DOC pool is one of the major reservoirs of carbon in the biosphere (Hansell and Carlson, 2002). Given the strong seasonal signals (ice cover, light, biological production, etc.) and the impact of these on the carbon cycle, the Arctic Ocean remains under-sampled for DOC.

The Chukchi Sea shelf waters are highly productive due to inflow of nutrient-rich Pacific water through Bering Strait (BS) and exchanges with the Canada Basin and adjacent Arctic shelves (via the East Siberian Current). The inflow of Pacific water

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*Corresponding author. Tel.: 305 421 4019; fax: 305 421 4689.
E-mail address: jmathis@rsmas.miami.edu (J.T. Mathis).

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to the Chukchi Sea is approximately 0.8 Sv ($1\,\mathrm{Sv} = 10^6\,\mathrm{m^3\,s^{-1}}$) (Coachman and Aagaard, 1988), primarily as the Anadyr Current and the Alaskan Coastal Current. These Pacific and Arctic shelf water masses are modified and blended within the Chukchi Sea, and some of this mixture is exported into the Canada Basin. The distribution and dynamics of DOC within the Chukchi Sea is complex, influenced by the transport and fate of terrigenous DOC from several different sources, in situ production, and consumption processes (Gosselin et al., 1997; Wheeler et al., 1997), and sea-ice melt processes. Along with the influx of Pacific water, the Alaskan Coastal Current brings a significant amount of terrigenous DOC from the Yukon River, which empties into the Bering Sea. Yukon River discharge ($210\,\mathrm{km^3\,yr^{-1}}$; Cauwet, 2002) has a DOC concentration range reported to be 357–733 μM (Degens et al., 1991), providing a potential DOC flux of $0.9 \times 10^{12}\,\mathrm{g\,yr^{-1}}$ to the Chukchi Sea (Telang et al., 1991). Another source of terrigenous DOC in the Western Arctic Ocean comes from the Mackenzie River, significant amounts of which can be entrained onto the Beaufort Sea shelf. Average discharge from the Mackenzie River of $249\,\mathrm{km^3\,yr^{-1}}$ and DOC concentrations of 375–863 μM (Degens et al., 1991; Gordeev et al., 1996; Pocklington, 1987; Telang et al., 1991) provide an influx of terrigenous DOC directly into the Canada Basin of $1.3 \times 10^6\,\mathrm{t\,yr^{-1}}$ (Telang et al., 1991). In addition to transport of terrigenous DOC, autochthonous production of DOC by marine phytoplankton (Davis and Benner, 2005) and bacterial degradation of particulate organic matter (POC) within the Chukchi Sea (Gosselin et al., 1997; Wheeler et al., 1997) contribute to the DOC pool. The dynamics of the DOC pool are further complicated by seasonal sea-ice melt and production processes. The role of sea-ice in biogeochemical cycles in the Arctic is still not understood, but here we show how the distribution of sea-ice melt affected salinity and DOC in the upper mixed layer.

The objective of this investigation is to improve understanding of the controls on distribution and variability of DOC in the Western Arctic Ocean. DOC was sampled during the 2002 spring and summer SBI process cruises and the 2003 summer SBI survey cruise. Waters in the BS, Chukchi Sea shelf and shelf-break, and deep Canada Basin were sampled. Relationships between DOC and hydrographic properties were characterized for each of the water masses found in the Western Arctic Ocean over the Chukchi Sea shelf, shelf break, and slope region. As previously described (Aagard and Carmack, 1994; Bauch et al., 1995; Munchow and Carmack, 1997), Arctic Ocean water masses can be classified based on their salinities: Bering Sea winter water (salinity ≈ 32.8); Upper Halocline (Pacific source) water (salinity ≈ 33.1), Lower Halocline water (Eurasian Basin shelf water source) (salinity ≈ 34.2), Atlantic water (salinity ≈ 34.8), deep Arctic waters (salinity >34.9). In this study, we recognize two conditions for the polar surface layer (PSL): wintertime (PSLw) water (salinity ≈ 30), present under the permanent ice cap or during winter under the seasonal ice cap; and summertime (PSLs) water (lowered to salinity <29, by sea-ice melt), present in summer. These analyses, and comparisons with DOC data previously collected in the Arctic Ocean, allowed us to evaluate seasonal changes of DOC in individual water masses, changes in terrigenous DOC contributions to the Chukchi Sea, and the influence of sea-ice melt processes on DOC distributions.

2. Methods

2.1. Field sampling

Physical, biogeochemical and biological measurements were made from the USCGC *Healy* during two cruises to the Chukchi Sea in 2002 and one from the Research Vessel *N.B. Palmer* during the 2003 SBI survey cruise, all as part of the Western Arctic SBI project.

During the spring cruise of 2002 (5 May–15 June 2002), 39 stations were occupied on the Chukchi Shelf and in the adjacent Canada Basin (Fig. 1A). Three sections were occupied from the Chukchi outer shelf into the Arctic basin, designated: (1) West Hanna Shoal (WHS); (2) East Hanna Shoal (EHS); and (3) Barrow Canyon (BC). In addition, isolated stations near Pt. Barrow and the inner shelf of the Chukchi Sea were occupied. With the exception of BS, ice cover in spring was $>90\%$. Heavy sea-ice limited sampling in the northwest portion of the Chukchi Sea (American territory) and along the easternmost (Barrow Canyon) line in the Beaufort Sea. No sampling was done in the territorial waters of Russia during the three cruises.

During the summer cruise of 2002 (17 July 26 August 2002), 45 stations were occupied (Fig. 1B). The three shelf break sections listed above were

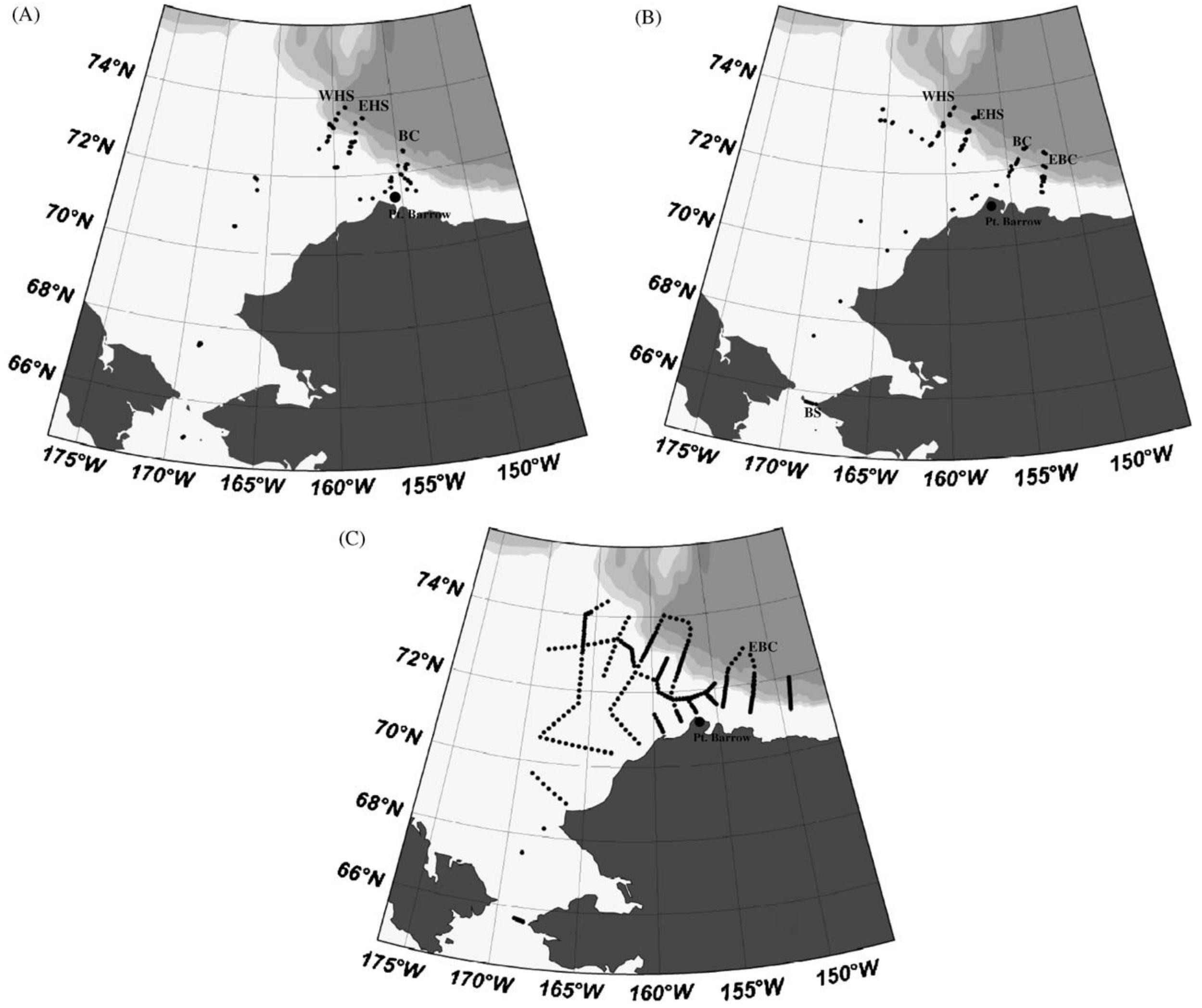

Fig. 1. Maps depicting station locations during the (A) spring 2002, (B) summer 2002, and (C) summer 2003 cruises. The hydrographic sections are designated West Hanna Shoal (WHS), East Hanna Shoal (EHS), Barrow Canyon (BC), East of Barrow Canyon (EB), and Bering Strait (BS).

reoccupied, as were additional inner shelf stations. A section east of Pt. Barrow, designated the East of Barrow Canyon (EB) line, was also occupied. Finally, the eastern (USA) sector of BS was occupied with five stations. Ice-free conditions were observed from BS to 70° N in the Chukchi Sea. Ice cover was $<25\%$ in the Barrow Canyon region, but heavier ice cover ($>75\%$) was present off the shelf and eastward into the Beaufort Sea.

During the summer survey cruise of 2003 (6 July–20 August 2003), 328 stations were occupied. DOC sampling was conducted on the above identified EB line only, with 22 stations being sampled (Fig. 1C) at higher horizontal and vertical densities than in previous years. Ice conditions during this cruise were moderate to light and did not affect sampling.

2.2. Dissolved organic carbon sampling and analysis

Samples were taken using a SeaBird 911+ CTD package. To ensure that particulate organic carbon (POC) did not contribute to estimates of DOC in the upper ocean, all samples from <300 m were filtered through an inline combusted GF/F filter held in acid-washed polycarbonate filter holders.

The filter cartridge was attached directly to the Niskin bottle with an acid-cleaned and MilliQ-water-rinsed silicone tube. Samples were collected into preconditioned and DOC-free, 60 ml HDPE bottles and frozen in organic-solvent-free freezers, then shipped to the shore-based laboratories. The filter cartridges were cleaned between uses and newly combusted GF/F filters were loaded prior to sampling each cast.

All samples were analyzed using the Shimadzu TOC-V system. Extensive conditioning and standardization procedures were performed prior to analyzing samples each day. Four-point standard curves of potassium hydrogen phthalate (KHP) were used to standardize DOC measurements. In addition, seawater DOC reference standards produced by the Hansell CRM program (http://www.rsmas.miami.edu/groups/organic-biogeochem/crm.html) were also analyzed each day. To maintain highest quality data control, samples were systematically checked against low-carbon water and deep and surface reference waters every sixth analysis (Hansell and Carlson, 1998). The between-day precision in the DOC measurement was 1–2 μM, or a CV of 2–3%.

3. Results

3.1. *General hydrography and near surface distribution of DOC*

The distributions of salinity and DOC at 10 m depth for the two cruises during 2002 are shown in Fig. 2. During the spring cruise of 2002 the lowest-salinity waters (<31) were in the northeast sector of the study area, in the Canada Basin (Fig. 2A). These waters generally had the highest DOC concentrations (>74 μM). The high-salinity Pacific water (>33) found in the western sector of BS had the lowest DOC concentrations (<68 μM) (Fig. 2A, B).

In summer of 2002 (Fig. 2C), the northern-most, off-shelf salinity at 10 m depth decreased to <29, apparently under the influence of ice melt. A drop in DOC to <70 μM in this area also was found. In contrast to spring, the highest DOC concentrations (<79 μM) were found in the eastern sector of BS and the southeastern Chukchi Sea shelf. In these regions, DOC concentrations increased by approximately 10 μM from spring to summer in the upper 10 m. Salinity was also reduced in BS during the summer cruise, suggesting a significant impact from Yukon River outflow.

3.2. *A representative shelf break section: West Hanna Shoal spring and summer comparison*

DOC and salinity in the upper 300 m of the West Hanna Shoal line during both occupations in 2002 are shown in Fig. 3. During spring, salinity in the surface 40 m decreased from >32 over the shelf to <31 over the basin (Fig. 3A). In contrast, DOC increased from ≈70 μM on the Chukchi Sea shelf to ≈78 μM over the basin (Fig. 3B). This covariation between salinity and DOC, with highest DOC values found in lower-salinity waters, is consistent with a riverine source (e.g., Mackenzie River) for the low-salinity, high-DOC surface basin water, referred to as PSLw water.

By summer, sea-ice melt reduced salinity in the upper 20 m to values of <30, with the lowest values farthest off the shelf (Fig. 3C). Off-shelf, DOC also was reduced (to ≈70 μM in the PSLs water; Fig. 3D). The % reduction of both salinity and DOC in the PSLs was similar in magnitude (≈10%), suggesting that the freshwater from sea-ice melt had a very low DOC concentration. The PSLw water (higher DOC and salinity of ≈29–31) remained offshore at depths of 10–40 m, but capped by the low-DOC ice-melt water (Fig. 3B, D). This wintertime layer below the surface sea-ice-melt layer, showed a reduction in DOC of approximately 5 μM over the basin. This could be attributed to the sea-ice melt dominated layer mixing vertically and diluting the DOC concentrations in the layer below it.

At depths of 60–100 m (Fig. 3), salinity and DOC showed little variability between spring and summer of 2002. Salinity and DOC values in this layer were approximately 32.5 and 65 μM, respectively.

3.3. *East of Barrow Canyon section: summer 2002 and 2003 interannual variability*

The EB line was occupied during the summer cruises of 2002 and 2003. During the 2002 cruise (Fig. 4A) the upper 20 m of water over the shelf region and the deep basin were fresher (28–29) than in the summer of 2003 (Fig. 4C) (29–30). This relative freshening was most likely due to the sampling line being occupied later in 2002 than in 2003, with more fresh water from ice melt being present. As expected, this salinity difference had an impact on the DOC concentrations in the surface layer, with values from 2002 being 8–10 μM less than those in 2003. This is another example of the

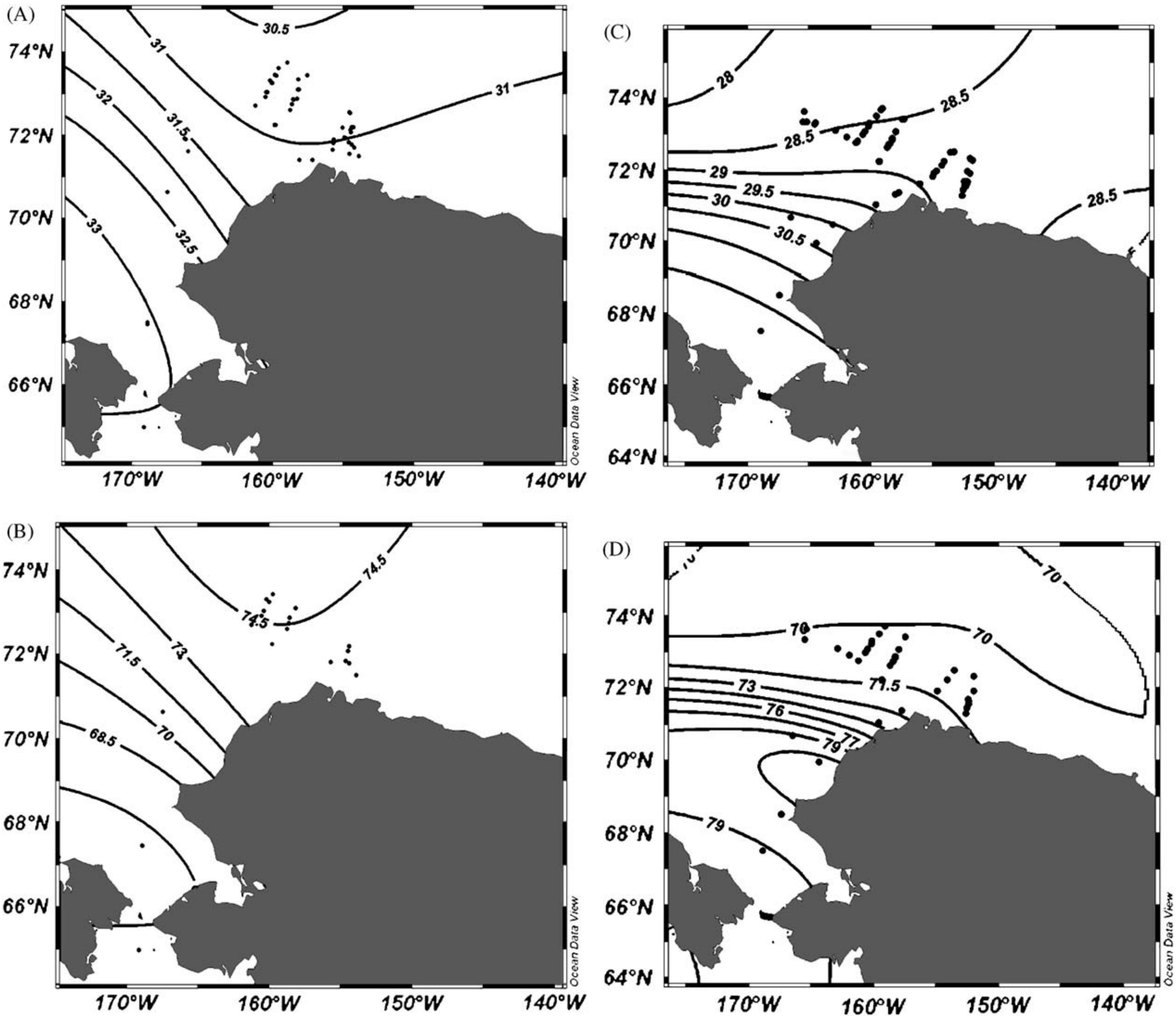

Fig. 2. Distribution of DOC (μM) at a depth of 10 m shown with salinity contour map: (A) Spring 2002 salinity; (B) spring 2002 DOC; (C) summer 2002 salinity; and (D) summer 2002 DOC.

effect that sea-ice melt has on DOC concentrations in the mixed layer of the Chukchi Sea.

DOC concentrations were also higher in the water mass above the shelf-break during the 2003 cruise (Fig. 4D). Between 50 and 100 m depth, DOC values were ≈70–75 μM during the 2003 cruise whereas values during the 2002 cruise were ≈65–70 μM (Fig. 4C). Again, there is a correlation here with salinity. The salinity was lower in this shelf break water during the 2003 cruise (≈32.5) compared to the values in 2002 (≈33). This area appears to contain high-DOC, low-salinity Alaskan coastal water flowing eastward along the shelf break in 2003 than 2002. This is perhaps due to time of sampling, or simply interannual variability. The higher DOC values and lower-salinity indicate a freshwater source of this water, most likely Yukon River water transiting near BC.

3.4. DOC in eastern Bering Strait

The BS is the portal for transfer of Pacific and Alaskan coastal current water to the Arctic. The waters passing through the strait are highly modified by the broad Bering Sea shelf crossed in the approach to the strait. Salinity in the eastern portion of the strait demonstrated the presence of the three water masses previously described (Coachman and Aagaard, 1988). Yukon River water dominated, low-salinity (<30.5) Alaskan Coastal

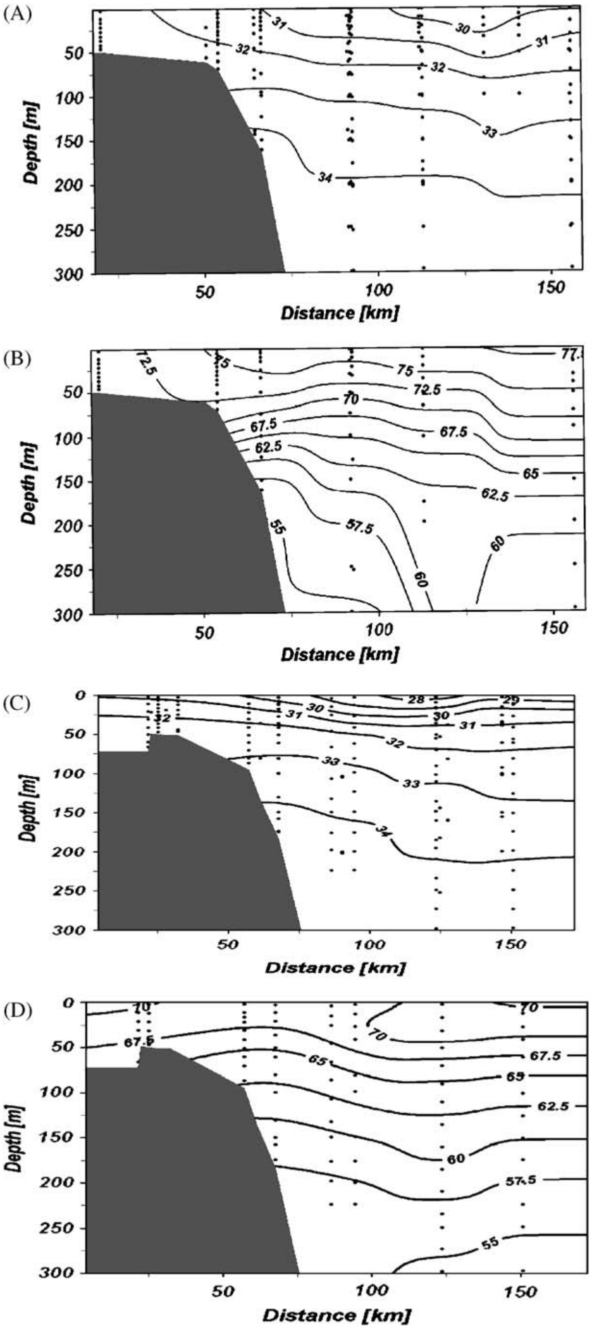

Fig. 3. Distribution of DOC (μM) with salinity contouring for the West Hanna Shoal section: (A) spring 2002 salinity, (B) spring 2002 DOC, (C) summer 2002 salinity, and (D) summer 2002 DOC. Note the presence of the off shore PSLs in C that is not present in A and the reduction in DOC between B and D. The PSLs is attributed to sea-ice melt.

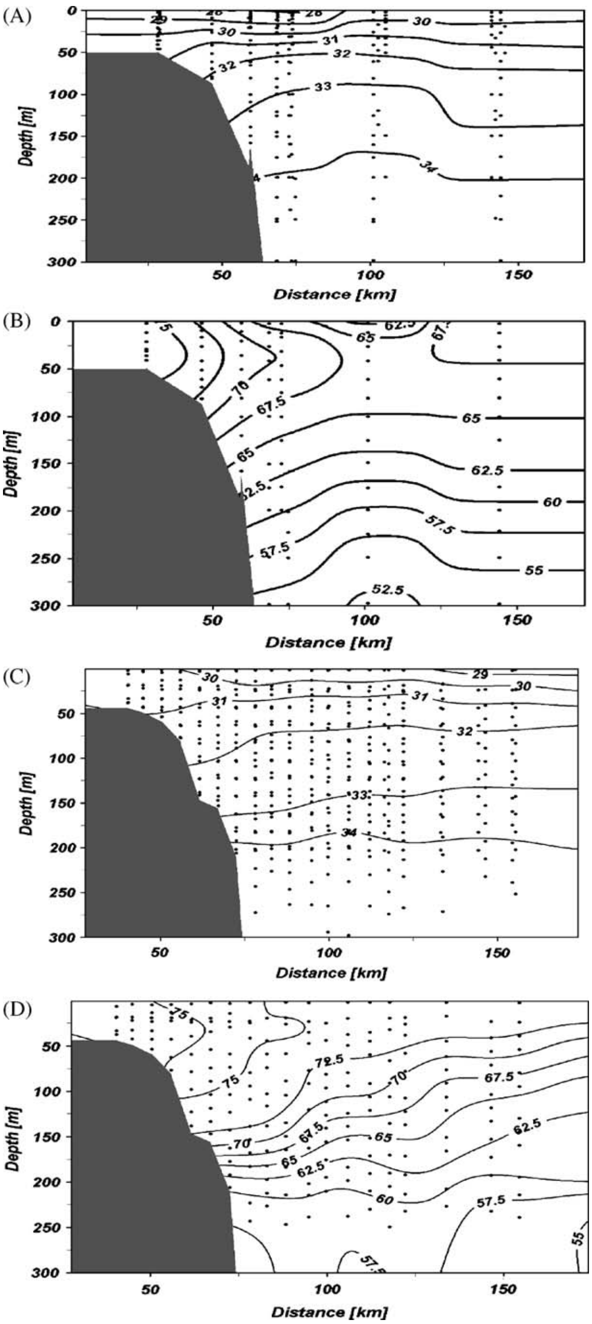

Fig. 4. Distribution of DOC (μM) with salinity contouring for the East of Barrow Canyon (EBC) section: (A) spring 2002 salinity; (B) spring 2002 DOC; (C) summer 2003 salinity; and (D) summer 2003 DOC.

water was present along the eastern boundary (Fig. 5A). In contrast, elevated salinity (>32) at depths >15 m (Fig. 5A) in the western-most part of the section indicated the influence of the Anadyr Current. The water mass intermediate in location and salinity to these two end-members was Bering Shelf water. The temperature distribution (Fig. 5B) allows Bering Shelf water to be subdivided

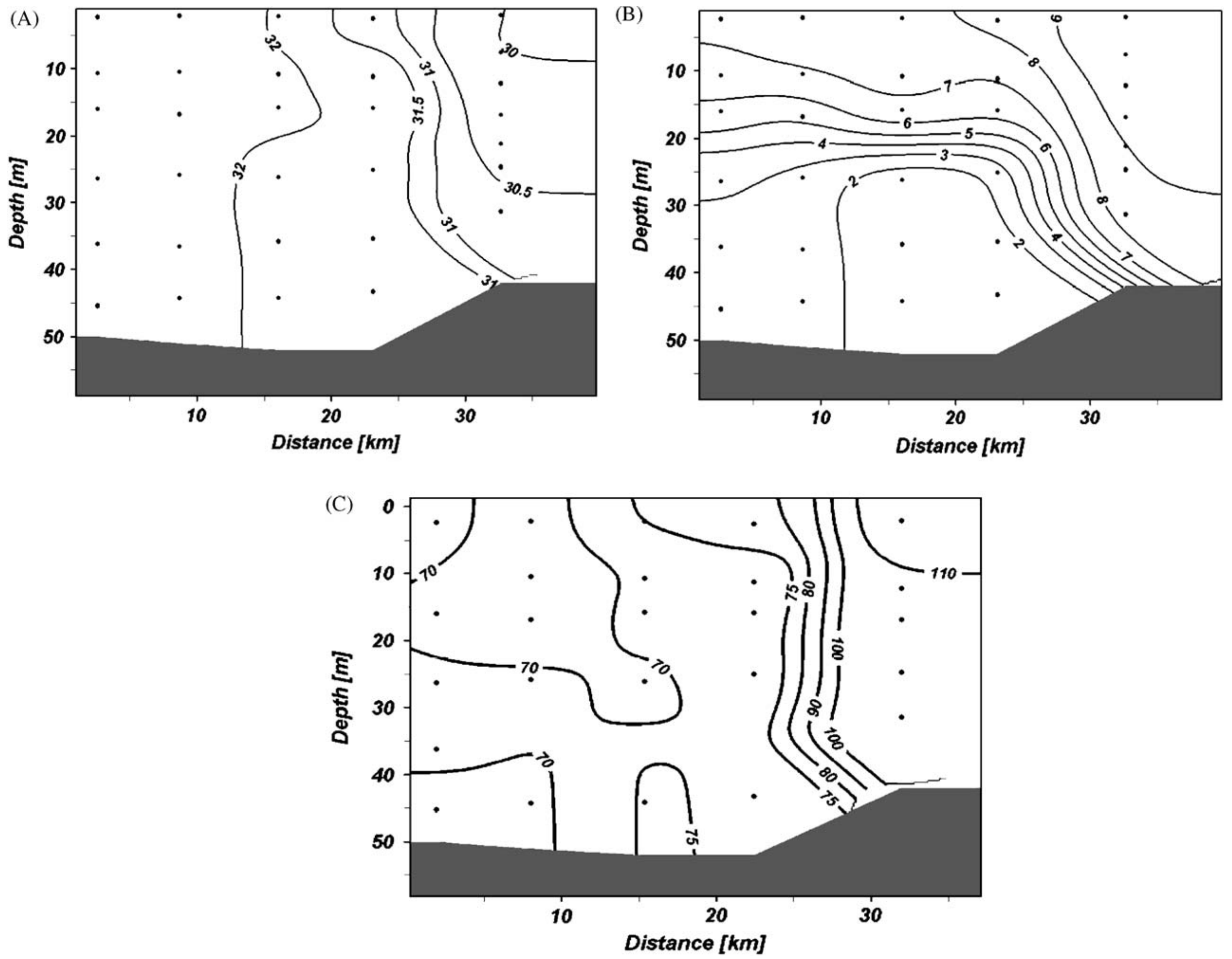

Fig. 5. Distribution of DOC (μM) with salinity and temperature contouring for the Bering Strait section during the summer of 2002: (A) salinity; (B) potential temperature (°C); and (C) DOC.

vertically, with the warm (>5 °C) summer Bering Shelf water present in the upper 20 m, and cold (<2 °C) winter Bering Shelf water reaching to the seafloor. DOC concentrations (Fig. 5C) showed a strong horizontal gradient, with highest concentrations (reaching >100 μM) in the coastal waters (riverine source) and lowest values near bottom in the highly marine Anadyr water (≈70 μM). A slight vertical gradient for DOC existed in the Bering Sea waters (Fig. 5C).

4. Discussion

4.1. Correlation of water masses and DOC concentrations

The distributions of temperature, salinity and nutrients in the Chukchi Sea have been well documented in previously published reports (Cota et al., 1996; McLaughlin et al., 1996; Cooper et al., 1997; Melling, 1998). Bates et al. (2005) provide a summary of the hydrographic conditions (salinity, temperature and nutrient patterns) found during the 2002 field season. The conditions were consistent with previously published reports.

Plots of DOC concentrations against salinity provide information on the relationship between Arctic hydrography and DOC (Fig. 6A, B). During spring of 2002, mixing between the offshore, low-salinity/high-DOC wintertime, river-water-dominated PSLw (salinity <31 and located over the basin) and the lower-DOC Pacific inflow water (salinity 33–34) was evident. The highest DOC concentrations (>74 μM) were found in the lowest-salinity (<31) surface waters, located over the basin. This low-salinity water was associated with

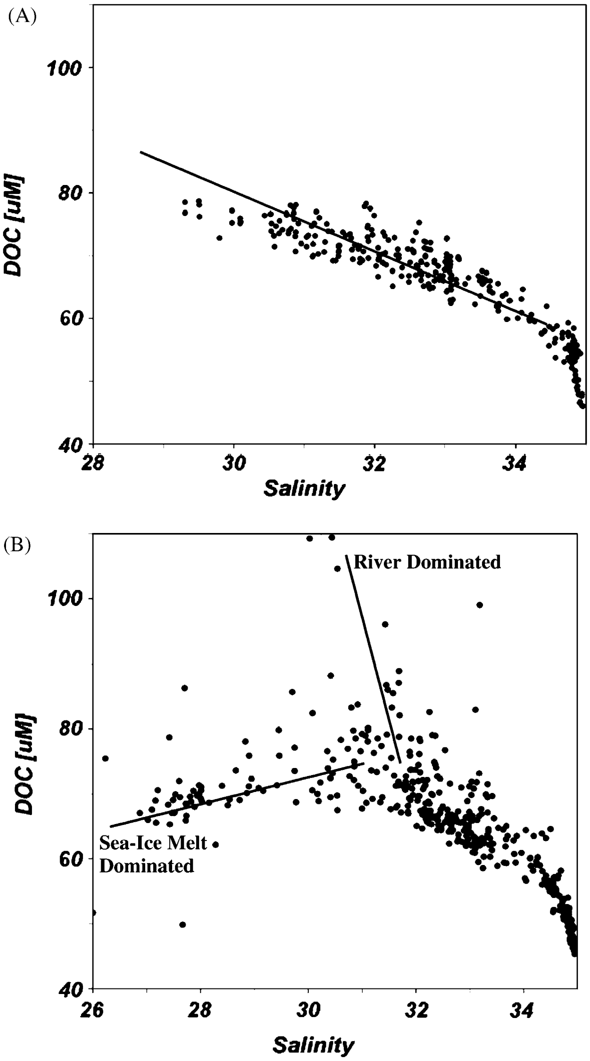

Fig. 6. Scatter plots of salinity and DOC (μM) identifying mixing curves: (A) spring 2002; and (B) summer 2002. Shown with apparent mixing lines.

PSLw water that was relatively enriched with DOC (Table 1). Increasing salinity in the DOC/salinity plot (Fig. 6A, B) generally corresponded to increasing water density and depth, which corresponded to decreasing mean DOC concentrations (Fig. 6A, B; Table 1). Atlantic water (salinity ~34.8) existed at depths >200 m and hence did not contribute significantly to the strong mixing found between the Pacific water and the PSLw (Fig. 6A).

During summer, mixing showed a clear bifurcation, with two new end-members evidently mixing with the Pacific end member (Fig. 6B). One new end-member was the Alaskan Coastal Current, dominated by high-DOC Yukon River inflow. During the summer cruise of 2002, the highest DOC concentrations (>100 μM) were found in waters with salinity from 30 to 31 (Figs. 5A, C and 6B), indicating the contribution from the low-salinity Yukon River water with DOC concentrations near 110 μM. The other direction of mixing was toward much lower salinities (<28) and lower DOC concentrations (<70 μM), indicating sea-ice-melt as the other new, seasonal end-member, located over the basin.

Here we compare the DOC concentrations and physical properties observed in the SBI study region to those previously published for the Western Arctic Ocean and the other Arctic basins. Table 1 shows the mean DOC concentrations found in each of the salinity-defined water masses for the three cruises during 2002 and 2003. Surface water over the basin had two states during the three cruises. A winter-time PSL (PSLw, target salinity ≈30) was found during the spring cruise. During the summer cruise, an ice-melt-dominated PSL (PSLs, target salinity <29) was present. The PSLw was still present during summer but had been capped by the new sea-ice melt layer of PSLs. During the spring 2002 and summer 2003 cruises, DOC concentrations in the PSLw were found to be approximately equal with a mean value of 75.2 ± 2.2 μM. During the two summer cruises of 2002 and 2003, respectively, the sea-ice melt-dominated surface layer had a lower DOC concentration than the PSLw, suggesting that sea-ice in the Chukchi Sea is low in DOC, thus causing a reduction of DOC in the upper mixed layer during the summer months. DOC concentrations and salinities in this layer during the summer of 2003 were found to be higher than in 2002, and a higher salinity was found in 2003, (73.2 ± 1.0 versus 67.6 ± 2.0, and 28.5 ± 0.5 versus 27.54 ± 0.3, respectively). The cause of this difference is most likely the degree of ice melt. The 2003 cruise was conducted early in the year with less ice melt present.

We found a reduction in DOC concentrations from 68.4 ± 3.3 μM to 63.9 ± 1.5 μM in Bering Sea winter water, from spring of 2002 to the summer of 2002, and through the summer of 2003. Variable residence times of BS water over the Bering and Chukchi shelves (~50 m depth) could allow varying fluxes of DOC from the sediments into the overlying waters, thus causing variations in concentrations. Variations in DOC concentrations also were found in the upper halocline waters. Concentrations were highest during the spring cruise of 2002, with a mean DOC concentration of 66.3 ± 2.7 μM. This

Table 1
Mean concentrations (±SD) of DOC (μM) and temperature (ITS-90) in salinity-defined water masses occupied near the shelf break of the western Arctic Ocean during the spring and summer 2002 cruises and the summer cruise of 2003

	Target salinity	Spring 2002			Summer 2002			Summer 2003		
		Measured salinity	Measured temp	DOC	Measured salinity	Measured temp.	DOC	Measured salinity	Measured temp.	DOC
Polar surface layer										
Winter-dominated (PSLw)	30	30.08 ± 0.48	−1.57 ± 0.01	75.3 ± 2.1 (10)	29.98 ± 0.37	−1.29 ± 0.20	70.1 ± 0.48 (11)	29.95 ± 0.31	0.35 ± 2.03	75.3 ± 2.30 (9)
Summer-dominated (PSLs)	< 29	—	—	—	28.54 ± 0.32	−0.67 ± 0.45	67.6 ± 2.0 (19)	28.47 ± 0.48	−0.85 ± 0.44	73.2 ± 0.97 (5)
Bering Sea winter water	32.8	32.75 ± 0.04	−1.69 ± 0.07	68.4 ± 3.3 (12)	32.82 ± 0.06	−1.34 ± 0.46	65.1 ± 1.4 (13)	32.78 ± 0.05	−1.56 ± 0.09	63.9 ± 1.50 (10)
Upper Halocline	33.1	33.11 ± 0.06	−1.69 ± 0.09	66.3 ± 2.7 (10)	33.09 ± 0.03	−1.63 ± 0.09	62.7 ± 1.6 (9)	33.11 ± 0.06	−1.51 ± 0.09	63.2 ± 2.5 (11)
Lower Halocline	34.2	34.18 ± 0.11	−0.78 ± 0.14	60.6 ± 2.1 (9)	34.17 ± 0.05	−0.90 ± 0.17	59.9 ± 1.6 (8)	34.16 ± 0.15	−0.84 ± 0.13	59.8 ± 2.9 (12)
Atlantic layer	34.8	34.81 ± 0.03	0.65 ± 0.08	54.6 ± 1.5 (28)	34.80 ± 0.01	0.62 ± 0.09	53. 8 ± 0.6 (11)	—	—	—
Deep Arctic layer	> 34.9	34.93 ± 0.02	−0.32 ± 0.09	47.2 ± 0.7 (9)	34.94 ± 0.01	−0.33 ± 0.09	46.5 ± 1.1 (10)	—	—	—

DOC data for this analysis were selected based on the target salinities used to designate the core of the water masses, with the actual (measured) salinities for each analysis given. Summer (PSLs) sea-ice melt-water data are from the West and East Hanna Shoal lines, selected at temperatures <0 °C for the target salinity. Target salinities are based on findings during the 2002 field season and literature values Bauch et al. (1995), Munchow and Carmack (1997), Aagard and Carmack (1994). Number of samples in parentheses. The Atlantic and deep Arctic layers were not sampled for DOC in 2003.

value decreased during the 2002 summer cruise to a mean value of 62.7 ± 1.6 μM (Table 1), while measured salinity of the water mass remained virtually unchanged. In the summer of 2003, the DOC concentration in the upper halocline was essentially unchanged compared to summer 2002, with a mean value of 63.9 ± 1.5 μM versus 62.7 ± 1.6 μM, respectively. Salinity remained constant between the two years at 33.1.

In water masses below the upper halocline, mean DOC concentrations did not vary seasonally or interannually (Table 1). During all three cruises the mean DOC concentration in the lower halocline layer, for example, was ≈60 μM, with a constant salinity of 34.17. In the Atlantic layer, DOC showed no seasonal variations, with concentrations being ≈54 μM, at salinity of 34.81. In the deep Arctic layer, again DOC concentrations showed no seasonal variation, remaining constant at ≈47 μM, with a salinity of 34.93. Observations taken from these water masses support the earlier findings that shelf water in the Arctic Basin does not affect deeper Arctic waters (Fransson et al., 2001; Ekwurzel et al., 2001).

We summarize the mean DOC concentrations for the water masses in the Western Arctic Ocean as: Bering Sea winter water DOC of 67 ± 2 μM (salinity ≈32.8); Upper Halocline (Pacific) water DOC of 66 ± 2 μM (salinity ≈33.1); Lower Halocline water (Eurasian Basin shelf water) 60 ± 2 μM (salinity ≈34.2). In the deeper layers, DOC averaged 54 ± 1 μM in the core of the Atlantic layer (salinity ≈34.8) and 47 ± 1 μM in the deep Arctic waters (salinity > 34.9).

A relatively large range of DOC values has been reported previously for the surface layer of the Arctic Ocean (Table 2). Compared to DOC means and ranges collected during this study, Opsahl et al. (1999) and Guay et al. (1999) found similar means and ranges. More recently, Bussmann and Kattner (2000) conducted a DOC survey in the central Arctic Ocean, finding a mean surface DOC concentration of 78 μM, but with an extremely large range from 43 to 225 μM. Wheeler et al. (1997)

Table 2
Comparison of mean DOC concentrations (μM) from the western Arctic Ocean reported in this study (from Table 1) with recent published values for the major water masses of the Arctic Ocean. Where seasonal variations existed in Table 1 data, the approximate mean and range is listed. Salinity definitions of water masses are given in Table 1

	This study	Published values	Location	Source
Surface layer	71 ± 4	78	Central Arctic	Bussmann and Kattner (2000)
		66–80	All basins	Opsahl et al. (1999)
		70 ± 10	Canada basin; 50 m	Guay et al. (1999)
		90 ± 25	Makarov basin; 50 m	Guay et al. (1999)
		34 ± 4	Chukchi shelf	Wheeler et al. (1997)
		76 ± 3	Chukchi slope	Wheeler et al. (1997)
		82 ± 15	Eurasian basin	Wheeler et al. (1997)
		101 ± 10	Canada basin	Wheeler et al. (1997)
		97	Central Arctic	Amon and Benner (2003)
Bering Sea winter water	66 ± 2	71 ± 20	Pacific inflow	Anderson (2002)
Halocline	63 ± 3	70 ± 6	Eurasian basin	Wheeler et al. (1997)
		67 ± 4	Chukchi slope	Wheeler et al. (1997)
		75 ± 8	Canada basin	Wheeler et al. (1997)
		70 ± 5	Eurasian basin	Wheeler et al. (1997)
Atlantic layer	53 ± 2	58 ± 5	Eurasian basin	Amon (2004)
		58 ± 4	Eurasian basin	Wheeler et al. (1997)
		53 ± 4	Canada basin	Wheeler et al., 1997
Deep Arctic layer	47 ± 1	50 ± 2	Eurasian basin	Amon (2004)
		55	Makarov basin	Bussmann and Kattner (2000)
		54	Amundsen basin	Bussmann and Kattner (2000)
		50	Nansen basin	Bussmann and Kattner (2000)
		53	Fram strait	Opsahl et al. (1999)
		51 ± 5	Eurasian basin	Wheeler et al. (1997)

reported a range of surface DOC concentrations from 34 to 101 μM across the Arctic Ocean (Table 2). We found a mean surface concentration of 71 μM but a smaller range of 50–90 μM. It is apparent that surface DOC concentrations throughout the Arctic Ocean have a high degree of variability. Based on the concentrations reported (Table 2) it seems likely that the surface concentration of DOC across the interior Arctic Ocean ranges between 70 and 90 μM. The variability in these data is likely due to several factors including different analytical methods and standardization, end-member mixing (Fig. 6B), ice conditions, biological production, and the influence of rivers. These complexities make it very difficult to generalize and predict DOC concentrations in the surface layer of the Arctic Ocean, particularly in the summer time.

In the halocline (both upper and lower), there appears to be no evidence for long-term variability in DOC concentrations. Wheeler et al. (1997) reported DOC concentrations in the halocline layer (upper and lower halocline averaged) over the Chukchi Slope of 67 ± 4 μM, compared to 63 ± 3 μM in this study (Tables 1 and 2). Furthermore, there appears to be little difference in DOC concentrations between the Canada and Eurasian Basins given the error range (Table 2).

However, there does seem to be a DOC concentration gradient between the Eurasian and Canada Basins in the deeper Atlantic and deep Arctic layers. In the Atlantic layer of the Canada Basin, a mean DOC concentration of 53 ± 2 μM (Table 2) is approximately 5 μM lower than values reported for the Eurasian basin by Amon and Benner (2003) and Wheeler et al. (1997). Similar DOC differences are also evident between the Eurasian and Canada Basins in the deep Arctic layer (Table 2). The difference in intermediate and deep DOC concentrations between both basins likely reflects greater aging of Canada Basin waters. The deep Canada Basin waters are approximately 500 years old (Macdonald and Carmack, 1993), whereas deep water of the Eurasian Basin are younger, between 163 and 287 years old (Schlosser et al., 1995). As shown in other basins (Hansell and Carlson, 1998), DOC concentration decreases with aging in the deep ocean, possibly explaining the gradient between the two basins.

Table 3 compares the slopes and intercepts of DOC/salinity regressions obtained with the data from the spring 2002 data to other published regressions using data taken in the Eurasian Basin. It is clear that the DOC/salinity relationship of the Canada Basin is very different than that of the Eurasian Basin. The DOC concentration in the freshwater end member (zero-salinity intercept of the y-axis) was 154 ± 7 μM in this study. The intercepts found in the Eurasian Basin have DOC concentrations in the freshwater end member ranging from 552 to 740 μM. Hansell et al. (2004) suggested that the difference in the zero-salinity intercepts is a result of significant removal of terrigenous DOC in the Western Arctic Ocean. There remains some uncertainty, however, about the initial DOC concentrations in the rivers contributing terrigenous DOC to the western Arctic. The Mackenzie River contributes approximately $1.9 \times 10^{12}\,\mathrm{g\,C\,yr^{-1}}$ and is the major source of freshwater in the southern sector of the Beaufort Gyre (Macdonald et al., 2002). DOC concentrations reported in this river are highly variable, ranging from 360 to 730 μM (Anderson, 2002). A summer (1993) survey of DOC in the Mackenzie River tributaries, when most of the river discharge occurs, indicated concentrations of 550 ± 122 μM (Droppo et al., 1998). Osborn et al. (2004, and pers. comm.) measured concentrations of 670 ± 7 and 512 ± 3μM at two stations on the Mackenzie River. Amon and Meon (2004) reported DOC values of 400 μM in the

Table 3
Slopes of DOC/salinity regressions (salinity are independent variable) and intercepts (DOC concentration (μM) at salinity = 0) from this study and published accounts

Slope	Intercept	Location	References
−5.1	154	Chukchi Sea shelf break	Spring 2002, this work
−18.5	705	East Siberian/Laptev Sea	Guay et al. (1999)
−12.8	600	Laptev Sea (SPASIBA 2)	Cauwet and Siderov (1996)
−11.8 to −16.4	552–617	Ob River, Kara Sea	Köhler et al. (2003)
−7.0 to −18.3	560–740	Yenisei River, Kara Sea	Köhler et al. (2003)
—	531	Lena River, Laptev Sea	Kattner et al. (1999)

Mackenzie River during the summer. Although there is some variability in these data, it is apparent that the Mackenzie is capable of contributing a significant load of DOC into the Beaufort Gyre, where this DOC can be entrained and circulated.

4.2. *DOC and sea-ice*

On the West Hanna Shoal section (Figs. 1A, 2A and 3), occupied during the spring cruise of 2002 (pre-ice melt), we found salinities in the surface layer ranging from 30 to 32 (Fig. 3A), with DOC concentrations ranging from 72.5 to 77 μM (Fig. 3B). When the same section was occupied later in the summer, after ice melt had occurred, a cap with lower salinities of 28–31 (Fig. 3C) was found with DOC concentrations being reduced to 70 μM (Fig. 3D).

Bussmann and Kattner (2000) reported that sea-ice melt in the central Arctic Ocean increased DOC concentrations in the surface layer. In contrast, during the SBI study, sea-ice melt-diluted surface layer DOC concentrations; sea-ice melt apparently did not contribute DOC to the PSLs (Table 1; Fig. 6B). Gianelli et al. (2001) indicate that the bulk of DOC is expelled during ice formation with the brine formed (and likely sinks into deeper layers), so the SBI results are not surprising.

Several studies done on sea-ice in the Arctic Ocean have found much higher DOC concentrations (through sea-ice diatom production) in certain types of ice than in the surface water below it (Thomas et al., 1995). For example, Mel'nikov and Pavlov (1978), Apollonio (1980), and Bunch and Harland (1990) measured mean DOC concentrations in the bottom layers of first year sea-ice 4 times greater than that of the underlying seawater. Thomas et al. (1995) suggested that these DOC concentrations, in conjunction with high NH_4^+ levels, indicated that a significant portion of the DOC was a result of decomposition/grazing of ice algae and/or detritus. Thomas et al. (1995) also showed depth distribution of DOC in various kinds of sea-ice (mixed columnar/granular, granular, and columnar) and how concentrations varied from each core sample taken. In some of the core samples, DOC concentrations were $<50\,\mu M$ throughout the entire ice sheet, while in others there was a strong DOC signal near the bottom layer ($>600\,\mu M$). The high accumulation of DOC in certain types of sea-ice indicates that there is an uncoupling of the DOC production and consumption processes (Thomas, 2003). Pomeroy and Wiebe (2001) reviewed this phenomenon and concluded that the reduced substrate affinity of bacteria at low temperatures may be responsible for the uncoupling, resulting in poor exploitation of the high concentrations of available organic substrates in the ice.

Due to the paucity of data for DOC in sea-ice in the western Canada Basin, it is uncertain whether the ice observed during the 2002 and 2003 cruises initially contained high concentrations of DOC. It could be that ice-melt water observed during our cruises to the Chukchi Sea was low in DOC while sea-ice melt in the central Arctic sampled by Bussmann and Kattner (2000) had much higher concentrations. This is one possible explanation for the discrepancies found in sea-ice melt and DOC concentrations in the upper mixed layer.

Another possible explanation of the variations in sea-ice DOC concentrations is related to the DOC versus ice thickness profiles shown by Thomas et al. (1995). These profiles showed that even ice that had higher DOC concentrations in the bottom layer was overlain by significantly more ice that had low DOC concentrations. If the entire ice flow melted, then the low-DOC ice on top of the flow would dilute the DOC signal from the bottom of the ice.

Immediate bacterial consumption of the DOC released could be another explanation for the apparent low concentration of DOC in sea-ice in the Chukchi Sea. If sufficient nutrients were available upon the ice flow breaking up then DOC could be consumed as it was released from ice. Further study is necessary to fully understand the relationship between sea-ice and DOC.

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