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Net community production in the northeastern Chukchi Sea

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ABSTRACT

To assess the magnitude, distribution and fate of net community production (NCP) in the Chukchi Sea, dissolved inorganic carbon (DIC), dissolved organic carbon (DOC) and dissolved organic nitrogen (DON), and particulate organic carbon (POC) and particulate organic nitrogen (PON) were measured during the spring and summer of 2004 and compared to similar observations taken in 2002. Distinctive differences in hydrographic conditions were observed between these two years, allowing us to consider several factors that could impact NCP and carbon cycling in both the Chukchi Shelf and the adjacent Canada Basin. Between the spring and summer cruises high rates of phytoplankton production over the Chukchi shelf resulted in a significant drawdown of DIC in the mixed layer and the associated production of DOC/N and POC/N. As in 2002, the highest rates of NCP occurred over the northeastern part of the Chukchi shelf near the head of Barrow Canyon, which has historically been a hotspot for biological activity in the region. However, in 2004, rates of NCP over most of the northeastern shelf were similar and in some cases higher than rates observed in 2002. This was unexpected due to a greater influence of low-nutrient waters from the Alaskan Coastal Current in 2004, which should have suppressed rates of NCP compared to 2002. Between spring and summer of 2004, normalized concentrations of DIC in the mixed layer decreased by as much as 280 μmol kg^{-1}, while DOC and DON increased by ~16 and 9 μmol kg^{-1}, respectively. Given the decreased availability of inorganic nutrients in 2004, rates of NCP could be attributed to increased light penetration, which may have allowed phytoplankton to increase utilization of nutrients deeper in the water column. In addition, there was a rapid and extensive retreat of the ice cover in summer 2004 with warmer temperatures in the mixed layer that could have enhanced NCP. Estimates of NCP near the head of Barrow Canyon in 2004 were ~1500 mg carbon (C) m^{-2} d^{-1} which was ~400 mg C m^{-2} d^{-1} higher than the same location in 2002. Estimates of NCP over the shelf-break and deep Canada Basin were low in both years, confirming that there is little primary production in the interior of the western Arctic Ocean due to near-zero concentrations of inorganic nitrate in the mixed layer.

1. Introduction

Arctic shelf seas contain some of the highest rates of primary production found in the ocean and play an important role in the cycling of carbon and nutrients in the Arctic Ocean. In the Chukchi Sea, nutrient-rich Pacific origin waters pass through Bering Strait (Fig. 1) to support a brief, but intense, photosynthetic season with rates of water-column primary production >300 g C m^{-2} yr^{-1} (Sambrotto et al., 1984; Hansell et al., 1993; Hill and Cota, 2005; Bates et al., 2005a). This production supports substantial benthic (Grebmeier et al., 1995) and pelagic biomass (Ashjian et al., 2008) that, in turn, supports higher trophic level organisms (e.g., fish, marine mammals, seabirds), including the native human population.

Primary production and net community production (NCP) in the northeastern Chukchi Sea are influenced by seasonal and interannual variability in light, ice and snow cover, as well as marine and coastal inputs. Because of the paucity of data in the region, the timing, extent, and controls of NCP are not well understood. This lack of understanding is particularly important because the Arctic Ocean has a heightened sensitivity to climate change, which could have an impact on ecosystems as warming and sea-ice loss continues (Walsh et al., 1990; Moritz and Perovich, 1996; Grebmeier and Whitledge, 1996; Manabe and Stouffer, 2000). It remains unclear how the warming of the atmosphere and sea-surface temperatures along with changes in stratification and thinning sea-ice might affect productivity and ecosystem dynamics in the region. Productivity over Arctic

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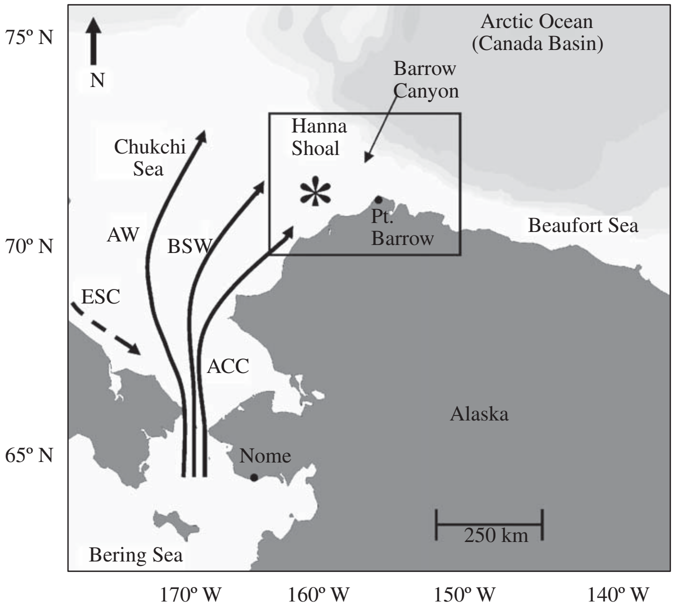

Fig. 1. Map of the western Arctic Ocean showing the northward flowing components of the major current system. The Alaska Coastal Current (ACC) dominates the eastern side of Bering Strait, while Bering Shelf Water (BSW) and Anadyr Current (AC) occupy the central and western channel of Bering Strait. The East Siberian Current (ESC) contributes some seasonal input to the region, but its impact is not well understood. The black box indicates the focus of the area in this study. The star is the approximate location of the head of Barrow Canyon and the biological hotspot in the region. A more detailed map showing the cruise track for spring and summer with station locations can be found at the SBI website (http://sbi.utk.edu/).

shelves could be enhanced in response to increased light availability as polar sea ice continues to diminish.

To date, limited *in vitro* measurements of primary productivity in the Chukchi Sea have been performed. Furthermore, it is difficult to extrapolate the measured rates, typically determined using dawn-to-dusk ^{14}C incubations (Williams, 1993), either spatially or temporally. An alternative approach to direct rate determinations involves observing changes in the *in situ* water-column inventories of the reactants and products (dissolved oxygen (DO), inorganic nutrients, dissolved inorganic carbon (DIC), dissolved organic carbon/nitrogen (DOC/N) and particulate organic carbon/nitrogen (POC/N) of photosynthesis. Estimates of NCP (Williams, 1993) can be determined from seasonal changes in DIC, thereby offering spatially and temporally integrative measures of productivity (Weiss et al., 1979; Codispoti et al., 1982, 1986; Karl et al., 1991; Chipman et al., 1993; Yager et al., 1995; Bates et al., 1998, 2005a; Lee, 2001; Lee et al., 2002).

As part of the Western Arctic Shelf–Basin Interactions (SBI) project (Grebmeier and Harvey, 2005), the timing, extent, and dynamics of production were evaluated during two cruises to the Chukchi Sea in 2004. In this study, the spatial and temporal patterns of NCP and its associated carbon parameters were observed over the northeastern Chukchi shelf and adjacent slope-basin of the Arctic Ocean and then compared to findings from similar cruises in the region in 2002 (Bates et al., 2005a).

A comparison of the 2004 hydrographic data with the results from 2002 revealed several similarities as well as some distinct differences in the two years. During both years dissolved inorganic nitrogen (DIN) (ammonium+nitrate+nitrite) was the limiting factor in phytoplankton growth, suggesting that the fixed-N transport through Bering Strait is a major control on biological productivity (Codispoti et al., 2009). We also found that the head of Barrow Canyon was a region of enhanced biological production over the northeastern shelf. In both years, particularly during summer, oxygen super-saturations were common in or just above the shallow nitracline with higher oxygen saturations observed in 2004 near Barrow Canyon (Codispoti et al., 2009). Finally, surface waters at the deepest stations occupied over the Canada Basin had near-zero concentrations of nitrate in both years indicating little to no potential for primary production in the Canada Basin.

In 2004, there was a greater influence of warm, relatively low-nutrient water from the Alaska Coastal Current (ACC) entering the region via Bering Strait (Codispoti et al., 2009). This increased inflow of ACC may have reduced photic zone nutrient concentrations. The differences in water temperature and nutrients were most pronounced in the upper ~100 m, and the increased influence of warm water in 2004 relative to 2002 was most evident in the area near and to the east of Barrow Canyon. Observations taken on the same days in late July–early August of both years showed that the surface layer was up to 5 °C warmer in 2004.

While the stronger inflow of Alaskan Coastal Water in 2004 may have reduced the autochthonous nutrient supply, rates of primary production and bacterial production were higher during 2004 (Kirchman et al., 2009). One possible explanation for this was an observed increased in light penetration in 2004, which may have allowed phytoplankton to increase utilization of nutrients deeper into the nutricline. In addition, more light combined with warmer water temperatures from the ACC could have enhanced NCP in the region. Sea ice over the northeastern shelf was thicker in 2004 than in 2002, but snow cover was significantly less and may compensated for the differences in ice thickness due to greater light penetration (Codispoti et al., 2009; Shirasawa et al., 2009). It is also possible that the rapid ice retreat and warmer temperatures in 2004 lead to an acceleration in the seasonal progression of biological processes such that the summer observations taken in 2004 might have existed a few weeks after the completion of the 2002 summer cruise. However, there is little doubt that hydrographic conditions in 2004 differed significantly from those in 2002, and this has given us a chance to analyze how these changes impacted NCP.

It has been hypothesized (Walsh and McRoy, 1986) that when the spring bloom occurs in the very cold waters of a shelf (<2 °C), zooplankton reproduction and growth are retarded, and the autotrophs are less susceptible to grazing. Hunt et al. (2002) followed with the suggestion that variability in ice extent, with impacts on SST and the timing of ice retreat, controls the structure of the ecosystem; these controls may be realized through retention of biomass in the upper layer (warm year) vs. the bottom waters (cold year) with a cascading effect through the ecosystem.

2. Hydrography and biogeochemistry

The continental margins of the western Arctic Ocean are important sites of biological activity as they are where the majority of primary production occurs in the Arctic. Ice algae and phytoplankton contribute significantly to primary production over the Chukchi shelf with ~90% of the total primary production occurring in the water column (Hill and Cota, 2005; Gosselin et al., 1997). Primary production in the water column is influenced by a variety of physical and biogeochemical factors including grazing, light, and sea-ice cover. However, the inflow of nutrient-rich Pacific water through Bering Strait has been considered the dominant mechanism controlling regional productivity.

Pacific and fluvial waters from the Bering Sea transit the narrow Bering Strait and fan out across the shallow (<60 m deep), broad Chukchi shelf (Fig. 1). The Bering Strait acts as a gateway for the influx of Pacific waters into the Arctic Basin (Coachman and

Aagaard, 1988; Björk, 1989), the mean inflow being ~0.8 Sv, with higher flow in summer and lower flow during winter (Roach et al., 1995; Woodgate et al., 2005a, b). The inflow through Bering Strait is composed of warmer, lower-salinity ACC waters in the east (Paquette and Bourke, 1974), Bering Shelf (BS) water in the central part of the channel, and colder, higher-salinity, nutrient-replete Anadyr Current (AC) water in the western part of the strait. Approximately 0.1 Sv flows into the Chukchi Sea in the intermittent East Siberian Current (ESC), but the impact of this water has on the system is not well understood (Woodgate et al., 2005a).

Seasonal sea-ice cover plays a major role in shaping both the water masses and biogeochemical processes of the Chukchi Sea. During winter, sea-ice covers most of the Chukchi Sea, extending south of Bering Strait and confining the water column to narrow temperature and salinity ranges (Woodgate et al., 2005a). In late spring and summer, sea ice recedes offshore, and nutrient-rich surface waters over the Chukchi shelf are exposed to near continuous sunlight causing a short, but intense, phytoplankton bloom to occur. During this bloom, rates of NCP can reach as high as 300 g C m^{-2} yr^{-1} (Walsh et al., 2005). At the termination of this bloom, nitrate has been exhausted in the surface layer (Codispoti et al., 2005); a plume of suspended POC/N extends from the shelf over the shelf-break (Bates et al., 2005b); and biologically produced DOC/N concentrations have increased in the mixed layer over the shelf by as much as 14 μmol kg^{-1} (Mathis et al., 2007).

3. Methods

Physical, biogeochemical, and biological measurements were made from the USCGC *Healy* during two cruises to the Chukchi and Beaufort Seas in 2004. During the spring (May/June) and summer (July/Aug) cruises, CTD stations were occupied in Bering Strait, over the Chukchi shelf and slope, and into the Arctic Basin. Detailed maps of the cruise tracks and station locations can be found on the SBI website (http://sbi.utk.edu/). At each CTD/rosette station, a suite of biological and chemical measurements were collected, including salinity, inorganic nutrients (ammonium, nitrate, nitrite, phosphate, reactive silicon, and urea), DIC, DOC/N, POC/N, and DO. All of these data are available to the pubic through the SBI homepage.

3.1. DIC analysis

Seawater samples for DIC were drawn from Niskin bottles into pre-cleaned ~300-ml borosilicate bottles. DIC samples were subsequently poisoned with Hg_2Cl_2 to halt biological activity, sealed, and returned to Bermuda Institute of Ocean Science (BIOS) for analysis. DIC samples were analyzed using a highly precise and accurate (~0.025%; <0.5 μmol kg^{-1}), gas extraction/Coulometric detection system (Bates et al., 1996, 1998; Bates, 2001). The analytical system consists of a single-operator multi-parameter metabolic analyzer (SOMMA) coupled to a CO_2 coulometer (model 5011; UIC Coulometrics). Routine analyses of Certified Reference Materials (CRM's provided by A.G. Dickson, Scripps Institution of Oceanography) ensured that the accuracy of the DIC measurements was within 0.05% (~0.5 μmol kg^{-1}).

3.2. DOC/N analysis

Many investigations of organic carbon in the Arctic have reported data on unfiltered samples and are therefore measurements of total organic carbon (TOC) concentrations (TOC = dissolved organic carbon+particulate organic carbon). In the central Arctic basin, where particle mass is very low, there is not a large difference between DOC and TOC measurements; however, in the coastal environment and in areas of high primary productivity the values can be considerably different. In this study, all reported values of DOC have been filtered to remove POC.

Samples for DOC/N were filtered through inline, pre-combusted GF/F filters held in acid-washed polycarbonate filter holders. The filter cartridge was attached directly to the Niskin bottle with acid-cleaned and MilliQ® water-rinsed silicone tubing. Samples were collected in preconditioned and DOC/DON-free, 60-ml HDPE bottles, frozen in organic solvent-free freezers, and then shipped to the shore-based laboratories. All samples were analyzed using a Shimadzu TOC-V/TN system. The DOC system was calibrated using potassium hydrogen phthalate and the total dissolved nitrogen (TDN) system using potassium nitrate, both in Milli-Q water and system performance was verified daily using Consensus Reference Water (http://www.rsmas.miami.edu/groups/biogeochem/CRM.html). This reference water is deep Sargasso Sea water (DSR) that has been acidified and sealed in 10 ml ampoules, the concentrations of which (of DOC and TDN) has been determined by the consensus of six independent laboratories. Low-Carbon Water (LCW) that has gone through the same acidification, sealing process, and consensus verification program as the DSR and has an agreed upon carbon concentration of 1–2 μmol C l^{-1} is also analyzed and used to determine the instrument blank. The sample analysis starts with a QW (Q Water) blank and a reference seawater analysis. Then six samples are analyzed, followed by another QW blank and reference seawater. This sequence is repeated until all samples for that run are analyzed. The run ends with a QW blank, reference water, and a QW blank that had not been acidified; this last blank verifies that the hydrochloric acid used to acidify the samples is not contaminated. QW blanks and reference water samples are used to evaluate system performance during the analytical run. If a problem is detected with the blanks or reference waters, the samples are reanalyzed. The between-day precision in the DOC measurement was 1–2 μmol kg^{-1}, or a CV of 2–3%. DON values were determined by subtracting the DIN from TDN (DON = TDN–DIN). For values reported here the between-day precision in the DON measurement was 0.3–0.7 μmol kg^{-1}, or a CV or ~5%.

3.3. POC/N analysis

For POC/N analysis, seawater was drawn from Niskin bottles into Nalgene bottles. Known volumes (1–4 l) of seawater were vacuum filtered through a funnel array onto pre-combusted GF/F filters (25 mm Whatman, 0.7 μm). Filters were then folded and placed into acid-washed, pre-combusted scintillation vials and stored until analysis. After acidification with HCl to remove inorganic carbon, filters were dried and samples analyzed for carbon and nitrogen. This analysis was done with a Control Equipment Corporation (CEC) 240-XA Elemental Analyzer at the Bermuda Institute of Ocean Science (BIOS) (Knap et al., 1997). Filter blanks represent the total blank associated with the pre-combusted GF/F filter and any DOC adsorption from ambient seawater due to the slight propensity of the filtering material to bind carbon compounds. Filter blanks for the suspended POM samples were ~0.4–0.6 μmol kg^{-1} for POC and ~0.08–0.10 μmol kg^{-1} for PON.

Suspended POC/N samples drained from the spigot of the Niskin sampler can underestimate the total suspended particulate organic matter (POM) samples due to the sinking of large particles within the Niskin bottle (Gardner, 1977). Gunderson et al. (2001) observed a mean 26% underestimation when comparing suspended POC drained from a Niskin spigot as compared to a whole water sample at the Bermuda Atlantic Times-series Study (BATS) site in the North Atlantic Ocean. Here, the suspended POC/N data are not corrected for this sampling bias, and therefore, most likely represent a lower estimate.

3.4. *Identification of water masses in the Western Arctic*

The upper several hundred meters of the Arctic Ocean and adjacent seas such as the Chukchi and Beaufort Seas are strongly stratified (Aagaard et al., 1981; Jones and Anderson, 1986; Anderson and Jones, 1992; Aagaard and Carmack, 1994; Schlosser et al., 1995). Identifiable signatures in temperature and salinity (Aagaard et al., 1981) and nutrient/oxygen distributions and stoichiometry (Wallace et al., 1987; Salmon and McRoy, 1994) were used to identify principal water masses in the study region (Codispoti et al., 2005). Water masses over the Chukchi and Beaufort Sea shelves and Arctic Basin included (1) the upper mixed layer (UML, 0–30 m over the shelf); (2) the polar mixed layer (PML; upper 0–50 m, over the Canada Basin, salinity typically <31); (3) the upper halocline (UH; 50–120 m deep; core layer salinity of 33.1, nitrate concentration of 14 ± 2 μmol kg^{-1} and phosphate concentration of 1.8 ± 0.2 μmol kg^{-1}); (4) the lower halocline (LH; 150–220 m deep; core layer salinity of 34.3, nitrate concentration of 12 ± 1 μmol kg^{-1} and phosphate concentration of 0.8 ± 0.2 μmol kg^{-1}); (5) the Atlantic layer (AL; >250 m deep, core layer salinity of 34.8, nitrate concentration of 14 ± 1 μmol kg^{-1} and phosphate concentration of 1.0 ± 0.1 μmol kg^{-1}); and (6) the deep Arctic layer (DAL; core layer salinity of 34.8, nitrate concentration of 15 ± 1 μmol kg^{-1}). At the Bering Strait, waters defined as ACC, Anadyr Water (AW), and Bering Shelf Water (BSW) (Coachman and Aagaard, 1988) (Fig. 1) were sampled during the summer cruise (Codispoti et al., 2005).

4. Results

4.1. *Distributions of DIC, DOC/N, and POC/N*

Waters of the UML and the UH were present over the Chukchi shelf during spring and summer of 2004. Water masses of the PML, UH, lower halocline (LH), Atlantic later (AL), and deep Arctic layer (DAL) were sampled over the deep Canada Basin during both cruises. During the spring cruise, most of the Chukchi shelf and slope-basin were heavily covered in sea ice. Temperatures in the UML over the shelf ranged from -1.80 to 1.50 °C, and salinity ranged from 28.9 to 32.9. Nitrate, phosphate, and silicate concentrations ranged from 0 to 8, 0–2, and 0–42 μmol kg^{-1}, respectively.

Approximately 6 weeks after the spring cruise observations were taken, the stations (as well as additional stations) were reoccupied. Temperatures in the surface layer over the shelf were warmer (-1.7 to 10.8 °C), and ice melt had caused a freshening of the UML with salinities ranging from <28 to 32.8. Inorganic nutrient concentrations, particularly nitrate, had been depleted in the UML (generally <0.2 μmol kg^{-1}).

4.1.1. *DIC observations*

In spring of 2004, DIC concentrations ranged from 1960 to 2240 μmol kg^{-1} (Fig. 2A) and averaged ~2135 μmol kg^{-1} over the shelf in the mixed layer (Table 1). Spatially, DIC concentrations in the mixed layer decreased from Bering Strait (~2020 μmol kg^{-1}) to the Canada Basin (~1965–2000 μmol kg^{-1}). Average DIC concentrations for all water masses over the shelf and Canada Basin in spring are shown in Table 1.

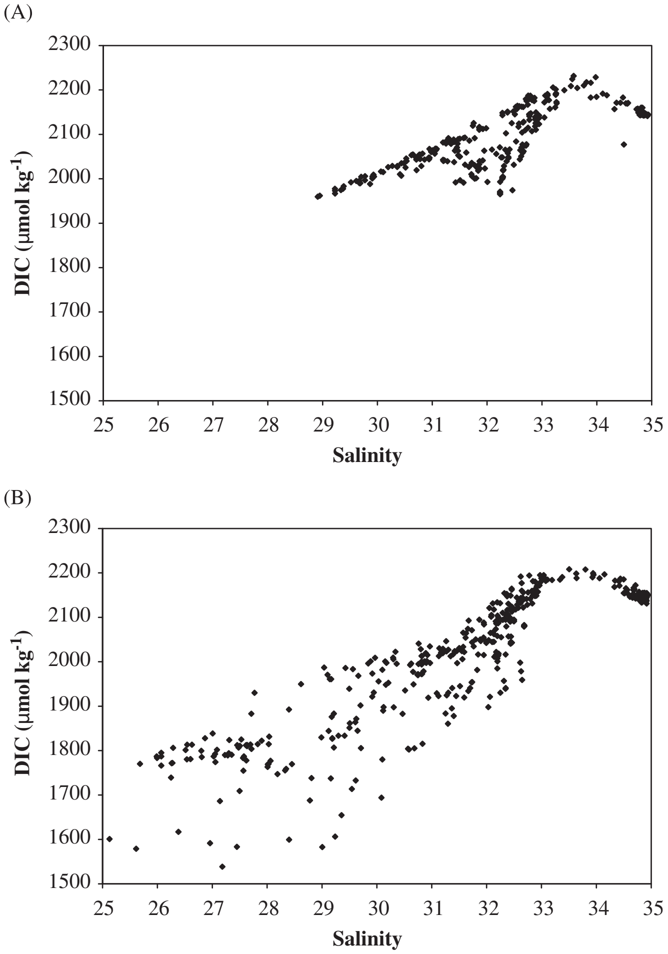

Fig. 2. Scatter plot of DIC (μmol kg^{-1}) versus salinity for (A) spring cruise 2004 and (B) summer cruise of 2004.

In summer, DIC concentrations over the shelf decreased and ranged from 1580 to 2240 μmol kg^{-1} (Fig. 2B). The lowest DIC concentrations (<1600 μmol kg^{-1}) were observed near Barrow Canyon. Over the Canada Basin, DIC concentrations showed very little seasonal variability (Table 1).

In spring and summer of 2004, DIC concentrations over the shelf were slightly lower than in 2002 (Bates et al., 2005a) (Table 1). Beneath the mixed layer and over the Canada Basin, concentrations of DIC did not vary (Table 1).

4.1.2. *DOC/N observations*

In spring, DOC concentrations (Fig. 3A) were tightly correlated with salinity both over the shelf ($y = -3.63x+186$) and Canada Basin. The zero salinity intercept of ~186 for DOC over the shelf is consistent with previous observations taken in the northeastern Chukchi Sea (Mathis et al., 2005). Over the shelf, there were two end members present: one had lower DOC concentrations (~65 μmol kg^{-1}) at a salinity of ~33.1; the other was surface water that had higher DOC concentrations (~75 μmol kg^{-1}) at lower salinity (~30.5). Over the Canada Basin, the appearance of a third end member coincided with the lower concentrations of DOC (~50 μmol kg^{-1}) in the waters of both the AL and DAL (Fig. 3A).

During summertime, DOC concentrations over the shelf (Fig. 3B) showed significant influence from two end members that were not present in spring. The first was from low-salinity (24.5–29.5), low DOC (~25 μmol kg^{-1}; Mathis et al., 2007) ice melt that diluted the DOC signal over the shelf. The second new end member was created by a combination of high DOC river

Table 1
Seasonal and interannual comparison of salinity, temperature (°C), and DIC (μmol kg^{-1}) for spring and summer of 2002 and 2004 in the western Arctic Ocean.

	CTDTMP ITS-90	CTDSAL	DIC (μmol kg^{-1})
Spring 2002			
Shelf			
0–30	1.7±0.1	32.1±0.7	2152±47
30–75	−1.7±0.1	32.8±0.4	2183±3
Canada Basin			
PSL	−1.4±0.4	31.4±0.6	2096±40
BS	−1.5±0.2	32.8±0.1	2180±9
UH	−1.6±0.1	33.3±0.2	2200±18
LH	−1.2±0.4	34.1±0.3	2204±32
AL	0.2±0.4	34.6±0.1	2161±12
DAL	0.2±0.4	34.9±0.1	2145±7
Summer 2002			
Shelf			
0–30	2.6±3.5	30.4±17	1932±106
30–75	0.40±2.2	32.1±0.7	2077±87
Canada Basin			
PSL	−1.1±0.4	28.3±11	1798±278
BS	−1.6±0.1	32.8±0.1	2168±44
UH	−1.6±0.1	33.3±0.2	2202±19
LH	−11±0.3	34.0±0.2	2199±28
AL	0.2±0.3	34.6±0.1	2166±43
DAL	0.2±0.4	34.9±0.1	2149±31
Spring 2004			
Shelf			
0–30	−1.3±0.5	31.6±0.8	2135±48
30–75	−1.2±0.5	32.2±0.6	2187±55
Canada Basin			
PSL	−1.4±0.2	31.3±0.8	2084±31
BS	−1.5±0.1	32.7±0.1	2165±18
UH	−1.6±0.1	33.2±0.2	2196±14
LH	−1.2±0.4	34.0±0.2	2211±29
AL	0.2±0.4	34.7±0.1	2160±15
DAL	0.2±0.4	34.9±0.1	2144±5
Summer 04			
Shelf			
0–30	3.7±3.9	30.9±1.0	1908±135
30–75	1.3±2.6	32.2±0.6	2063±69
Canada Basin			
PSL	1.9±2.0	28.1±1.2	1758±208
BS	−1.5±0.1	32.7±0.2	2180±31
UH	−1.5±0.1	33.2±0.1	2207±17
LH	−0.9±0.3	34.1±0.2	2195±23
AL	0.2±0.3	34.6±0.1	2168±40
DAL	0.2±0.4	34.9±0.1	2150±30

runoff and *in situ* DOC production from phytoplankton in the upper mixed layer (Mathis et al., 2007). Elevated concentrations of DOC were observed over some parts of the adjacent Canada Basin. This DOC likely came either from riverine sources or was produced by phytoplankton over the shelf and transported offshore.

On average, DOC concentrations increased between spring and summertime in the mixed layer (Table 2) by as much as 12 μmol kg^{-1}. Below the mixed layer over the shelf and Canada Basin, DOC concentrations showed little seasonal variability. Average values for DOC concentrations for each of the water masses are shown in Table 2.

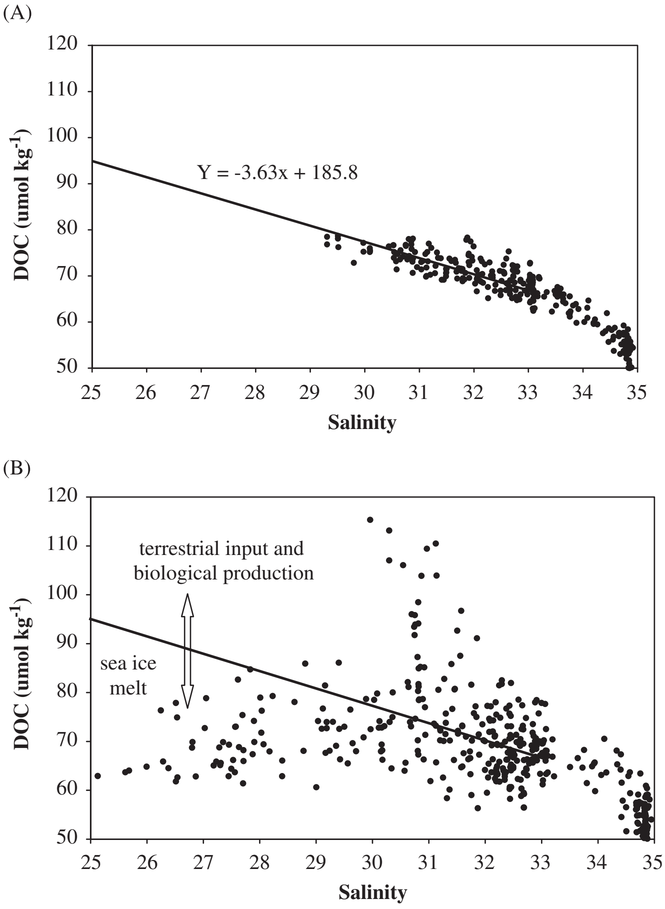

Fig. 3. DOC concentrations (μmol kg^{-1}) over the Chukchi shelf and Canada Basin for (A) spring 2004 and (B) summer 2004. The black line indicates conservative mixing between the incoming Pacific/Bering Sea water and the waters of the Chukchi shelf with a *y*-intercept of 186. Deviations from this line in summer are due to the complex nature of DOC in the Chukchi Sea. Points above the line are a result of high DOC influx from rivers and *in situ* production from phytoplankton. Points below the line are due to dilution from low DOC ice melt.

Averaging values of DON for spring and summer in the mixed layer over the shelf showed that there was a seasonal increase of DON. Concentrations over the shelf increased by ~3.6 μmol kg^{-1} (Table 2). Over the Canada Basin, DON concentrations decreased with depth with the highest values (~4.6 μmol l^{-1}) near the surface and the lowest values (~2.6 μmol l^{-1}) present in the DAL (Table 2).

DOC/N concentrations in the mixed layer over the shelf were higher in 2004 than in 2002 (Mathis et al., 2005) (Table 2). However, concentrations beneath the mixed layer did not vary considerably (Table 2).

4.1.3. *POC/N observations*

POC/N concentrations increased between spring and summer of 2004, and a plume of suspended POC (>20 μmol kg^{-1}; depth ~30 m; density ~25.8 kg m^{-3}) and PON (>2.0 μmol l^{-1}; depth ~30 m; density ~25.8 kg m^{-3}) extended from the shelf over the shelf-break. These suspended particles are likely transported off the shelf in subsurface waters, supporting the heterotrophic community in the UH of the Canada Basin.

Taking the average values of suspended POC/N in the Chukchi Sea for spring and summertime (Table 2) shows the seasonal increase in concentrations, particularly over the shelf. Average concentrations of suspended POC below the surface and over the shelf increased from 3.5 to >20 μmol kg^{-1} between spring and

Table 2
Seasonal and interannual comparison of salinity, DON (μmol kg^{-1}), DOC (μmol kg^{-1}), POC (μmol kg^{-1}), and PON (μmol kg^{-1}) for spring and summer of 2002 and 2004 in the western Arctic Ocean.

	CTDSAL	DON (μmol kg^{-1})	DOC (μmol kg^{-1})	PON (μmol kg^{-1})	POC (μmol kg^{-1})
Spring 2002					
Shelf					
0–30	32.1 ± 0.7	4.1 ± 1.3	68.4 ± 4.2	0.6 ± 0.3	3.5 ± 1.6
30–75	32.8 ± 0.4	4.6 ± 1.1	69.3 ± 2.7	0.6 ± 0.3	3.3 ± 1.1
Canada Basin					
PSL	31.4 ± 0.6	4.1 ± 0.7	71.6 ± 3.1	0.3 ± 0.2	1.5 ± 0.9
BS	32.8 ± 0.1	4.1 ± 1.2	66.9 ± 2.2	0.1 ± 0.1	0.9 ± 0.5
UH	33.2 ± 0.2	4.5 ± 1.1	65.1 ± 2.1	0.1 ± 0.1	0.9 ± 0.3
LH	34.1 ± 0.2	4.0 ± 1.1	61.7 ± 2.3	0.2 ± 0.1	1.1 ± 0.7
AL	34.6 ± 0.1	3.4 ± 1.0	56.8 ± 2.2	0.1 ± 0.1	0.8 ± 0.6
DAL	34.9 ± 0.1	2.6 ± 1.0	52.2 ± 3.7	0.1 ± 0.2	0.7 ± 1.0
Summer 2002					
Shelf					
0–30	30.8 ± 1.7	6.5 ± 1.6	72.5 ± 12.0	2.2 ± 3.0	14.1 ± 21.9
30–75	32.1 ± 0.7	4.6 ± 1.6	70.9 ± 8.2	3.5 ± 3.4	21.8 ± 21.0
Canada Basin					
PSL	31.4 ± 0.8	5.1 ± 1.1	70.9 ± 5.2	0.9 ± 0.6	5.3 ± 3.8
BS	32.8 ± 0.1	4.2 ± 1.3	65.0 ± 1.6	0.5 ± 0.5	2.7 ± 2.5
UH	33.3 ± 0.2	4.5 ± 1.2	63.8 ± 2.7	0.4 ± 0.2	2.3 ± 1.3
LH	34.0 ± 0.2	3.9 ± 1.3	60.8 ± 2.6	0.2 ± 0.1	1.2 ± 0.8
AL	34.6 ± 0.1	3.4 ± 1.3	54.4 ± 3.1	0.1 ± 0.1	0.9 ± 0.5
DAL	34.9 ± 0.1	2.6 ± 1.4	49.4 ± 2.0	0.1 ± 0.1	0.5 ± 0.3
Spring 2004					
Shelf					
0–30	31.6 ± 0.8	4.4 ± 1.3	68.2 ± 3.9	0.5 ± 0.2	3.7 ± 1.0
30–75	32.2 ± 0.6	4.3 ± 1.4	69.4 ± 4.0	0.6 ± 0.3	3.6 ± 1.5
Canada Basin					
PSL	31.3 ± 0.8	4.3 ± 1.6	68.5 ± 3.1	0.2 ± 0.1	1.4 ± 1.0
BS	32.7 ± 0.1	4.8 ± 1.1	66.8 ± 4.3	0.1 ± 0.1	1.0 ± 0.4
UH	33.2 ± 0.2	4.4 ± 1.8	70.6 ± 3.6	0.1 ± 0.1	0.9 ± 0.3
LH	34.0 ± 0.2	3.9 ± 1.7	58.5 ± 5.1	0.2 ± 0.1	1.1 ± 0.7
AL	34.7 ± 0.1	3.4 ± ± 1.9	53.3 ± 2.5	0.1 ± 0.1	0.9 ± 0.6
DAL	34.9 ± 0.1	2.7 ± 2.1	50.7 ± 3.3	0.1 ± 0.1	0.7 ± 0.9
Summer 2004					
Shelf					
0–30	30.6 ± 2.0	8.4 ± 1.1	79.7 ± 9.5	2.9 ± 3.2	19.9 ± 23.6
30–75	32.2 ± 0.6	4.7 ± 1.0	72.6 ± 6.9	3.9 ± 4.0	22.7 ± 24.1
Canada Basin					
PSL	31.7 ± 0.6	4.7 ± 1.6	70.1 ± 5.3	0.9 ± 0.6	5.9 ± 3.1
BS	32.7 ± 0.2	4.5 ± 1.7	65.3 ± 2.3	0.5 ± 0.4	2.8 ± 2.3
UH	33.2 ± 0.1	4.7 ± 1.6	65.8 ± 2.6	0.4 ± 0.2	2.3 ± 1.2
LH	34.1 ± 0.2	3.9 ± 1.7	59.9 ± 2.6	0.2 ± 0.1	1.2 ± 0.7
AL	34.6 ± 0.1	3.4 ± 1.6	55.4 ± 1.7	0.1 ± 0.1	0.9 ± 0.6
DAL	34.9 ± 0.1	2.6 ± 1.4	53.6 ± 2.7	0.1 ± 0.1	0.5 ± 0.3

The shelf values were calculated by averaging measurements taken at stations where the water depth was less <75 m. The shelf stations were then further divided by mixed layer depth (0–30 m) and water beneath the mixed-layer (30–75 m). Stations over the continental slope and deep Canada Basin (>75 m) were broken down by water masses. See Section 3.1 of the text for a description of each water mass.

summer. Suspended PON concentrations also increased from 0.55 μmol kg^{-1} in spring to >3.5 μmol kg^{-1} in summer. Over the Canada Basin, small increases were observed between spring and summer in the BS and UH waters, likely due to lateral advection off of the shelf. These increases diminish with depth, and there was very little seasonal variability in the waters of the LH, AL, or DAL (Table 2).

POC/N showed similar trend to DOC/N with higher concentrations in the mixed layer over the shelf in 2004 compared to 2002 (Table 2).

5. Discussion

5.1. Estimates of NCP

5.1.1. Chukchi shelf productivity estimate

DIC concentrations are influenced by a variety of physical and biogeochemical factor that include (1) NCP and ice melt, which both decrease DIC concentrations, and (2) air–sea gas exchange of CO_2 and remineralization of organic matter, which both increase DIC concentrations (Bates et al., 2005a). Between the spring and summer observations in 2004, large decreases (<100–280 μmol kg^{-1}) of DIC were observed in the water column over the shelf. A large component of the observed decrease was the dilution by ice melt; although, this was largely restricted to the upper 5 m. The contribution of ice melt to DIC changes can be negated by normalizing DIC to a constant salinity of 35. This correction assumes that the ice melt contributed negligible amounts of DIC to the upper mixed layer, and that there was an absence of mixing with new water mass sources (Bates et al., 2005a). By normalizing to a constant salinity, the impacts of ice melt are removed, and the spatial and temporal distributions of normalized DIC (nDIC) reflect the influence of factors such as NCP and air–sea gas exchange of CO_2.

In spring of 2004, nDIC concentrations in the surface waters over the Chukchi shelf and slope-basin ranged from 2300 to 2370 μmol kg^{-1} (Fig. 4A). Spatially, there was an onshore to offshore gradient in nDIC concentrations noted in the upper 30 m, with the highest values present over the Canada Basin (Fig. 5A). Later, during the summer occupation, decreases in nDIC (100–450 μmol kg^{-1}) (Fig. 4B) were observed over much of the Chuckchi shelf and were highest near the biological hotspot near Barrow Canyon, where nDIC concentrations decreased to 2140 μmol kg^{-1} in the mixed layer (Fig. 5B). Previous studies have also shown similar seasonal drawdown of DIC and seawater pCO_2 in the mixed layer near Barrow Canyon (Pipko et al., 2002; Murata and Takizawa, 2003; Bates et al., 2005a).

5.1.2. Estimates of productivity over the Chukchi shelf and Canada Basin

The observed drawdown of nDIC in the upper mixed layer over the shelf can be attributed to primary production. Estimates of NCP were determined from changes in the inventory of nDIC over time (t) as follows:

$$\mathrm{NCP} = ({}^{\mathrm{spring}}\mathrm{nDIC}_{(0-30\,\mathrm{m})} - {}^{\mathrm{summer}}\mathrm{nDIC}_{(0-30\,\mathrm{m})})/t \tag{1}$$

The rate of NCP is expressed as mg C m^{-2} d^{-1}, with an error of ~24–40 mg C m^{-2} d^{-1} due to imprecision and inaccuracy of ~1 μmol kg^{-1} associated with the DIC analysis (Bates et al., 2005a). At each station, rates of NCP were computed from nDIC data integrated over 0–30 m depth.

During the spring cruise of 2004, mixed-layer nDIC concentrations were fairly uniform over much of the Chukchi shelf (Table 3).

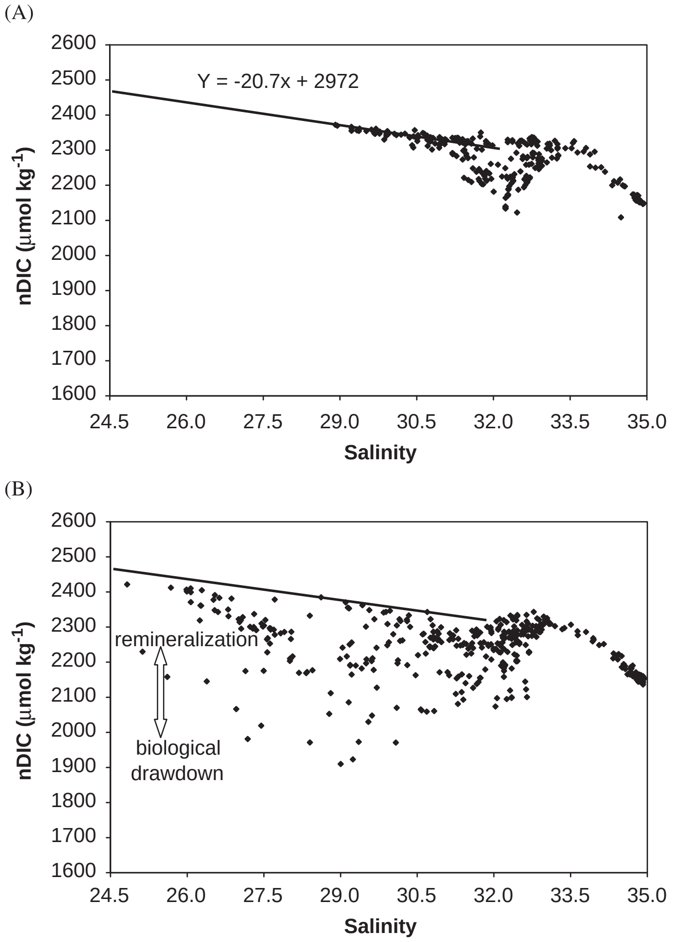

Fig. 4. Concentrations of DIC (μmol kg^{-1}) normalized (nDIC) to a constant salinity of 35 for (A) spring 2004 and (B) summer 2004. The black line shows the conservative mixing in spring between the incoming Pacific/Bering Sea water and the waters of the Chukchi shelf with a y-intercept of 2747. In summer, the decreases in nDIC values are due to consumption by phytoplankton during photosynthesis with subsequent production of organic carbon. At the same time, but at a slower rate remineralization is converting this organic carbon back into its inorganic constituents. While the photosynthetic drawdown of nDIC occurs over a few weeks, the remineralization takes 6–10 months to return nDIC to its pre-bloom concentrations.

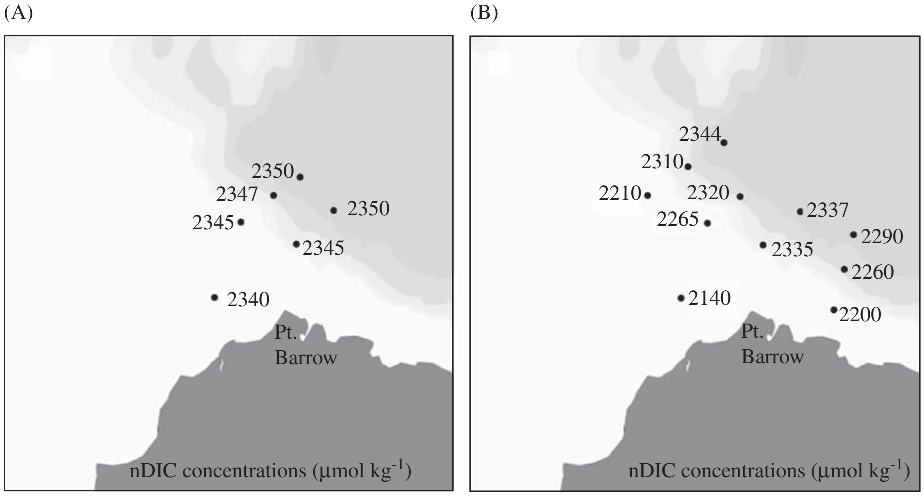

Fig. 5. nDIC (μmol kg^{-1}) shown spatially in the study area (see black box in Fig. 1) for (A) spring and (B) summer.

The spring nDIC values were used to determine the subsequent nDIC changes and rates of NCP observed between the spring and summer cruises (52–86 days). An average value (2246 ± 4 μmol kg^{-1}) for springtime nDIC was used to calculate nDIC drawdown over shelf and deep basin between the two cruises.

Rates of NCP integrated over the upper 30 m determined for the spring-summer period were highly variable (Table 4), ranging from low values of 8 mg C m^{-2} d^{-1} over the basin to >2000 mg

Table 3
Average values for nDIC (μmol kg^{-1}) in spring 2002 in the Chukchi Sea.

Station	Location	Date	Mean nDIC (μmol kg^{-1})
Barrow Canyon			
23	Shelf	11 June 2004	2341 ± 3
26	Slope	13 June 2004	2345 ± 6
27	Slope/Basin	15 June 2004	2350 ± 4
East Hanna Shoal			
9	Shelf	24 May 2004	2344 ± 7
12	Shelf	28 May 2004	2346 ± 2
13	Shelf	30 May 2004	2343 ± 3
16	Slope	29 May 2004	2347 ± 3
17	Slope	30 May 2004	2349 ± 2
19	Slope/Basin	03 June 2004	2350 ± 1
20	Basin	05 June 2004	2350 ± 1
Average			2346 ± 4

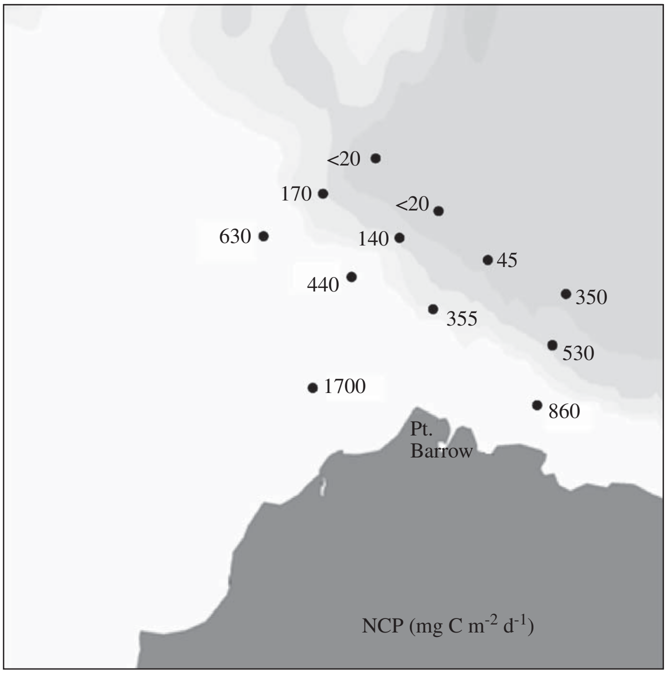

Fig. 6. NCP (mg C m^{-2} d^{-1}) shown spatially in the study area (see black box in Fig. 1).

Table 4
Mean nDIC concentrations for the mixed layer (0–30 m) during summer cruise of 2004.

Station	Location	Date	Mean nDIC (μmol kg^{-1})	ΔnDIC	Days	NCP (mg C m^{-2} d^{-1})
Barrow Canyon						
14	Shelf	22 July 2004	2170	176	52	1338 ± 38
15	Shelf	23 July 2004	2120	226	53	1690 ± 40
18	Shelf	24 July 2004	2065	281	54	2057 ± 41
22	Shelf	26 July 2004	2212	134	56	950 ± 32
23	Slope	27 July 2004	2336	10	57	72 ± 37
24	Slope	28 July 2004	2338	8	58	43 ± 8
35	Slope/Basin	07 Aug 2004	2337	9	68	47 ± 2
36	Slope/Basin	08 Aug 2004	2337	9	69	47 ± 2
East of Barrow Canyon						
25	Shelf	29 July 2004	2204	142	67	837 ± 37
26	Shelf	30 July 2004	2198	148	66	887 ± 37
29	Slope	30 July 2004	2250	96	64	594 ± 35
32	Slope/Basin	03 Aug 2004	2275	71	60	471 ± 36
33	Slope/Basin	05 Aug 2005	2282	64	59	427 ± 31
34	Slope/Basin	6 Aug 2005	2304	42	60	275 ± 20
East Hanna Shoals						
38	Shelf	10 Aug 2004	2245	101	71	562 ± 38
42	Shelf	11 Aug 2004	2305	41	72	223 ± 22
44	Shelf	12 Aug 2004	2246	100	73	541 ± 39
47	Slope	13 Aug 2004	2319	27	74	143 ± 21
West Hanna Shoals						
59	Shelf	23 Aug 2004	2251	94	85	439 ± 29
60	Shelf	24 Aug 2004	2167	179	86	825 ± 38
56	Slope	22 Aug 2004	2311	35	83	164 ± 31
58	Slope	22 Aug 2004	2308	38	84	178 ± 30
53	Basin	19 Aug 2004	2341	5	80	24 ± 18
54	Basin	19 Aug 2004	2344	2	80	8 ± 2

NCP rates (mg C m^{-2} d^{-1}) integrated over the upper 30 m were estimated for each station using the nDIC change (compared to the average spring nDIC of 2346 μmol kg^{-1}) observed since springtime. The error estimates for NCP were calculated with the standard deviation of the spring nDIC concentrations. For stations along the EBC section, which was not sampled in spring due to sea-ice cover, it was assumed that these waters originated west of Point Barrow either from the Chukchi shelf or interior basin. Geostrophic flow along the shelf and shelf break was from west to east.

$\mathrm{C\,m^{-2}\,d^{-1}}$ over the shelf. Fig. 6 shows the gradient in NCP over the Chukchi shelf extending out into the Canada Basin.

The highest rates of NCP (~950–2060 $\mathrm{mg\,C\,m^{-2}\,d^{-1}}$) in 2004 as in 2002, were found over the shelf near the head of Barrow Canyon. However, rates in 2004 were elevated by as much as 400 $\mathrm{mg\,C\,m^{-2}\,d^{-1}}$ in this area. Rates of NCP in 2004 (~850 $\mathrm{mg\,C\,m^{-2}\,d^{-1}}$) were also similar to those observed in 2002 to the east of Barrow Canyon. This is interesting because this area showed the maximum influence from the enhanced ACC water as temperatures in the mixed layer were 5 °C warmer than in 2002. Waters from the ACC are lower in inorganic nutrients than those derived from the AC, which should have diminished rates of NCP in the region. The fact that NCP stayed consistent, or in some instances increased in 2004, indicates that other factors such as light availability, ice and snow cover, and water temperatures play an important role in the controlling ecosystem production as several key differences were observed in these conditions in 2004. For instance, while ice thickness was similar over the shelf in both years, the amount of snow cover on the ice was less in 2004 (Shirasawa et al., 2009), allowing for increased light penetration. The ice cover in 2004 also experiences a rapid retreat off the shelf, exposing the warmer (+5 °C) surface waters. In 2004, autotrophs were able to utilize nitrate deeper into the water column compared to 2002, thus increasing the potential for NCP. From these observations, it appears that these changes in hydrographic conditions were enough to maintain and exceed rates of NCP even with the diminished nutrient supply through Bering Strait.

As expected, low rates of NCP were observed at locations over the outer shelf-break and Canada Basin due to the lack of inorganic nitrate in the mixed layer. There was a west to east gradient offshore with the highest rates of NCP found off the shelf east of Barrow Canyon (Fig. 6).

Assuming that the growing season of the Chukchi Sea shelf is approximately 120 days, ^{14}C-based productivity measurements (Hill and Cota, 2005) can be extrapolated to give an annual productivity of ~35–50 $\mathrm{g\,C\,m^{-2}\,yr^{-1}}$. However, the ^{14}C-based productivity measurements probably missed the bulk of the productivity between spring and summer, as the bloom had significantly diminishes by late July and August. NCP rates, estimated from the inventory change of nDIC, yield considerably higher annual production estimates of ~300 $\mathrm{g\,C\,m^{-2}\,yr^{-1}}$. This, however, might also be an underestimate, as remineralization of organic matter occurs between our sampling in spring and summer. While remineralization is a slower process than primary production, it is contributing DIC back into the system that we are not able to account for in our mass balance. A shorter time between sampling intervals would help to alleviate this problem.

The carbon mass balance used here to estimate NCP does not account for air–sea gas exchange of CO_2 and vertical diffusion between the spring and summer cruises. Although both of these processes add CO_2 to the mixed layer, the contribution to the nDIC inventory is small, and this topic is discussed in detail in Bates et al. (2005a).

5.1.3. *Early growing season productivity estimates*

It is difficult to determine the rates of NCP on the Chukchi shelf prior to the spring cruise due to lack of wintertime DIC data. In spring, DIC (nDIC) concentrations in the upper mixed layer were fairly uniform across most of the shelf and deep basin. nDIC concentrations were lower in Bering Strait and in the southern Chukchi Sea where ice cover was <80%, which could indicate early season production in this area. However, these waters were replete in inorganic nutrients (nitrate ~10–15 $\mu\mathrm{mol\,kg^{-1}}$), and the relatively low nDIC concentrations may represent the DIC-salinity properties of the influx of Pacific origin and terrestrial waters that have been modified by early season production in the Bering Sea (Bates et al., 2005a).

5.1.4. *Fate of NCP*

We must now determine if there was any change in the partitioning (retention in the mixed layer vs. export) of organic matter produced during NCP given the observed changes in the hydrography and other environmental conditions. We have developed a mass balance for the northeastern Chukchi Sea (Mathis et al., 2007) using salinity and δ^{18}O as conservative traces to determine the fractions of river water, ice melt, and marine water present at a station. By knowing the concentrations of DOC and POC in each of these components, we can calculate the seasonal increases in DOC and suspended POC due to NCP. The remaining carbon, when biologically produced DOC and suspended POC are subtracted from the normalized drawdown of DIC, is considered export production, or carbon that is removed from the mixed layer and deposited in the sediments either on the shelf or in the slope-basin.

We performed a similar analysis with the 2004 data, as was done for 2002 (Mathis et al., 2007), and determined that more DOC and suspended POC was produced by phytoplankton over the shelf and retained in the mixed layer. From our mass balance, we determined that in areas where NCP increased export production also increased, and rates of benthic metabolism were higher, indicating that more organic carbon was deposited to shelf sediments in 2004 (Grebmeier et al., 2006; Lepore et al., 2006). However, we found that a disproportionate amount of NCP was retained in the mixed layer in 2004 as DOC and suspended POC. In 2002, near Barrow Canyon, we determined that ~10% of NCP was converted to DOC and ~15% was converted to suspended POC (Mathis et al., 2007), meaning that ~75% of NCP was removed from the mixed layer as export production. In 2004, our mass balance showed that ~17% of NCP was converted to DOC, and 19% was converted to suspended POC, leaving ~64% as export production. To the east of Barrow Canyon, where rates of NCP were consistent between 2002 and 2004, we also observed an increase (2–4%) in the percentage of NCP that was converted to DOC and suspended POC, with a slight decrease in export production in these areas. This supports the hypothesis that more NCP is retained and remineralized in the mixed layer rather than being exported when the bloom occurs in warmer waters.

We have shown that NCP can be strongly influenced by several factors other than the inflow of waters onto the northeastern Chukchi shelf. Ice and snow cover, light availability, and water temperatures also play an important role in the cycling and fate of carbon in the region. As environmental conditions in the region continue to change, it will be important to monitor the rates of NCP and the fate of the organic carbon that is produced as they will have a definite impact on the ecosystem of the northeastern Chuckchi Sea.

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