

## Determining net dissolved organic carbon production in the hydrographically complex western Arctic Ocean

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### Abstract

Each spring and summer, the Chukchi Sea in the western Arctic Ocean experiences a short but intense phytoplankton bloom that is controlled by sea ice cover, nutrient availability, and river runoff. During the bloom, dissolved inorganic carbon (DIC) concentrations are drawn down in the mixed layer (shelf,  $\sim\Delta 100 \mu\text{mol kg}^{-1}$ ; shelf-break,  $\sim\Delta 50 \mu\text{mol kg}^{-1}$ ; basin,  $<\Delta 5 \mu\text{mol kg}^{-1}$ ) and converted to particulate organic carbon (POC) and dissolved organic carbon (DOC). We use  $\delta^{18}\text{O}$  and salinity to estimate DOC inputs by river and sea ice melt, allowing the marine portion of the DOC pool to be compared between seasons and to facilitate estimates of net DOC production in the region. We estimate that  $\sim 10\%$  of the DIC consumed during net community production is converted to DOC. The remaining carbon deficit (90% of DIC drawdown) is most likely exported from the mixed layer as POC. In 2002 a carbon (C) mass balance was developed for the Chukchi Sea that showed that rates of vertical export were highest over the Chukchi Shelf near Point Barrow ( $64 \text{ mmol C m}^{-2} \text{ d}^{-1}$ ), but more commonly ranged from 10 to  $35 \text{ mmol C m}^{-2} \text{ d}^{-1}$  over the remainder of the shelf. At the shelf-break and in the Canada Basin export production was  $<10 \text{ mmol C m}^{-2} \text{ d}^{-1}$ . DOC plays a relatively small role as a carbon sink in the system, but quantifying its contributions provides more robust estimates of export production in the Arctic.

A predominant geographical feature of the Arctic Ocean is its extensive continental shelves, constituting  $\sim 50\%$  of its total surface area and accounting for  $\sim 85\%$  of all primary productivity in the Arctic Ocean (Stein and MacDonald 2004). Strong physical and biogeochemical forcing on these shelves, such as sea ice formation and high primary and secondary production, play an important role in modifying and conditioning the waters of the interior Arctic Basin.

In the central Chukchi Sea, north of the Bering Strait, rates of primary production during late spring and summer are among the highest measured globally (Springer and McRoy 1993). These blooms are controlled by the availability of inorganic nutrients, light intensity, ice cover, and river runoff. At the termination of these blooms, inorganic nutrients, particularly nitrate, have been exhausted in the surface layer, and a fraction of dissolved

inorganic carbon (DIC) that was present in the surface layer before the onset of the seasonal bloom has been converted to dissolved and particulate organic carbon (DOC and POC, respectively). A strong gradient exists in primary productivity between the shelves and the interior Arctic basins. Thus, the transformations and shelf–basin exchange of carbon have the potential to significantly affect the carbon budget for the Arctic Ocean.

In remote, open-ocean regions away from land, DOC production originates from several in situ biological processes, but it is ultimately derived from primary production. In the western Arctic, however, a complex set of hydrographic conditions exists that provide a variety of sources of DOC to the region. In late spring and summer the upper mixed layer of the Chukchi Sea is strongly influenced by river-water runoff and ice melt, which both affect DOC concentrations. During the height of terrestrial input and sea ice melt primary production converts DIC to DOC and POC in the mixed layer. Significant amounts of newly produced DOC have been shown to accumulate during or after phytoplankton blooms (Carlson et al. 1994), and several studies have shown that DOC is an important component of the “biological pump” (Carlson et al. 1994). However, DOC export in lower latitudes, such as the Sargasso Sea, is not considered to be a long-term carbon storage mechanism because of limited potential for physical transport (Carlson et al. 1994). On the other hand, in polar environments such as the Ross Sea (Carlson et al. 1998)

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and the Chukchi Sea, where conditions exist for intermediate and deep-water formation, DOC can be advected to greater depths and thus removed from contact with the surface.

The objective of this work was to determine the seasonal production of marine DOC by phytoplankton in the western Arctic Ocean by correcting for the influence of river runoff and sea ice melt using salinity and  $\delta^{18}\text{O}$  data. Once the river-water and ice melt components are removed, marine DOC data were compared between spring (pre-bloom) and summer (late/postbloom) to calculate the seasonal DOC accumulation due to primary productivity. Finally, we developed a carbon mass balance for the Chukchi Sea based on the seasonal drawdown of DIC and the production of DOC and POC.

### Regional hydrography and biogeochemistry

**Regional hydrography**—On average, 0.8 Sv (1 Sv =  $10^6 \text{ m}^3 \text{ s}^{-1}$ ) of nutrient-rich Pacific and fluvial waters flow through the Bering Strait into the Chukchi Sea (Woodgate et al. 2005). While crossing the Chukchi Shelf, this water undergoes modifications through seasonal primary production, respiration, and remineralization; physical forcing (i.e., cooling in winter, with densification through brine rejection); and interactions with the sediments (Cooper et al. 1997). This area is subject to strong seasonal and interannual variability in sea ice cover, freshwater input from rivers, light availability, and atmospheric forcing.

On the eastern side of the Bering Strait, the inflow of water is dominated by the warm, relatively fresh Alaskan Coastal Current (Woodgate et al. 2005). The western side of the inflow contains water from the Anadyr Current, with the lowest temperatures, highest salinities, and highest nutrient concentrations. The central Bering Strait contains Bering shelf water that is intermediate in temperature and salinity. Observations indicate that water flows across the Chukchi Shelf as two or three distinct branches dictated by the bathymetry of the shoals and canyons (Woodgate et al. 2004; Weingartner et al. 2005), consistent with recent model results (Winsor and Chapman 2004) (Fig. 1). North of the Bering Strait some seasonal flow also enters the region from the East Siberian Current (Weingartner et al. 1999), but the effect this water has on the system is highly variable (e.g., Münchow et al. 1999) (Fig. 1).

When these waters reach the outer shelf of the Chukchi Sea, geostrophic constraints drive the flow into an eastern boundary current flowing along the shelf-break toward the Beaufort Sea (e.g., Pickart et al. 2005). There is evidence for eddy formation from this boundary current (Pickart et al. 2005), which propagates nutrient- and carbon-rich waters into the interior Canada Basin. The lateral exchange of waters between the continental shelf and interior basin is evident throughout the Arctic Ocean and is an important mechanism for transport of nutrients, organic carbon, and suspended particulate matter to the interior Arctic basins (e.g., Carmack et al. 1997). These interactions along the outer shelves of the Chukchi and Beaufort Seas control the rate of exchange between Pacific water entering through the Bering Strait and the interior Arctic Ocean.

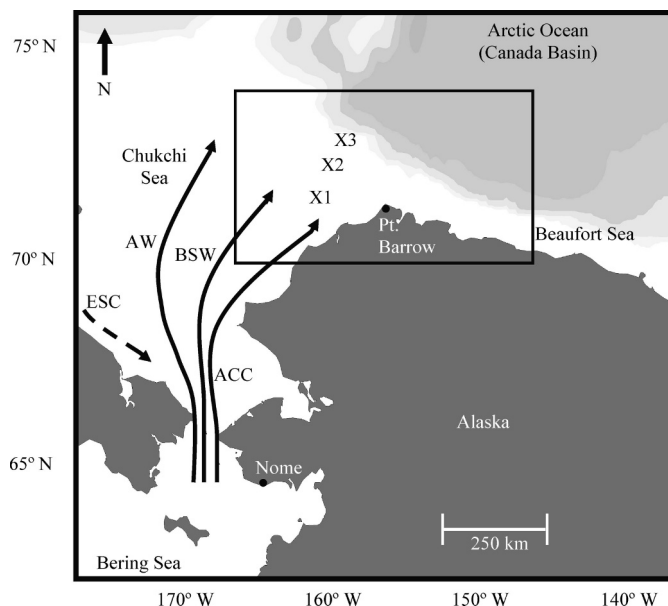


Fig. 1. The western Arctic Ocean including the Chukchi and Beaufort Seas. X1, X2, and X3 are locations of ice cores that were sampled for DOC in spring of 2004. ACC, Alaskan Coastal Current; BSW, Bering Sea Water; AW, Anadyr Current; ESC, East Siberian Current. The box defines the area used in Figs. 7 and 8.

The combination of waters from the Pacific Ocean, the Bering Sea, terrestrial runoff, and sea ice melt create a hydrographically complex water mass over the Chukchi Shelf. In winter, the mixed layer (0 to  $\sim 30$  m; temperature  $[T] = \sim -1.3^\circ\text{C}$ ; salinity  $[S] = \sim 31\text{--}32$ ) over the Chukchi Shelf is dominated by lower salinity water from the Bering Sea and remnant river-water runoff. During late spring, the onset of sea ice melt and increased river runoff lowers the salinity and raises the temperature of the mixed layer ( $T > 0$ ;  $S < 31$ ) and creates a freshwater lens at the surface (0–5 m). Beneath the mixed layer are waters of the Upper Halocline Layer (UHL). The UHL layer is typically  $> \sim 30$  m deep and has a core layer with a salinity of 33.1 and a temperature of  $-1.5^\circ\text{C}$ . The UHL flows off the shelf and can be traced to the Eurasian basin exits from the Arctic Ocean Region (e.g., Jones et al. 2003).

**DOC in the western Arctic Ocean**—DOC enters the western Arctic Ocean through several different pathways. There are three physical pathways that bring DOC into the Chukchi Sea; marine DOC transits through the Bering Strait with waters of Pacific origin; terrestrial DOC is imported through river runoff; and marine DOC exchanges between the East Siberian/Chukchi Sea and the Canada Basin/Chukchi Sea through physical processes such as upwelling. Within the Chukchi Sea there exist active DOC production and consumption throughout the year (i.e., in situ production of DOC from net community production [NCP], production of DOC from sinking and suspended POC, consumption of DOC by the microbial community both in the Polar Mixed Layer (PML) and UHL, and the breakdown of DOC in the benthos). The highest concen-

trations of DOC in source waters are found in arctic river runoff, with a reported range of 375 to 900  $\mu\text{mol kg}^{-1}$  (Anderson 2002). These high concentrations of riverine DOC are substantial because the Arctic Ocean receives a disproportionately high amount (approximately 10%) of the total global river runoff (Lobbes et al. 2000). Most of the organic carbon present in arctic river runoff is derived from the carbon-rich soils and vegetation in the high-latitude regions of North America and Eurasia (Dixon et al. 1994). Future warming could thaw the permafrost present in the Arctic, accelerating carbon loss from soils. The increase in carbon availability from the soil coupled with increased river discharge could lead to an increase in the amount of terrigenous DOC that is delivered to the Arctic Ocean. The Yukon River (357–733  $\mu\text{mol kg}^{-1}$  DOC) (Anderson 2002) is the major contributor of terrigenous DOC to the Chukchi Sea. However, other rivers, such as the Mackenzie River (375–863  $\mu\text{mol kg}^{-1}$  DOC) (Anderson 2002) and the Colville River, which had a DOC concentration of  $\sim 900 \mu\text{mol kg}^{-1}$  in September 2004 (this study), can also deliver large seasonal fluxes of DOC to the Chukchi Shelf. The fate of terrestrial DOC once it reaches the marine environment is not well defined. A portion of it is consumed by microbial activity, but  $\sim 35\%$  of the total annual discharge of DOC from arctic rivers can be transported into the North Atlantic (Hansell et al. 2004; Benner et al. 2005).

Concentrations of marine DOC entering the western Arctic Ocean with Pacific waters through the Bering Strait are much lower ( $\sim 70 \mu\text{mol kg}^{-1}$ ; Mathis et al. 2005) than in arctic rivers. However, the volume flux is  $>50$  times higher than continental runoff, making it the most significant source of marine DOC to the western Arctic Ocean.

Several factors affect the distribution of DOC in the Chukchi Sea. Concentrations in the upper mixed layer over the Chukchi Shelf are strongly influenced by freshwater input from river runoff and sea ice melt (Mathis et al. 2005) as well as by biological activity. River runoff provides a strong seasonal flux of terrestrial DOC to the surface waters of the Chukchi Sea (Anderson 2002), and the Yukon River is the largest source of terrestrial DOC to the Chukchi Shelf. Low-salinity water from ice melt, on the other hand, dilutes the DOC pool in the upper 5 m over the Chukchi Shelf and in the polar surface layer of the western Arctic Ocean (Mathis et al. 2005). These two factors have made it difficult to determine the seasonal net production of marine DOC. The inability to account for DOC production in spring and summer has made it difficult to develop an accurate carbon budget for the Chukchi Shelf and the adjacent Canada Basin.

Here, we use  $\delta^{18}\text{O}$  and salinity to correct for the river runoff and sea ice melt components of the mixed layer, allowing the marine fraction of the DOC pool to be compared seasonally. Once the rate of net DOC production and the seasonal accumulation of POC (Bates et al. 2005b) are determined, the rates of vertically exported POC over the shelf, shelf-break, and Canada Basin are calculated using a seasonal carbon budget determined by mass balance.

## Biogeochemical conditions in 2002

During a survey of the region in 2002, surface waters were ice-covered at all stations occupied in the spring (May/June), whereas waters over the Chukchi Shelf and slope were largely ice-free in summer (July/August). Temperature and salinity in the upper 50 m ranged, respectively from  $-1.8$ – $1^\circ\text{C}$  and 29–33 in spring to  $-1.8$ – $0.2^\circ\text{C}$  and 18–35 in summer (Codispoti et al. 2005).

In 2002, the euphotic zone, defined by the 1% light layer, averaged  $37 \pm 14$  m in the spring and  $38 \pm 13$  m in the summer; it was shallower ( $\sim 25$ ) over the shelf in areas of high productivity near Barrow Canyon (Hill and Cota 2005). Chlorophyll *a* concentrations increased from minima of  $\sim 0.1$ – $0.3 \text{ mg m}^{-3}$  to maxima ranging from  $\sim 0.5$  to  $4.0 \text{ mg m}^{-3}$  between the spring and summer cruises (Hill and Cota 2005). Dissolved nitrate ranged from  $\sim 1$  to  $4 \mu\text{mol kg}^{-1}$  in waters over the shelf in spring but was below detection limits in summer (Codispoti et al. 2005).

Primary productivity in the spring ( $<0.3 \text{ g C m}^{-2} \text{ d}^{-1}$ ) was light-limited as a result of sea ice cover over most of the shelf, but rates as high as  $8 \text{ g C m}^{-2} \text{ d}^{-1}$  were observed in association with surface bloom conditions during the initial ice breakup (Hill and Cota 2005). Rates of production observed during summer (late bloom to postbloom) were  $0.8 \text{ g C m}^{-2} \text{ d}^{-1}$  on the shelf and  $0.3 \text{ g C m}^{-2} \text{ d}^{-1}$  at the shelf-break, with an estimated total annual production of  $90 \text{ g C m}^{-2} \text{ yr}^{-1}$  in the study area (Hill and Cota 2005). The highest rates of NCP, based on the drawdown of DIC between spring and summer, were  $1$ – $3 \text{ g C m}^{-2} \text{ d}^{-1}$  near Barrow Canyon and east of Point Barrow in the western Beaufort Sea (Bates et al. 2005a). A total NCP of  $8.9$ – $17.8 \times 10^{12} \text{ g C}$  was determined for the eastern Chukchi Sea shelf and slope region (Bates et al. 2005a). Very low inorganic nutrient concentrations and low rates of NCP ( $<15$ – $25 \text{ mg C m}^{-2} \text{ d}^{-1}$ ) in the adjacent Canada Basin indicate that this area is perennially oligotrophic (Bates et al. 2005a).

POC accumulated between spring and summer in the mixed layer of the Chukchi Sea, and this organic matter was transported from the shelf into the Canada Basin in a POC-enriched layer at the top of the upper halocline (Bates et al. 2005b). POC not suspended in the water column sinks out of the upper mixed layer, where it is remineralized at depths below the mixed layer or deposited in the sediments (Grebmeier and Dunton 2000). Seasonally high rates of primary productivity and POC export on the Chukchi Shelf support elevated rates of benthic carbon respiration, causing bottom waters to become depleted in dissolved oxygen and enriched in remineralized nutrients.

## Methods

*Field sampling*—Physical, chemical, and biological measurements were taken during two cruises on the USCGC *Healy* to the Chukchi and Beaufort Seas in 2002 (May/June and July/August; Fig. 1) as part of the Shelf Basin Interactions (SBI) Program (see Grebmeier and Harvey [2005] for research overview). Physical and chemical measurements were taken at stations over the Chukchi/Beaufort Shelves and at the shelf-break and in the deep

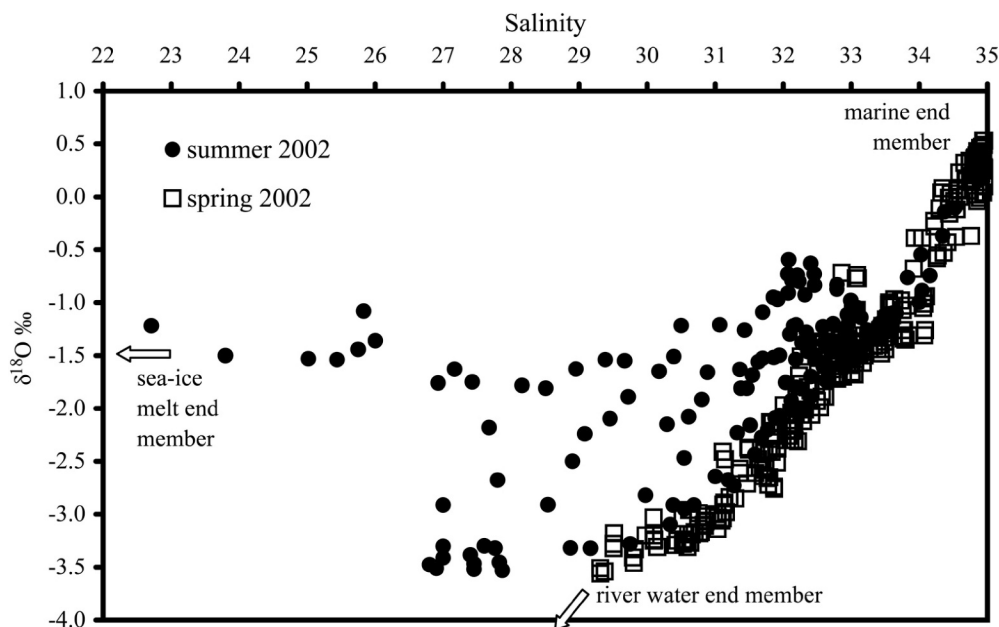


Fig. 2.  $\delta^{18}\text{O}$  versus salinity in spring and summer of 2002. Three end-members (marine: salinity = 35,  $\delta^{18}\text{O}$  = 0.3; sea ice: salinity = 4.5,  $\delta^{18}\text{O}$  = -1.9; river: salinity = 0,  $\delta^{18}\text{O}$  = -20.3) were used to determine the fraction of each component in the mixed layer.

Canada Basin. During the spring cruise (May/June), most (>90%) of the Chukchi Sea was ice-covered, predominantly by first-year sea ice. By summer (July/August) the Chukchi Shelf was mostly ice-free, with only small amounts of drifting pack-ice observed. However, there was still heavy ice over the Chukchi shelf-break and adjacent Canada Basin in mid-summer.

*Analytical methods*—Hydrographic measurements and water sampling were undertaken with a Seabird 911+ conductivity/temperature/depth (CTD) unit mounted on a 24-position frame with 10-liter Niskin bottles. Standard CTD quality control was performed to produce 1-db average downcast temperature and salinity profiles, which are discussed in Codispoti et al. (2005).

Samples for DOC were filtered through inline precombusted GF/F filters 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 tubing. Samples were collected into pre-conditioned and DOC-free, 60-mL bottles and frozen in organic solvent-free freezers, then shipped to the shore-based laboratories. All DOC samples were analyzed using a Shimadzu TOC-V/TN system. Extensive conditioning and standardization procedures were performed prior to analyzing samples each day. In addition, seawater DOC reference standards produced by the Hansell Certified Reference Material program were also analyzed each day. To maintain the highest quality data control, samples were systematically checked against low-carbon water and deep and surface reference waters every sixth analysis. The between-day precision in the DOC measurement was 1–2  $\mu\text{mol kg}^{-1}$ , or a coefficient of variation of 2–3%.

Water for  $\delta^{18}\text{O}$  analysis was collected from the Niskin bottles and sealed in 8-mL glass vials to prevent isotopic fractionation as a result of evaporation. Samples were stored under cool conditions until time of analysis. The oxygen isotope composition of the seawater samples was measured using an automated equilibration unit linked to a Finnigan Delta Plus dual-inlet mass spectrometer at the University of Tennessee. Data are reported in the standard delta notation, where  $\delta^{18}\text{O} = [({}^{18}\text{O}/{}^{16}\text{O}_{\text{sample}}/{}^{18}\text{O}/{}^{16}\text{O}_{\text{V-SMOW}}) - 1] \times 1,000$  (V-SMOW is Vienna-Standard Mean Ocean Water). Precision, based upon repeated measurements of an internal standard, was <0.05%.

Sea ice samples were taken during the spring cruise of 2002. Ice cores were obtained in three different locations (Fig. 1). The cores were then partitioned into 10-cm sections and allowed to melt. The melt water was then filtered to remove particulate matter using precombusted GF/F filters held in acid-washed polycarbonate filter holders, and the filtrate was transferred into pre-conditioned, DOC-free, 60-mL HDPE bottles and frozen in organic solvent-free freezers. The samples were shipped to the shore-based laboratories for DOC analysis using a Shimadzu TOC-V/TN system, as described above.

$\delta^{18}\text{O}$  and salinity (Fig. 2) were used to determine the fractions of seawater, ice melt, and river water present in the system following the approach used by MacDonald et al. (1999), among others. The three end-members were defined as river water (salinity = 0,  $\delta^{18}\text{O}$  = -20.3), ice melt (salinity = 4.5,  $\delta^{18}\text{O}$  = -1.9), and Atlantic layer seawater (salinity = 35,  $\delta^{18}\text{O}$  = 0.3). The fraction of each component in the water column was determined using Eqs. 1–3 ( $f$  is the fraction of each component and  $S$  is the salinity).

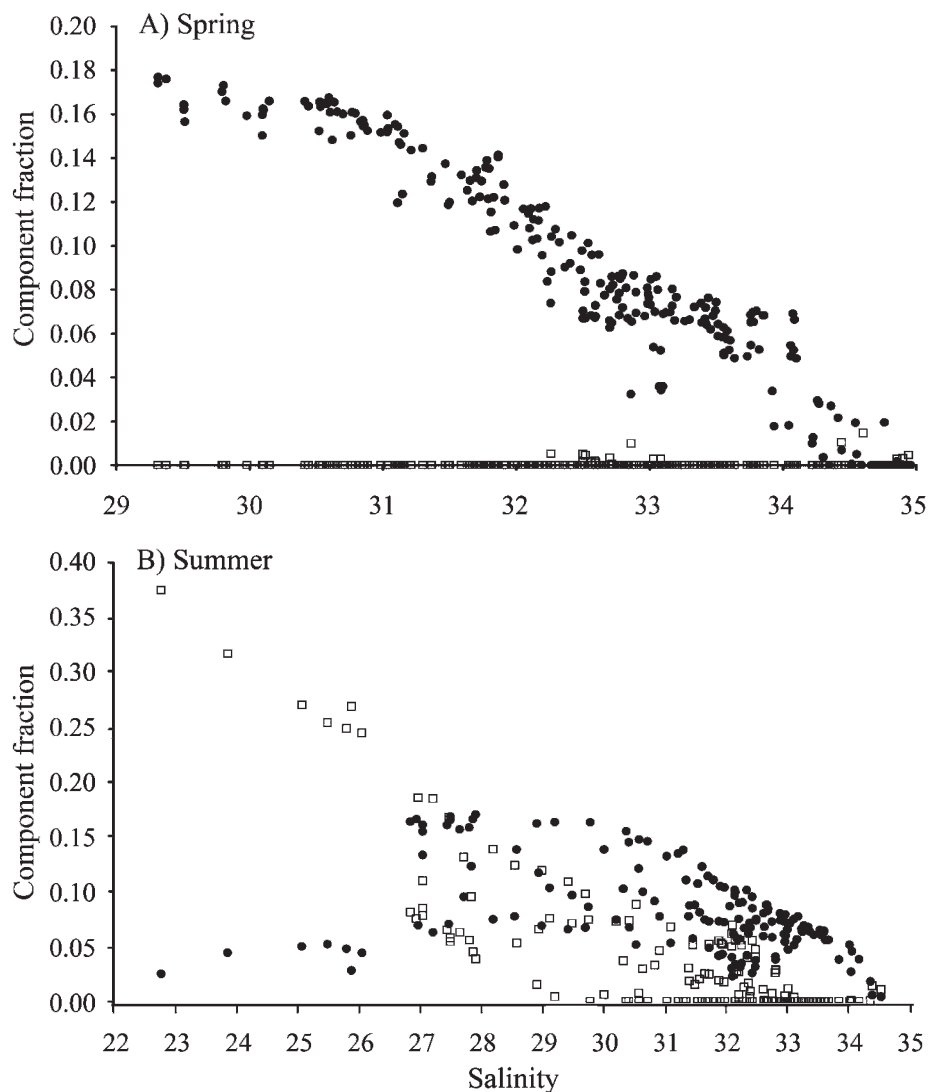


Fig. 3. Fractions of sea ice melt and river water in the mixed layer (upper 30 m) in (A) spring and (B) summer of 2002.  $^{18}\text{O}$  isotopic data were used to partition the upper mixed layer into three fractions: river water, sea ice melt, and marine water. During spring, there was little sea ice melt present over the Chukchi Sea or adjacent Canada Basin. Remnant river water made up as much as 18% of the surface water. During summer, sea ice melt was present at  $>30\%$  over the Chukchi Shelf and shelf-break. River water contributed as much as 20% to the mixed layer at a salinity of 27.

$$\text{Salinity} = f_{rw} \times S_{rw} + f_{im} \times S_{im} + f_{sw} \times S_{sw} \quad (1)$$

$$\delta^{18}\text{O} = f_{rw} \times \delta^{18}\text{O}_{rw} + f_{im} \times \delta^{18}\text{O}_{im} + f_{sw} \times \delta^{18}\text{O}_{sw} \quad (2)$$

$$1 = f_{rw} + f_{im} + f_{sw} \quad (3)$$

## Results

*Seasonal components of the mixed layer*—The salinity of the upper mixed layer (upper 30 m) of the Chukchi Sea changes seasonally. In winter and early spring, sea ice covers most of the Chukchi Sea ( $>95\%$ ), and the salinity of

the mixed layer below the ice ranges from  $\sim 29.2$  to  $31.5$  (Mathis et al. 2005). This water mass is a mixture of lower salinity marine surface water from the Bering Sea and river water that has remained on the shelf from the previous summer's runoff. The fraction of river water in this upper layer reaches 18% at the surface; isotopic evidence indicates that no ice melt component was present (Fig. 3A). The lowest salinity water was found over the shelf-break and adjacent Canada Basin, where the highest concentrations of river water were found in surface waters (Fig. 4A).

In late spring and throughout the summer, sea ice melt reduces salinity in the upper layer over the Chukchi Shelf and Canada Basin. The sea ice melt mixes with fresh river runoff, creating a low-salinity lens occupying the upper 5 m

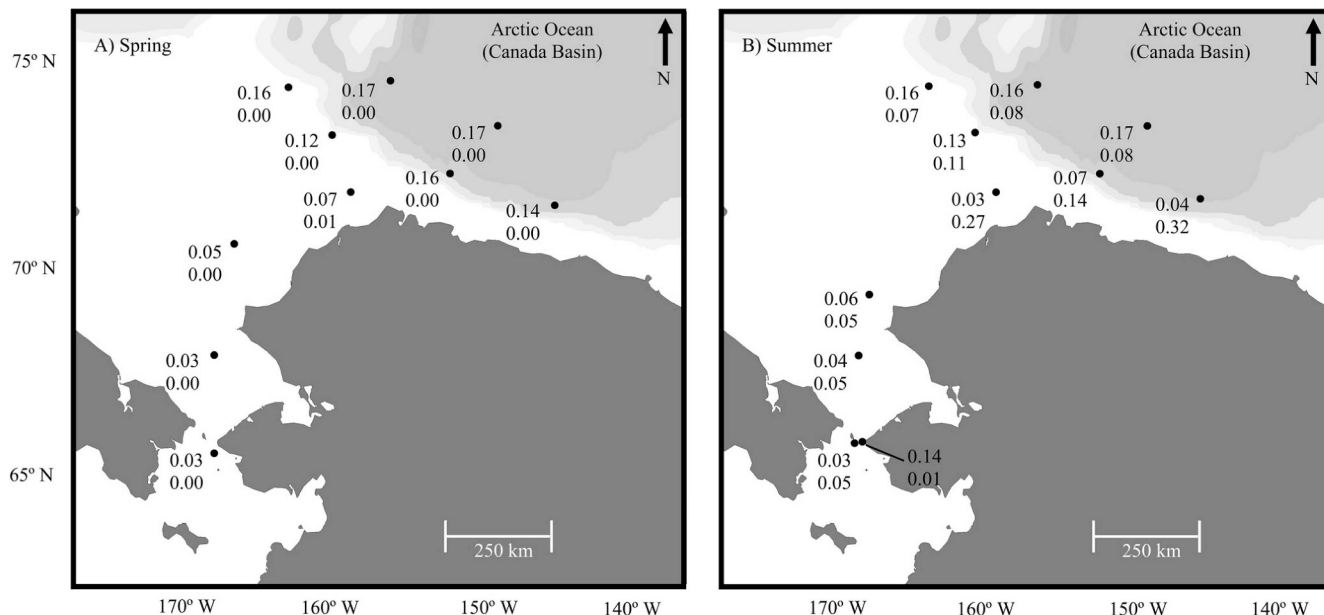


Fig. 4. The data presented represent the calculated contributions of river water (top value) and ice melt (bottom values) to surface water (upper 5 m) for (A) spring and (B) summer.  $\delta^{18}\text{O}$  data were used to determine the fraction of each component (see text for details).

of the water column. At the lowest salinities (22.5), the contribution of ice melt can be as great as 35% (Fig. 4B). In the upper 5 m of this layer (salinity 22–27) there was a small fraction of river water (<5%), but below 5 m in depth the contribution of river water increased to 5–20% in the salinity range of 27–31.5 (Fig. 3B). The highest concentrations of river water in the mixed layer in summer were still located over the shelf-break and deep basin, while the highest contributions of sea ice to the mixed layer were found along the northern coast of Alaska (Fig. 4B).

*DOC in sea ice*—During the spring cruise (May/June), three ice core samples were obtained in the central Chukchi Sea (Fig. 1; locations X1, X2, and X3) to determine DOC profile (Fig. 5) and the effect that its melting might have on the surface layer. The total thicknesses of the ice cores were 95, 105, and 130 cm for locations X1, X2, and X3, respectively. The DOC concentrations in the cores ranged from  $18.5 \mu\text{mol kg}^{-1}$  to  $24.5 \mu\text{mol kg}^{-1}$ , with an average value of  $21.5 \mu\text{mol kg}^{-1}$ . When the cores were collected, very little ice melt had occurred in the Chukchi Sea (<10%).

*Seasonal increases in the marine DOC pool*—Inputs of sea ice melt and river water complicate interpretations of net DOC production generated by in situ biological activity. Here,  $\delta^{18}\text{O}$  and salinity were used to determine these components of the water column and to remove the impact of allochthonous inputs on DOC concentrations (Eq. 4). A concentration of  $350 \mu\text{mol kg}^{-1}$  was taken for initial DOC concentrations in river runoff in the Chukchi Sea. This value is consistent with historic observations taken in the Yukon River, which is the largest contributor of terrigenous DOC to the Chukchi Sea. A DOC concentration of  $21.5 \mu\text{mol kg}^{-1}$  was used to correct for

the influence of sea ice melt in surface waters. Salinity (to determine the salinity of the marine end-member) was also corrected for dilution by river runoff and ice melt components (Eq. 5) in order to develop a consistent interseasonal comparison of the water masses in the Chukchi Sea and adjacent Canada Basin.

$$\text{Marine DOC} = \text{Measured DOC} - (f_{rw} \times \text{DOC}_{rw} + f_{im} \times \text{DOC}_{im}) \quad (4)$$

$$\text{Corrected salinity} = (\text{Measured salinity}) / (1 - f_{rw} - f_{im}) \quad (5)$$

Employing these equations allowed for interseasonal comparison of the marine DOC pool. In spring, a regression

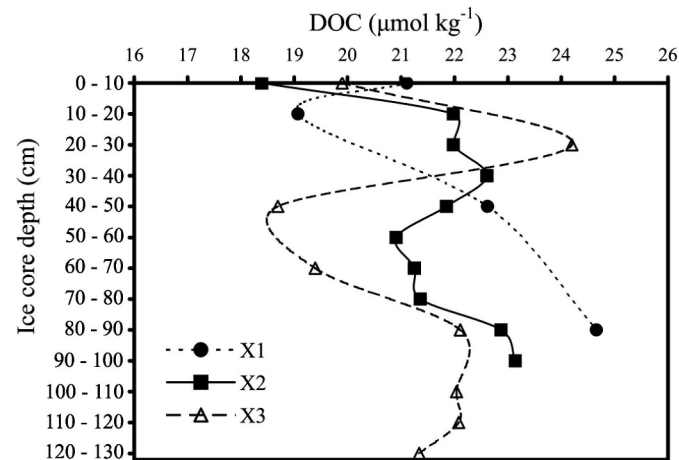


Fig. 5. Concentrations of DOC ( $\mu\text{mol kg}^{-1}$ ) in three ice cores taken over the Chukchi Shelf in spring of 2002 (see Fig. 1 for locations). The total thickness of the ice cores was 95 cm, 105 cm, and 130 cm for locations X1, X2, and X3, respectively.

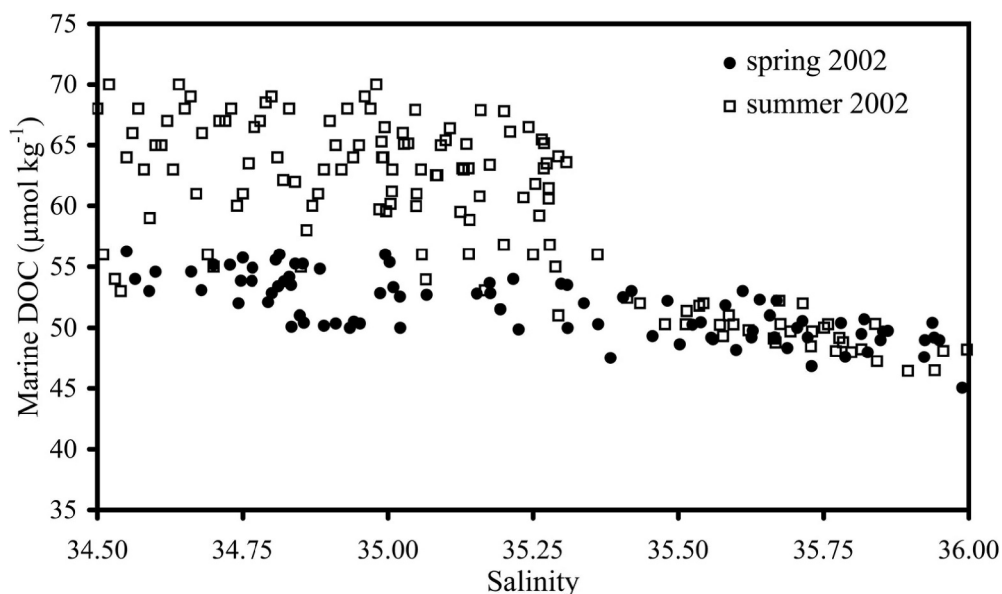


Fig. 6. Marine DOC ( $\mu\text{mol kg}^{-1}$ ) versus salinity for spring and summer of 2002. Measured DOC values were corrected for ice melt and river water leaving the marine portion of the DOC pool. Salinity was also corrected for the removal of the freshwater ice melt and river runoff. In spring, a regression of marine DOC versus salinity was linear in the range of 34–36. In summer, DOC values in the mixed layer (salinity = 34–35) became nonlinear, providing evidence for the net production of DOC by marine organisms. Below the mixed layer a regression of summer DOC versus salinity was similar to spring, in the salinity range of 35–36, where little biological transformation of DOC occurs.

of marine DOC concentrations versus salinity was essentially linear (Fig. 6). During summer, the marine DOC concentrations became nonlinear in the upper mixed layer (corrected salinity = 34.5–35.25) but were similar to spring concentrations in deeper waters (corrected salinity = 35–36) (Fig. 6). The increases in DOC concentrations between spring and summer (Fig. 7) ranged from  $14 \mu\text{mol kg}^{-1}$  at a corrected salinity of 34.5 (surface water) (Fig. 8) to  $0 \mu\text{mol kg}^{-1}$  at corrected salinities of  $>35.25$  (deep water) (Fig. 6).

## Discussion

The global marine DOC pool is estimated to be 685 Gt-C (Hansell and Carlson 1998), which is comparable to the

reservoir of  $\text{CO}_2$  in the atmosphere. Therefore, small perturbations in the net production or consumption rates of oceanic DOC could affect the equilibrium between atmospheric and marine  $\text{CO}_2$ . This could be particularly true in the Arctic, a system that is more sensitive to climate changes than are areas at lower latitudes (Smetacek and Stephen 2005). Marginal arctic seas, such as the Chukchi, experience short but intense periods of biological production that could therefore play an important role in Arctic and, ultimately, global ocean carbon budgets.

The transformation of DIC to DOC may be an important component of biogeochemical carbon cycles in the open ocean and in continental shelf ecosystems, but this transformation is poorly constrained in the Arctic. DOC represents a significant byproduct of biological productiv-

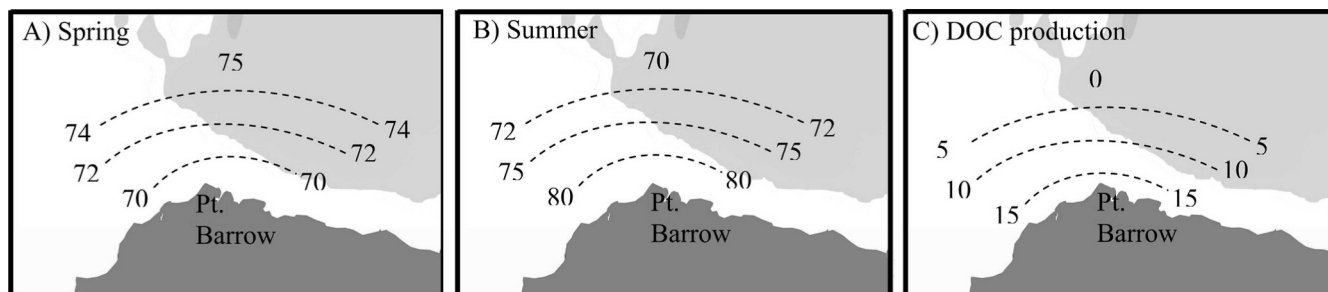


Fig. 7. (A) Distribution of DOC ( $\mu\text{mol kg}^{-1}$ ) in spring 2002. (B) Distribution of DOC ( $\mu\text{mol kg}^{-1}$ ) in summer 2002. (C) Distribution of the in situ production of DOC ( $\mu\text{mol kg}^{-1}$ ) between spring and summer of 2002 in the upper mixed layer. See Fig. 1 for location of area.

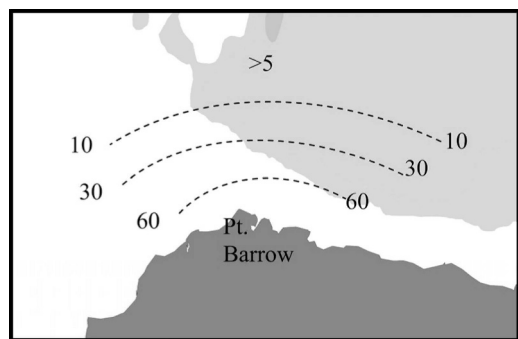


Fig. 8. Rates of export production of carbon ( $\text{mmol m}^{-2} \text{d}^{-1}$ ) on the Chukchi and Beaufort Shelves. These values were calculated by determining the reduction of DIC in the water column at each location between spring (prebloom) and summer and then subtracting the net DOC and suspended POC produced. Export production was highest over the shelf west of Point Barrow. Higher rates of export production extended farther off the shelf to the east of Point Barrow. See Fig. 1 for location of area.

ity and a substrate that supports heterotrophic bacterial growth in the open oceans and in coastal margins (Ducklow and Carlson 1992). DOC that is resistant to microbial degradation can accumulate in the surface layer, where it is available for export out of the surface ocean (Hansell and Carlson 2001).

During late spring and summer in 2002, rates of NCP over the Chukchi Shelf ranged from 83 to 238  $\text{mmol C m}^{-2} \text{d}^{-1}$  (Bates et al. 2005a), with the highest rates observed near Barrow Canyon. In summer, DIC concentrations in the mixed layer over the shelf were drawn down by  $>100 \mu\text{mol kg}^{-1}$  compared to spring (prebloom) values (Bates et al. 2005a), and there was an accumulation of POC (Bates et al. 2005b) in the upper mixed layer. Marine DOC concentrations increased up to  $14 \mu\text{mol kg}^{-1}$  (Figs. 6, 7) compared to prebloom concentrations, with the highest increases in the upper mixed layer, where the maximum drawdown of DIC occurred. Here, we develop a seasonal carbon budget (Table 1) for spring and summer of 2002 in the Chukchi Sea to determine the transformations and fate of carbon in this shelf system. This work is a check on previously reported budgets for the system (Hill and Cota 2005; Moran et al. 2005), which did not include direct measurements of net DOC production.

Using  $\delta^{18}\text{O}$  and salinity values for spring and summer of 2002 (Fig. 2) we determined that approximately 10% of the DIC consumed during photosynthesis is converted into DOC (Table 1). Approximately 20% of the seasonal DIC drawdown in the mixed layer is converted to POC that accumulates in the mixed layer (upper 30 m) during summer (Bates et al. 2005b).

*Vertical export of carbon*—Rates of export production for the interior Arctic Ocean have been consistently reported to be low (e.g., Moran and Smith 2000; Anderson et al. 2003). However, seasonally high export rates have been observed over the continental shelves of the Arctic (e.g., Moran et al. 2005). In this study we used a seasonal

carbon mass balance to determine the potential vertical export of organic carbon from the mixed layer. Rates of export production were determined by subtracting the seasonal biological production of DOC and the observed accumulation of marine POC in the mixed layer from the net deficit of DIC (Eq. 6)

$$\text{Export production} = \Delta\text{DIC} - \Delta\text{Marine DOC production} - \Delta\text{Marine POC production} \quad (6)$$

For this calculation we assumed that all of the POC accumulation that occurred between spring and summer observations was due to biological production (Bates et al. 2005a). To convert export production to the units of  $\text{mmol C m}^{-2} \text{d}^{-1}$  we used the density of seawater, the integrated marine DOC and POC accumulation in the upper 30 m of the water column, and the number of days between observations, yielding a conversion factor from  $\mu\text{mol kg}^{-1}$  to  $\text{mmol C m}^{-2} \text{d}^{-1}$  of  $\sim 0.51$ .

Rates of export production in 2002 varied spatially over the Chukchi Shelf and Canada Basin, with the highest fluxes of carbon ( $\sim 50 \text{mmol C m}^{-2} \text{d}^{-1}$ ) found over the shelf near Point Barrow in the vicinity of Barrow Canyon (Fig. 8). The range of export production over the entire shelf was 10–64  $\text{mmol C m}^{-2} \text{d}^{-1}$  (Fig. 8; Table 1). Over the Canada Basin, export production was  $>10 \text{mmol C m}^{-2} \text{d}^{-1}$  (Fig. 8; Table 1), with the exception of stations to the east of Point Barrow, where export was slightly higher ( $\sim 20 \text{mmol C m}^{-2} \text{d}^{-1}$ ) over the shelf-break and Canada Basin.

There is no evidence of long-term (interannual) accumulation of organic carbon in the waters over the Chukchi Shelf or in the Canada Basin. Therefore, it must be remineralized either on the shelf or once it is transported into the deep Arctic Ocean. POC that is exported from the mixed layer can be entrained in winter-modified Pacific water (Pickart et al. 2005) as it flows northward off the shelf. When this plume of dense water reaches the shelf-break it turns eastward, contributing to the shelf-break current (Pickart et al. 2005; Mathis et al. in press). This organic carbon gives the shelf-break current a strong “shelf signal.” This current has been shown to be unstable and capable of generating eddies that move water from the current into the Canada Basin. One such eddy was surveyed in 2004 and contained elevated amounts of DOC and POC compared to waters outside the eddy in the Canada Basin (Mathis et al. in press). The remineralization of this organic carbon, once it is in the Canada Basin, supports heterotrophy in the upper halocline and maintains the biogeochemical properties of the interior Arctic Ocean.

*The effect of sea ice on DOC*—The direct role that sea ice plays in Arctic DOC dynamics is largely unknown, mostly because of a paucity of data. In this study, concentrations of DOC in ice cores were substantially lower than previously reported in the Chukchi Sea and other parts of the Arctic Ocean. DOC in sea ice has been attributed mostly to ice algae production (Smith et al. 1997), with a much smaller amount coming from terrige-

Table 1. Carbon mass balance developed for the shelf, shelf-break, and deep basin of the Chukchi Sea from data collected in 2002. The table shows the net drawdown of DIC between spring (prebloom) and summer (postbloom) and the subsequent in situ production of marine DOC and POC. Export production was determined by subtracting the net DOC and POC production (data from Bates et al. 2005b) from the DIC deficit (the normalized decrease in DIC in the upper 30 m) between spring and summer (Export Production = DIC Deficit – Net DOC Production – POC Production).\*

Location	$\Delta$ DIC ( $\mu\text{mol kg}^{-1}$ )	$\Delta$ DOC ( $\mu\text{mol kg}^{-1}$ )	$\Delta$ POC ( $\mu\text{mol kg}^{-1}$ )	% DIC converted to DOC	% DIC converted to POC	Export production ( $\text{mmol C m}^{-2} \text{d}^{-1}$ )
Near Point Barrow (Barrow Canyon)						
Shelf	94.0	9.1		9.6		
Shelf	172.1	14.0	33.4	8.1	19.4	64.0
Shelf	101.4	11.2		11.1		
Shelf	116.2	10.4	24.0	9.0	20.7	41.9
Slope	82.6	8.4		10.1		
Slope/basin	41.2	3.1	7.9	7.5	19.2	15.5
Basin	2.1	0.0	0.5	0.0	21.6	0.8
East of Point Barrow						
Shelf	94.4	12.0	18.3	12.7	19.4	32.9
Slope	122.0	12.3	25.1	10.1	20.6	43.5
Slope	58.6	6.2	11.3	10.5	19.3	21.1
Slope/basin	46.2	4.2	8.6	9.1	18.6	17.2
East of Hanna Shoals						
Shelf	159.2	14.0	30.3	8.8	19.0	59.0
Shelf	34.2	4.1	7.2	12.1	20.9	11.8
Slope	18.7	2.0	3.9	10.8	20.8	6.6
Basin	21.7	0.0	3.5	0.0	16.0	9.4
West of Hanna Shoals						
Shelf	85.8	9.4	17.6	11.0	20.5	30.2
Shelf	65.2	7.2	12.9	11.0	19.8	23.2
Slope	27.5	2.1	5.1	7.5	18.4	10.5
Slope	10.0	0.0	1.8	0.0	17.5	4.3
Basin	3.1	0.0	0.7	0.0	21.0	1.3

\* DIC, dissolved inorganic carbon; DOC, dissolved organic carbon; POC, particulate organic carbon.

nous DOC. The highest reported concentrations of DOC have been observed in the bottom of the ice sheet near the ice–water interface and exceed  $3,000 \mu\text{mol kg}^{-1}$  (Smith et al. 1997), but above the bottom few centimeters of the core concentrations drop sharply to  $<100 \mu\text{mol kg}^{-1}$ . DOC release rates from ice have been reported to be  $<25 \mu\text{mol m}^{-2} \text{d}^{-1}$  (Gosselin et al. 1997). Anderson (2002) calculated that melting sea ice would increase DOC concentrations in the surface layer of the Arctic Ocean by  $6 \mu\text{mol kg}^{-1}$ . However, the results reported here and elsewhere (Mathis et al. 2005) has shown that sea ice melt dilutes DOC concentrations in the mixed layer of the Chukchi Shelf and in the Canada Basin. The variability of DOC in sea ice is most likely related to where the ice forms, the biogeochemical properties of the water immediately below the ice, and the degree of biological activity that occurs in the ice during winter. Nutrients and light will be the limiting factors in DOC production in the bottom layer of the ice. Our findings indicate that the major effect that sea ice has on DOC dynamics in the Chukchi Sea is to dilute its concentration in the surface layer.

*Qualifying statements for production estimates*—The estimates of DOC and POC production presented here do

not take into account the general northeast flow of surface waters over the shelf between spring and summer. However, in spring, DOC and POC concentrations are uniform over the shelf. If we assume an average current speed near the surface of  $5 \text{ cm s}^{-1}$ , then over the approximately 2-month period between the spring and summer observation, the water would have traveled  $\sim 250 \text{ km}$ . The distance from the Bering Strait to Point Barrow is on the order of  $900 \text{ km}$ . Therefore, we make the assumption that water transported into the region between the spring and summer observations was similar to our measurements during the spring cruise.

The Arctic Ocean and its extensive area of continental margins are sensitive to climate changes (MacDonald et al. 2005; Smetacek and Stephen 2005). Arctic soils are warming (Foley 2005), perhaps mobilizing additional stored terrestrial carbon, and ice cover is projected to continue to recede in the coming decades, further affecting organic carbon cycles. Quantifying the transformations and fate of organic carbon in the Arctic marginal seas is important to understanding the carbon cycle of the region. Our work shows that  $\sim 10\%$  of NCP over an arctic shelf is converted into DOC,  $\sim 20\%$  is converted to POC, and the remaining  $70\%$  is exported from the mixed layer, where it is

either deposited in the sediments or transported offshore along with dense northward-flowing bottom waters. Changing environmental conditions could disrupt or change the partitioning and distribution of organic carbon in the region, thus affecting the overall carbon budgets in the Arctic. With the budget determined here, a reference point for change is established.

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