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Air-sea CO_2 fluxes and the continental shelf pump of carbon in the Chukchi Sea adjacent to the Arctic Ocean

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[1] The Chukchi Sea, a shallow sea-ice covered coastal sea adjacent to the Arctic Ocean, exhibits an intense bloom of phytoplankton each year due to the exposure of nutrient-laden surface waters during the brief summertime retreat and melting of sea-ice. The impact of phytoplankton production and other factors on the seasonal dynamics of carbon and air-sea CO_2 fluxes were investigated during two survey cruises (5 May–15 June 2002, and 17 July–26 August 2002), as part of the Western Arctic Shelf-Basins-Interactions (SBI) project. In springtime, most of the Chukchi Sea was sea-ice covered (>95%) and remnant winter water was present across the shelf. Surface layer seawater partial pressure of CO_2 ($p$$CO_2$) ranged from ~200–320 μatm, indicative of undersaturation with respect to atmospheric $p$$CO_2$, although sea-ice cover kept rates of air-to-sea CO_2 flux generally low (<1 mmoles CO_2 m^2 d^{-1}). By summertime, after sea-ice retreat, seawater $p$$CO_2$ contents had decreased to very low values (<80–220 μatm) in response to high rates of localized primary and net community production (NCP) and biological uptake of dissolved inorganic carbon (DIC). In the seasonally sea-ice free regions of the Chukchi Sea shelf, rates of air-to-sea CO_2 fluxes, determined using the quadratic wind speed-transfer velocity relationships of Wanninkhof (1992), were high, ranging from ~30–90 mmoles CO_2 m^{-2} d^{-1}. In regions of the Chukchi Sea slope (and western Beaufort Sea shelf and Arctic Ocean basin) where sea-ice cover remained high (>80%), air-to-sea CO_2 fluxes remained generally low (<2 mmoles CO_2 m^{-2} d^{-1}). Seasonal (i.e., May to September) and annual net air-to-sea CO_2 fluxes from the Chukchi Sea shelf were estimated at ~27 ± 7 Tg C yr^{-1}, and 38 ± 7 Tg C yr^{-1}, respectively. The Chukchi Sea represents the largest oceanic CO_2 sink in the marginal coastal seas adjacent to the Arctic Ocean. An active continental shelf pump of carbon, driven by the northward transport of nutrient-rich water of Pacific Ocean origin, high rates of primary and net community production during the sea-ice free period, and lateral export of organic carbon, maintains the Chukchi Sea shelf and slope as a perennial ocean CO_2 sink.

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1. Introduction

[2] The coastal ocean is the active interface where the terrestrial, ocean and atmosphere components of the Earth's biogeochemical system interact. However, CO_2 dynamics, and CO_2 sink or source status of the coastal ocean domain remains poorly understood due to past undersampling and limited historical studies. The CO_2 source or sink status of the coastal ocean continues to be highly debated. In early papers, Walsh first suggested that the continental margins sequestered significant amounts of CO_2 and that the global coastal ocean was a significant sink of atmospheric CO_2 [*Walsh et al.*, 1985; *Walsh*, 1991]. In contrast, *Smith and Hollibaugh* [1993] argued that the coastal ocean (and open ocean) was net heterotrophic and thus a potential source of CO_2 to the atmosphere. More recently, other studies have suggested that the CO_2 source or sink status [*Borges*, 2005; *Borges et al.*, 2005], and the metabolic status of continental shelves is highly variable in time and space [e.g., *Wollast*, 1998; *Gattuso et al.*, 1998]. High-latitude and temperate coastal seas tend to be net annual sinks of atmospheric CO_2, while nearshore, upwelling dominated, and subtropical to tropical coastal environments tend to release CO_2 to the atmosphere [*Borges et al.*, 2005] (see references in Table A1 of *Borges et al.* [2005]). In a recent review, *Ducklow and McAllister* [2005] concluded that the global coastal ocean is presently net autotrophic, and a potential sink for atmospheric CO_2.

[3] There are multifold and complex factors that influence the CO_2 sink or source status of the coastal ocean. The net metabolism (either net autotrophy or heterotrophy) of a continental shelf region is influenced by a balance of transports and exchanges, such as: the input of organic matter (OM) from terrestrial sources, OM production and

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consumption in the coastal ocean, retention or export of OM from the shelf and, the net air-sea exchange of CO_2. The balance of these processes dictates the metabolic status (i.e., autotrophic or heterotrophic) of the continental shelf, but can also influences the potential CO_2 sink or source status. The spatiotemporal variability of CO_2 on the coastal ocean is driven by a complex interplay of connected and quasi-independent physical and biological factors. For example, the physicochemical process of air-sea CO_2 exchange can proceed independently of the biological processes (e.g., production versus consumption of OM) that dictate the metabolism of the coastal ocean. Thus, as *Ducklow and McAllister* [2005] point out, the variability of pCO$_2$ (or ΔpCO$_2$, difference between seawater and atmospheric pCO$_2$) and separation of biological and physical influences can lead, for example, to a net heterotrophic open (or coastal) ocean still being a sink for atmospheric CO_2.

[4] In high-latitude and temperate coastal oceans that act as sinks for atmospheric CO_2, the causes for undersaturation of seawater pCO$_2$ are complex and uncertain. For example, in the temperate East China Sea (ECS) and west European continental shelves, seawater pCO$_2$ concentrations remain below atmospheric CO_2 values for most of the year and these shelves are net sinks for atmospheric CO_2 [e.g., *Tsunogai et al.*, 1999; *Frankignoulle and Borges*, 2001; *Borges and Frankignoulle*, 2002a; *Borges*, 2005]. As an explanation, *Tsunogai et al.* [1999] proposed the ''continental shelf pump'' hypothesis, in which winter cooling on the ECS shelf depressed seawater pCO$_2$ below saturation. Inputs of nutrients and continued CO_2 drawdown in the summer due to primary production, and the subsequent vertical export of OM and horizontal export of CO_2 as dissolved inorganic carbon (DIC) maintains the CO_2 sink status of the shelf throughout the year. Although there is sparse data to support this idea [e.g., *Wang et al.*, 2000; *Liu et al.*, 2000], the west European continental shelves appear to function in this manner [e.g., *Thomas et al.*, 2004; *Bozec et al.*, 2005; *Borges*, 2005]. However, other continental shelves may act as sources of CO_2 [e.g., *Cai et al.*, 2003; *Cai and Dai*, 2004; *Zhai et al.*, 2005] and the nearshore coastal and estuarine systems of the West European shelf region are thought to be sources of CO_2 to the atmosphere [e.g., *Borges and Frankignoulle*, 1999, 2002a; *Borges et al.*, 2005].

[5] In high-latitude polar and subpolar coastal ocean environments, *Yager et al.* [1995] put forward the ''seasonal rectification hypothesis'' to explain seasonal seawater pCO$_2$ variability. For example, in the North East Water (NEW) polynya [*Yager et al.*, 1995], Ross Sea [*Bates et al.*, 1998; *Sweeney et al.*, 2000; *Sweeney*, 2003], and east of Baffin Island [*Miller et al.*, 2002], there are brief but large drawdowns of seawater pCO$_2$ (and DIC) due to intense primary production during the ice-free periods of summertime (austral summer in Antarctica). During the remainder of the year, *Yager et al.* [1995] suggested that the sea-ice cover prevented gas exchange in the NEW polynya, thereby allowing wintertime rectification of seawater pCO$_2$ to near equilibrium values through remineralization of OM produced earlier. The seasonal asymmetry in the air-sea CO_2 fluxes, driven by primary production and wintertime sea-ice cover, is thought to cause these coastal regions to be net sinks for atmospheric CO_2 [*Yager et al.*, 1995; *Miller et al.*, 2002]. However, it is not clear whether these shelves are weak or strong sinks, since this depends on whether OM is preferentially retained and remineralized to CO_2 on the shelf (weaker CO_2 sink) or OM (and DIC) is preferentially exported to the open ocean (stronger CO_2 sink) during the sea-ice covered period.

[6] In the Arctic Ocean and adjacent coastal seas, knowledge about the distribution of CO_2, air-sea CO_2 fluxes and the net metabolism of the region is uncertain due to a lack of sufficient observations. The Arctic Ocean and adjacent coastal seas such as the Chukchi Sea and Beaufort Seas have an important role in the global freshwater cycle [e.g., *Aagaard and Carmack*, 1989; *Wijffels et al.*, 1992; *Woodgate and Aagaard*, 2005] and Atlantic overturning circulation [e.g., *Aagaard and Carmack*, 1994; *Walsh and Chapman*, 1990; *Mysak et al.*, 1990; *Häkkinen*, 1993; *Wadley and Bigg*, 2002]. Arctic Ocean coastal shelf seas are important sites of biological production, particularly during the brief, seasonally sea-ice free periods. For example, flow of nutrient-rich Pacific and Alaskan coastal waters through the Bering Strait into the Chukchi Sea from the Bering Sea supports a brief but intense photosynthetic season in the Chukchi and Beaufort Seas with rates of water column ^{14}C primary and net community production (NCP) at >300 g C m^2 y^{-1} (0.3–2.8 g C m^2 d^{-1} [*Hameedi*, 1978; *Cota et al.*, 1996; *Sambrotto et al.*, 1984; *Hansell et al.*, 1993; *Wheeler et al.*, 1996; *Gosselin et al.*, 1997; *Chen et al.*, 2002; *Hill and Cota*, 2005; *Bates et al.*, 2005a]). This production supports substantial pelagic and benthic biomass that, in turn, supports higher trophic levels (e.g., fish, marine mammals, seabirds) and important human sociocultural and economic activities. The Arctic Ocean and adjacent seas are also particularly sensitive to global climate change and potentially to ecosystem changes associated with warming and sea-ice loss [e.g., *Walsh and Chapman*, 1990; *Moritz and Perovich*, 1996; *Grebmeier and Whitledge*, 1996; *Manabe and Stouffer*, 2000].

[7] Despite the importance and highly dynamic physical and biological nature of the Chukchi, Beaufort and Bering Seas, knowledge about the distribution of CO_2, air-sea CO_2 fluxes and the net metabolism of the region is limited due to a lack of sufficient observations. For example, in the Bering Sea (an important preconditioner for the Chukchi Sea and Arctic Ocean basin), early studies suggest that surface waters of the highly productive ''Green belt'' of the shelf [e.g., *Springer et al.*, 1996; *Springer and McRoy*, 1993] are potential sinks for atmospheric CO_2 [*Codispoti et al.*, 1982, 1986]. More recent studies have focused on the southwestern periphery of the Bering Sea, for example, seawater pCO$_2$ or dissolved inorganic carbon (DIC) data has only been collected close to the western Aleutian Islands [e.g., *Murphy et al.*, 2001; *Nedashkovskii and Sapozhnikov*, 2001] or outside the Bering Sea in the subarctic gyre of the North Pacific [*Midorikawa et al.*, 2002; *Andreev and Watanabe*, 2002].

[8] On the Chukchi and Beaufort Sea continental shelves, studies on CO_2 distributions or air-sea CO_2 fluxes are also extremely limited. For example, inorganic carbon data were collected at a few conductivity-temperature-pressure (CTD) stations in the Chukchi Sea during the Arctic Ocean Section in 1994 [*Anderson et al.*, 2003]. In September 1996, seawater pCO$_2$ and DIC were calculated from measurements of pH and total alkalinity (TA) in the Laptev, East Siberian and

Chukchi Seas [*Semiletov*, 1999; *Pipko et al.*, 2002]. On several cruises between 1998 and 2001, *Murata and Takizawa* [2003] measured surface seawater pCO_2 and DIC. In this paper, we report the surface distributions of seawater DIC, TA, and calculated seawater pCO_2 data in the Chukchi and western Beaufort Sea shelves, collected as part of the 2002 field surveys of the Western Arctic Shelf-Basin Interactions (SBI) project. The seasonal distributions of seawater pCO_2, air-sea CO_2 fluxes and the net metabolism of the Chukchi Sea shelf are examined in context of a comprehensive suite of supporting water column physical and biological carbon measurements [e.g., *Codispoti et al.*, 2005; *Bates et al.*, 2005a] obtained during the SBI survey cruises. The spatiotemporal CO_2 data collected in the Chukchi Sea will be used to evaluate the attributes and drivers of carbon dynamics in the region, and comparisons to the "continental shelf pump" and "seasonal rectification" hypotheses. In the Chukchi Sea, it is hypothesized that the region is a perennial oceanic sink of atmospheric CO_2 and that the CO_2 sink-source status does not oscillate seasonally compared to the Bering Sea, for example.

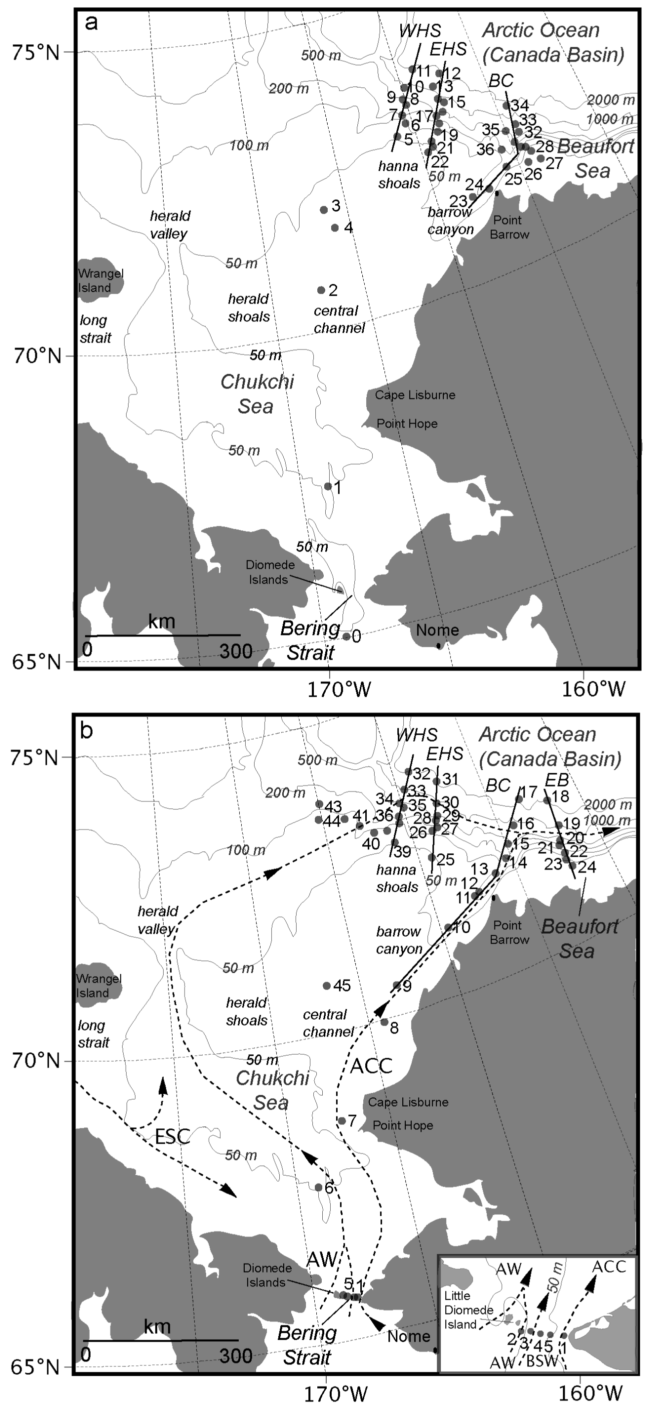

Figure 1. Location map of the Chukchi Sea shelf, Bering Strait, and western Beaufort Sea. (a) Springtime CTD/rosette stations from the HLY 02-01 cruise to the Chukchi Sea (5 May–15 June 2002). Three sections were sampled from Chukchi outer shelf into the Arctic basin, included: (1) West Hanna Shoal (WHS); (2) East Hanna Shoal (EHS) transect, and; (3) Barrow Canyon (BC) transect. (b) Summertime CTD/rosette stations from the HLY 02-03 summer cruise to the Chukchi Sea (17 July–26 August 2002). Four sections were sampled from Chukchi outer shelf into the Arctic Ocean basin, included: (1) West Hanna Shoal (WHS), stations 32–39; (2) East Hanna Shoal (EHS) transect; (3) Barrow Canyon (BC) transect, and; (4) East of Pt. Barrow (EB). Five stations were also sampled at Bering Strait. ACC, Alaskan Coastal Current; AW, Anadyr Water; BSW, Bering Shelf Water; ESC, East Siberian Coastal Current.

2. Overview of Physical Circulation and Water Masses in the Chukchi Sea and Adjacent Arctic Ocean Basin

[9] Pacific Ocean waters from the sub-polar Bering Sea transit through the narrow Bering Strait and enter the Chukchi Sea, fanning out across the shallow (<50 m deep), expansive Arctic marginal sea (Figure 1). The Bering Strait acts as the Pacific Ocean gateway to the Arctic Ocean [*Coachman et al.*, 1975; *Björk*, 1989], with a mean inflow of ~0.8 Sv, with higher flow in summer and lower flow in winter [*Roach et al.*, 1995; *Woodgate et al.*, 2005a, 2005b; *Woodgate and Aagaard*, 2005]. Water transiting Bering Strait is largely composed of warmer, fresher, Alaskan Coastal Current (ACC) waters in the east [*Paquette and Bourke*, 1974], Bering Shelf water (central Bering Strait) and colder, saltier, more nutrient-rich water of the Anadyr Current in the west [*Coachman et al.*, 1975]. Bering Shelf Water (BSW) and Anadyr Water (AW) are thought to merge into Bering Seawater within the Chukchi Sea [*Woodgate et al.*, 2005a; *Codispoti et al.*, 2005]. Another inflow of ~0.1 Sv [*Woodgate et al.*, 2005a] to the Chukchi Sea is the intermittent East Siberian Coastal (ESC) Current through Long Strait [*Weingartner et al.*, 1999]. The four major outflows (~0.1–0.3 Sv each [*Woodgate et al.*, 2005a]) from the Chukchi Sea into the Canada Basin of the central Arctic Ocean occur through Long Strait, Central Channel, Herald Valley and Barrow Canyon [*Paquette and Bourke*, 1974; *Weingartner et al.*, 1998, 2006; *Woodgate et al.*, 2005b], although the outflow through Barrow Canyon can be as high as ~1 Sv [*Münchow and Carmack*, 1997].

[10] Physical transformations and seasonal sea-ice cover play a major role in shaping the Chukchi Seawater masses

and ecosystem. During the winter and much of the year, sea-ice covers much of the Chukchi and Beaufort Sea shelf areas. Furthermore, the water column on the Chukchi Sea shelf is confined to a small range of temperature-salinity space [*Woodgate et al.*, 2005a], indicating mixing and homogenization by ventilation, brine rejection and mixing. During the summer, the sea-ice briefly retreats northward from the Bering Sea, through Bering Strait into the Chukchi and Beaufort Seas to the shelf break and beyond into the Canada Basin of the Arctic Ocean. On the Chukchi Sea shelf, local sea-ice melt transforms water of Pacific Ocean origin to relatively warm, fresher Polar Mixed Layer (PML) water (upper 0–~30 m, salinity typically <31; temperature > −1.5). In the later part of the sea-ice free season, the temperature and salinity properties of the PML on the Chukchi Sea shelf widens from wintertime T-S space. The surface water of the Chukchi Shelf, outflows through the major shelf-slope conduits (i.e., Barrow Canyon, Herald Valley), merges and interjects with the Arctic Ocean basin PML waters off the slope of the Chukchi and western Beaufort Seas. On the continental shelf of the Chukchi Sea, beneath the mixed layer, are waters of the Upper Halocline Layer (UHL). The UHL layer is typically > ~30 m deep, and has a core layer with a salinity of 33.1, nitrate concentration of ~14 ± 2 μmoles kg^{-1} and phosphate concentration of ~1.8 ± 0.2 μmoles kg^{-1} [*Codispoti et al.*, 2005]. The UHL is also transported off the shelf into the Canada Basin, and can be traced to the Eurasian Basin exits from the Arctic Ocean region [e.g., *Jones et al.*, 2003].

3. Methods

3.1. Sampling and Analyses

[11] Comprehensive sampling of seawater physical, biogeochemical and biological properties on the Chukchi and Beaufort Sea shelves and Canada Basin of the central Arctic Ocean were conducted from the icebreaker USCGC *Healy* during spring (HLY 02-01) and summer (HLY 02-03) cruises, as part of the 2002 field phase of the SBI project [*Grebmeier and Harvey*, 2005]. Forty and forty-five CTD/rosette stations were occupied during spring (5 May–15 June 2002) and summer (17 July–26 August 2002), respectively. Both cruises sampled at the Bering Strait, over the Chukchi and Beaufort Sea shelves, the shelf-slope region and into the central Arctic Ocean (Figure 1). Three sections, extending across the Chukchi and Beaufort Sea shelf and slope into the Arctic Ocean, were repeated each cruise, including: (1) West Hanna Shoal (WHS); (2) East Hanna Shoal (EHS) transect, and; (3) Barrow Canyon (BC) transect. In addition, during summer field activities, a fourth section East of Pt. Barrow (EBC), and a section extending from the Alaskan side of the Bering Strait to the Diomede Islands were also taken.

[12] At each CTD/rosette station, hydrocasts and rate measurements provided physical data, (e.g., salinity), inorganic nutrients (ammonium, nitrate, nitrite, phosphate, reactive silicon, and urea), dissolved oxygen [*Codispoti et al.*, 2005], in situ ^{14}C primary production [*Hill and Cota*, 2005], export production [*Moran et al.*, 2005], suspended particulate organic matter (sPOM [*Bates et al.*, 2005b]), dissolved organic matter [*Mathis et al.*, 2006], DIC and total alkalinity. CTD, bottle and rate data are available at the Joint Office for Science Support (JOSS) web site (http://www.joss.ucar.edu/sbi/), and archived at the National Snow and Ice Data Center (NSIDC;http://nsidc.org/).

[13] Seawater samples for DIC and total alkalinity were drawn from the Niskin samplers into precleaned ~300 mL borosilicate bottles, poisoned with $HgCl_2$ to halt biological activity, sealed, and returned to the Bermuda Biological Station For Research (BBSR) for analysis. DIC samples were analyzed using a highly precise (~0.025%; <0.5 μmoles kg^{-1}) gas extraction/coulometric detection system [*Bates et al.*, 1996, 1998; *Bates*, 2002; *Bates et al.*, 2005a]. Total alkalinity samples were analyzed using an automated potentiometric method with a precision of <~1 μmoles kg^{-1} and potential inaccuracy of ~0.1% (~2 μmoles kg^{-1}). Routine analyses of Certified Reference Materials (provided by A. G. Dickson, Scripps Institution of Oceanography) ensured that the accuracy of the DIC and TA measurements was 0.05% (~0.5 μmoles kg^{-1}) and 0.1% (~2 μmoles kg^{-1}) respectively.

[14] Seawater pCO$_2$ concentrations were calculated from DIC, TA, temperature and salinity data using the algebraic relationships given in *Peng et al.* [1987], the CO_2 solubility equations of *Weiss* [1974], and dissociation constants for carbonic acid (i.e., pK$_1$ and pK$_2$), borate [*Dickson*, 1990], phosphate[*Dickson and Goyet*, 1994]. The carbonic acid dissociation constants of *Mehrbach et al.* [1973] (as refit by *Dickson and Millero* [1987]) were used to determine seawater pCO$_2$, although other dissociation constants were also used [*Goyet and Poisson*, 1989; *Roy et al.*, 1993] (F. J. Millero et al., Dissociation constants of carbonic acid in seawater as a function of salinity and temperature, submitted to *Marine Chemistry,* 2006) (hereinafter referred to as Millero et al., submitted manuscript, 2006) to examine the potential inaccuracy of the seawater pCO$_2$ calculation. It should be noted that since the experimental determinations of carbonic acid dissociation constants [i.e., *Mehrbach et al.*, 1973; *Goyet and Poisson*, 1989; *Roy et al.*, 1993; Millero et al., submitted manuscript, 2006] had lower limits of −1°C or 0°C, equations governing pK$_1$ and pK$_2$ were extrapolated to temperatures colder than −1°C. The difference in calculated seawater pCO$_2$ between different pK$_1$ and pK$_2$ values was relatively small (<5 μatm) at temperatures less than 0°C. For example, seawater pCO$_2$ data were calculated using the carbonic acid dissociation constants of *Mehrbach et al.* [1973] (as refit by *Dickson and Millero* [1987]) and *Goyet and Poisson* [1989]. The majority of samples from the Chukchi Sea were collected from waters with a temperature range of ~−1.8°C to 0°C, and computed seawater pCO$_2$ was slightly higher for the carbonic acid dissociation constant of *Mehrbach et al.* [1973] compared to *Goyet and Poisson* [1989], with an average difference of ~2.5 μatm. The difference in calculated seawater pCO$_2$ was very small relative to the large ΔpCO$_2$ values observed in the region (−100 to −250 μatm). This, in turn, has minor impact on air-sea CO_2 fluxes. The difference between seawater pCO$_2$ computed from *Mehrbach et al.* [1973] and *Goyet and Poisson* [1989] pK$_1$ and pK$_2$ constants was higher (i.e., ~5–10 μatm) for the few samples collected in warmer waters (i.e., ~6–10°C in water at Bering Strait or in southernmost stations of the Chukchi Sea). Overall, the inaccuracy of seawater pCO$_2$ calculations was less than 10 μatm.

Table 1. Seasonal, Annual, and Geographic Net Air-to-Sea CO_2 Fluxes (Tg C) for the Chukchi Sea Bounded by the Areal Range of 65–75°N and 150–170°W (an Area of 595000 km^2)[a]

	Net Air-to-Sea CO_2 Fluxes, Tg C or 10^{12} g C
Annual and Seasonal	
Jan	−0.04
Feb	−0.06
Mar	−0.05
Apr	−0.04
May	−0.3
Jun	−1.7
Jul	−5.1
Aug	−11.2
Sep	−8.6
Oct	−7.3
Nov	−3.4
Dec	−0.2
May to Sep	−27.1 ± 7[b]
Annual	−38.1 ± 7[b]
Geographic(150°W–175°W)	
65.0°N–67.5°N (119800 km^2)	−3.2 ± 2[b]
67.5°N–70.0°N (225190 km^2)	−15.4 ± 2[b]
70.0°N–72.5°N (239300 km^2)	−12.4 ± 2[b]
72.5°N–75.0°N (217500 km^2)	−7.1 ± 2[b]

[a]Net air-to-sea CO_2 fluxes were calculated using NNR wind speed and $\Delta p CO_2$ data sets for each 2.5° by 2.5° area of the coastal sea. $\Delta p CO_2$ were determined from seawater pCO_2 data across the Chukchi and western Beaufort Sea shelves, and atmospheric pCO_2 data from Point Barrow Alaska (data from http://www.cmdl.noaa.gov). Steady/long-term wind speed k formulation (equation (3)) of *Wanninkhof* [1992]) was used in the calculation of CO_2 flux. Negative values denote CO_2 flux into the ocean.

[b]Details of the error calculation are given in the methods section.

3.2. Air-Sea CO_2 Gas Exchange Considerations

[15] The net air-sea CO_2 flux (F) was determined by the following formula:

$$F = k\, s(\Delta p\mathrm{CO_2}) \tag{1}$$

where k is the transfer velocity, s is the solubility of CO_2 and, ΔpCO_2 is the difference between atmospheric and oceanic partial pressures of CO_2. The ΔpCO_2, or air-sea CO_2 disequilibrium, sets the direction of CO_2 gas exchange while k determines the rate of air-sea CO_2 transfer. Here, gas transfer velocity-wind speed relationships for short-term and long-term wind conditions based on a quadratic (U^2) dependency between wind speed and k [i.e., *Wanninkhof*, 1992] were used to determine air-sea CO_2 fluxes:

$$k = 0.31\ U_{10}^2 (Sc/660)^{-0.5} [\text{steady/short} - \text{term wind}] \tag{2}$$

$$k = 0.39\ U_{10}^2 (Sc/660)^{-0.5} [\text{steady/long} - \text{term wind}] \tag{3}$$

where U_{10} is wind speed corrected to 10 metres, and Sc is the Schmidt number for CO_2. The Schmidt number was calculated using the equations of *Wanninkhof* [1992] and s (solubility of CO_2 per unit volume of seawater) was calculated from the observed temperature and salinity using the equations of *Weiss* [1974].

[16] The ΔpCO_2 data sets used here to estimate air-sea CO_2 fluxes were computed from seawater pCO_2 data across the Chukchi and western Beaufort Sea shelves, and atmospheric pCO_2 data from Point Barrow in Alaska. The atmospheric data was downloaded from http://www.cmdl.noaa.gov (National Oceanographic and Atmospheric Administration, NOAA, Climate and Meteorological Diagnostics Laboratory, CMDL), and corrected for water vapor pressure.

[17] Daily averaged 6-hourly wind speed data from the NCEP (National Centers for Environmental Prediction)/ NCAR (National Center for Atmospheric Research) reanalysis 2 data assimilation model was used to calculate k values (http://www.cdc.noaa.gov/cdc/data.ncep.html). NCEP/NCAR Reanalysis 2 (i.e., NNR) data were used rather than shipboard meteorological data reports in order to allow regional estimates of air-sea CO_2 fluxes to be made. The spatial resolution of the NNR data assimilation model is 2.5° by 2.5° (for example, 167.5°W–170°W, 70°N–72.5°N).

[18] In the Chukchi Sea, western Beaufort Sea and Arctic Ocean (i.e., Canada Basin), rates of air-sea CO_2 fluxes were determined at each CTD/rosette station. Net air-sea CO_2 fluxes were calculated using observed ΔpCO_2 data and k values (using equation (2) for short-term winds) calculated from mean daily NNR wind speed in the nearest 2.5° by 2.5° box for the duration of each relevant cruise (i.e., 5 May–15 June 2002 and 17 July–26 August 2002). Rates of net air-sea CO_2 flux were initially calculated assuming sea-ice free conditions (i.e., 0% sea-ice). It is assumed here that sea-ice provides an effective barrier to air-sea CO_2 gas exchange, and that air-sea CO_2 fluxes are a linear function of sea-ice coverage. Thus, air-sea CO_2 fluxes were corrected to observed sea-ice coverage (shipboard reports and satellite data;http://www.joss.ucar.edu/sbi/). For example, in sea-ice coverage conditions of 95%, 50%, and 0%, multipliers of 0.05, 0.5 and 1.00, respectively were applied to the air-sea CO_2 fluxes. In those regions with 100% sea-ice coverage, it is possible that air-sea CO_2 gas exchange can occur through leads and fractures in the ice, and also directly through sea-ice [*Semiletov et al.*, 2004]. In these regions, a multiplier of 0.01 (equivalent to 99% sea-ice cover) was used to allow for minor rates of air-sea CO_2 exchange through leads, fractures and brine channels [*Semiletov et al.*, 2004].

[19] Net air-sea CO_2 fluxes were also calculated for the Chukchi Sea bounded by the geographic range of 65–75°N, and 150–170°W (an area of 595000 km^2). Although the SBI cruises only spanned a four-month period (May to August), physical and biogeochemical observations captured the full seasonal range of wintertime (complete sea-ice coverage) to summertime (sea-ice minima) conditions. On the spring SBI cruise, mixed layer water had a very narrow range in temperature, salinity, and density across most of the Chukchi Sea. The physical data collected for the spring SBI cruise was also similar to wintertime data (i.e., December to May) collected from mooring locations at Bering Strait and across the Chukchi Sea slope [*Woodgate et al.*, 2005a, 2005b]. Mixed-layer DIC concentrations observed over most of the Chukchi Sea shelf and slope during the spring SBI cruise also had a small range, with the average salinity normalized DIC in the 0–30 m layer of 2357 ± 4 μmol kg^{-1} [*Bates et al.*, 2005a]. As such, spring DIC (and TA) data were chosen as representative of sea-ice covered, wintertime conditions and, seawater pCO_2 values

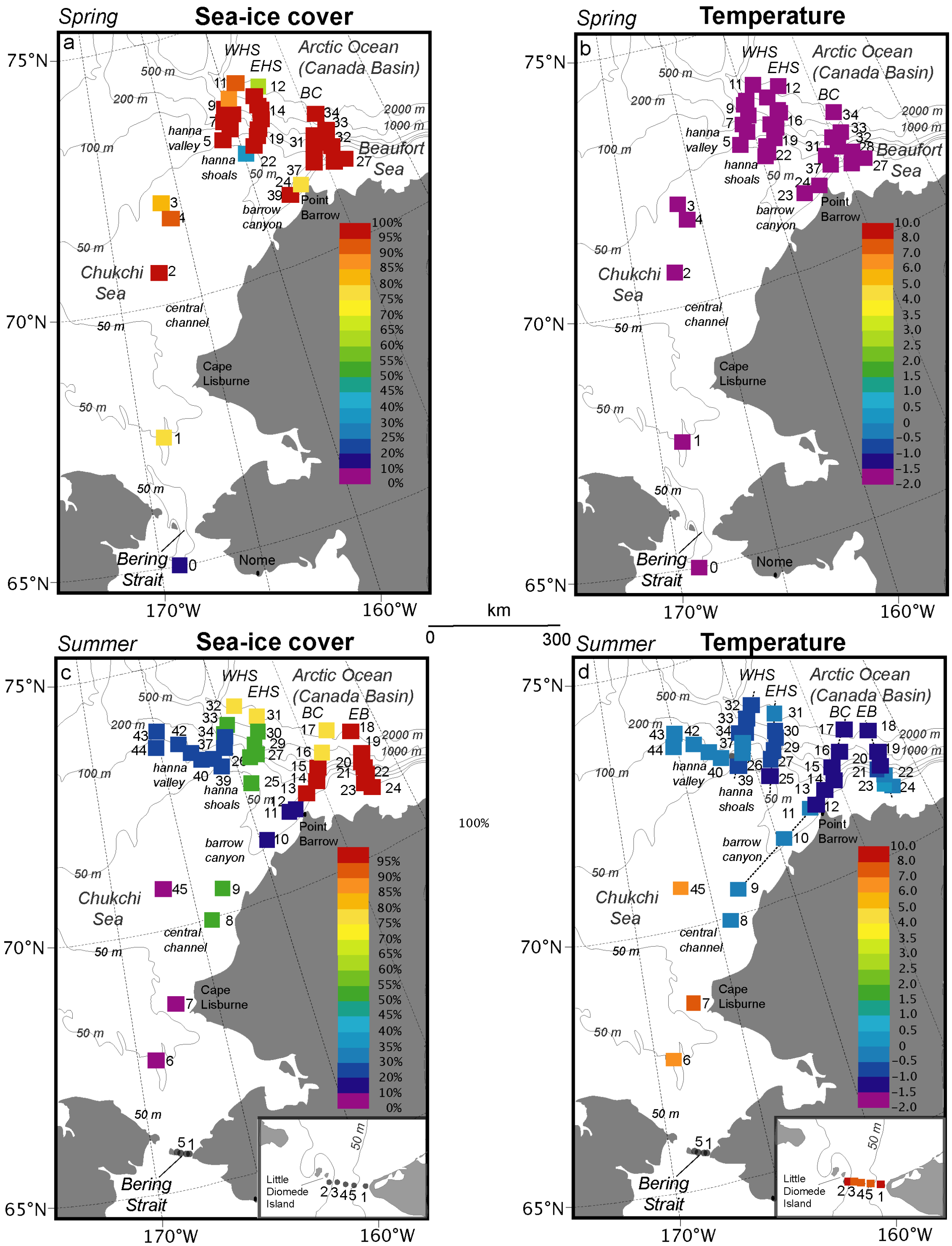

Figure 2. Sea-ice (% cover) and surface temperature (°C) distributions in the Chukchi Sea, Bering Strait, and western Beaufort Sea. (a) Springtime sea-ice cover distributions and (b) summertime sea-ice cover. Sea ice cover was determined from individual CTD/rosette stations reports, as well as remotely sensed sea-ice products (http://www.joss.ucar.edu/sbi). (c) Springtime surface temperature and (d) summertime surface temperature. Inset shows sea-ice cover and surface temperatures at Bering Strait.

were calculated for each 2.5° by 2.5° area of the Chukchi Sea region for the December to May period (Table 1). Seawater pCO_2 values observed in summertime (i.e., July and August; HLY 02-03 cruise) during the seasonal minima in sea-ice coverage (and after inorganic nutrient exhaustion) were chosen as representative of the seasonal minima in seawater pCO_2. Mean seawater pCO_2 values for each 2.5° by 2.5° area of the Chukchi Sea region was determined from station data or the nearest representative stations. At other times, during seasonal transitions (i.e., June to July, and September to November), seawater pCO$_2$ values were estimated using simple linear interpolation between wintertime and summertime conditions. Net air-sea CO_2 fluxes were thus calculated for each 2.5° by 2.5° area of the Chukchi Sea region in 2002 using monthly averaged seawater and atmospheric pCO$_2$ data (i.e., monthly values of ΔpCO$_2$) and NNR wind speed data. Average sea-ice coverage each month (from shipboard reports and satellite data composites; http://www.joss.ucar.edu/sbi/) for each 2.5° by 2.5° area of the Chukchi Sea region was used as multiplier to correct air-sea CO_2 fluxes for sea-ice cover. If an error of seawater pCO$_2$ data (e.g., 20 μatm higher) and wind speed (e.g., 0.2 m s^{-1} higher) is assumed, net annual air-sea CO_2 fluxes for the entire Chukchi Sea have an error of 7 Tg C yr^{-1} and 2 Tg C yr^{-1}, respectively. In addition, air-sea CO_2 gas exchange is allowed for during 100% sea-ice coverage by using a multiplier of 0.01 (equivalent to 99% sea-ice coverage). If no air-sea CO_2 gas exchange through 100% sea-ice coverage occurs, net annual air-sea CO_2 fluxes would be lower by ~0.04 Tg C yr^{-1}.

4. Results

4.1. Springtime Physical and Biogeochemical Distributions

[20] The seasonal physical and biological transformations on the Chukchi Sea and western part of Beaufort Sea shelves during the 2002 SBI field program are described in detail elsewhere [*Codispoti et al.*, 2005; *Bates et al.*, 2005a, 2005b]. During the springtime, sea-ice cover was high at >80–100% over much of the Chukchi Sea shelf (Figure 2a), except in the region of Bering Strait. Mixed layer and UHL temperatures (−1.8°C to −1.5°C; Figure 2c), and salinities (>32.5–33.2; Figure 3a) were confined to a small range in temperature and salinity space. TA concentrations ranged from ~2150–2350 μmoles kg^{-1}, with similar spatial gradients to surface salinity (Figure 3b). Nitrate (~10–15 μmoles kg^{-1}) and phosphate (~1.8 μmoles kg^{-1}) concentrations in the PML and UHL were fairly uniform across the Chukchi Sea shelf [*Codispoti et al.*, 2005; *Bates et al.*, 2005b], and similar to nutrient concentrations in the UHL measured at Bering Strait. Chlorophyll *a* concentration was also generally low (<0.8 μg L^{-1} [*Hill and Cota*, 2005]). In summary, across much of the Chukchi Sea shelf and slope regions, the physical properties of water present on the shelf did not appear to have been significantly transformed from wintertime conditions.

[21] During springtime, surface DIC concentrations across the Chukchi Sea shelf ranged from ~2100–2200 μmoles kg^{-1}, with concentrations decreasing northward into the Arctic Ocean basin (Figure 4a [*Bates et al.*, 2005a]). However, over the Chukchi Sea shelf, DIC corrected to a constant salinity (i.e., nDIC) had a very small range (~2200–2230 μmoles kg^{-1}; Figure 4c) at the surface. Furthermore, the mean nDIC concentration in the surface layer (0–30 m deep) also had a very small range of 2357 ± 4 μmoles kg^{-1}. The nDIC data is corrected to the mean salinity of the UHL (i.e., 33.1) from which the PML is modified, and it is assumed that normalizing DIC and TA data to a constant salinity does not introduce potential biases [*Friis et al.*, 2003]. The homogeneity of the nDIC data across the Chukchi Sea shelf, slope and Arctic Ocean basin also suggests that remnant winter waters were still present on the shelf during the springtime field survey.

[22] The springtime distributions of surface seawater pCO$_2$ showed distinct spatial variability. On the central Chukchi Sea shelf, seawater pCO$_2$ (~300–350 μatm; Figure 5a) values were slightly undersaturated with respect to atmospheric pCO$_2$ conditions (~370 ppm). Surface seawater pCO$_2$ values, however, decreased northward from the Chukchi Sea shelf and slope stations to the Arctic Ocean stations. At the Arctic Ocean stations under near perennial sea-ice cover, seawater pCO$_2$ values were highly undersaturated (~200–250 μatm; Figure 5a) with respect to atmospheric pCO$_2$ conditions.

4.2. Summertime Physical and Biogeochemical Distributions

[23] Two months later in August 2002, the physical and biological properties of the Chukchi Sea were transformed from springtime conditions. Seasonal sea-ice retreat had occurred, with most of the Chukchi Sea shelf sea-ice free. In the northern areas of the Chukchi Sea shelf, ~30–50% sea-ice coverage remained, with a higher sea-ice coverage (>80%) in the region of the Chukchi Sea slope, Beaufort Sea shelf and Arctic Ocean (Figure 2b). Seasonal warming of the surface layer was evident from the Bering Strait across the Chukchi Sea shelf to ~71°N (Figure 2d), with surface layer salinities highly variable (<10 to 32) due to sea-ice melt (Figure 3b). Surface total alkalinities were more variable compared to spring (Figure 3d), with low values (<1600 μmoles kg^{-1}) in areas of significant freshening due to sea-ice melt. The biological transformation was also evident, with inorganic nutrient concentrations exhausted, reduced to less than 0.2 μmoles kg^{-1} at all stations [*Codispoti et al.*, 2005; *Bates et al.*, 2005b]. Across much of the Chukchi Sea shelf (and western Beaufort Sea shelf), large concentrations of chlorophyll *a* were present, and high rates of in situ ^{14}C primary production and net community production (>0.3–2.8 g C m^2 d^{-1} [*Hill and Cota*, 2005; *Bates et al.*, 2005a]), high rates of vertical organic matter export [*Moran et al.*, 2005] and horizontal export of suspended particulate organic matter from the Chukchi Sea shelf into the Arctic Ocean [*Bates et al.*, 2005b] were observed.

[24] The summertime DIC distributions in the mixed layer of the Chukchi Sea were also transformed from springtime conditions. Surface DIC concentrations had a very wide range of concentrations (~526–1900 μmoles kg^{-1}) with the lowest values occurring at stations where large amounts of sea-ice melt have diluted DIC and salinity. The changes in nDIC between springtime and summer were used to estimate rates of net community production [*Bates et al.*, 2005a]. The highest rates of NCP (~1–2.8 g C m^2 d^{-1}) and in situ primary production [*Hill and Cota*, 2005] occurred on the shelf in the Barrow Canyon region of the Chukchi Sea and east of Point Barrow in the western Beaufort Sea. A total NCP rate of 20 x 10^{12} g C for the growing season (~120 d) in 2002 was estimated for the eastern Chukchi Sea shelf and slope region (area of 13.9 x 10^4 km^2 [*Bates et al.*, 2005a]). At the Arctic Ocean stations,

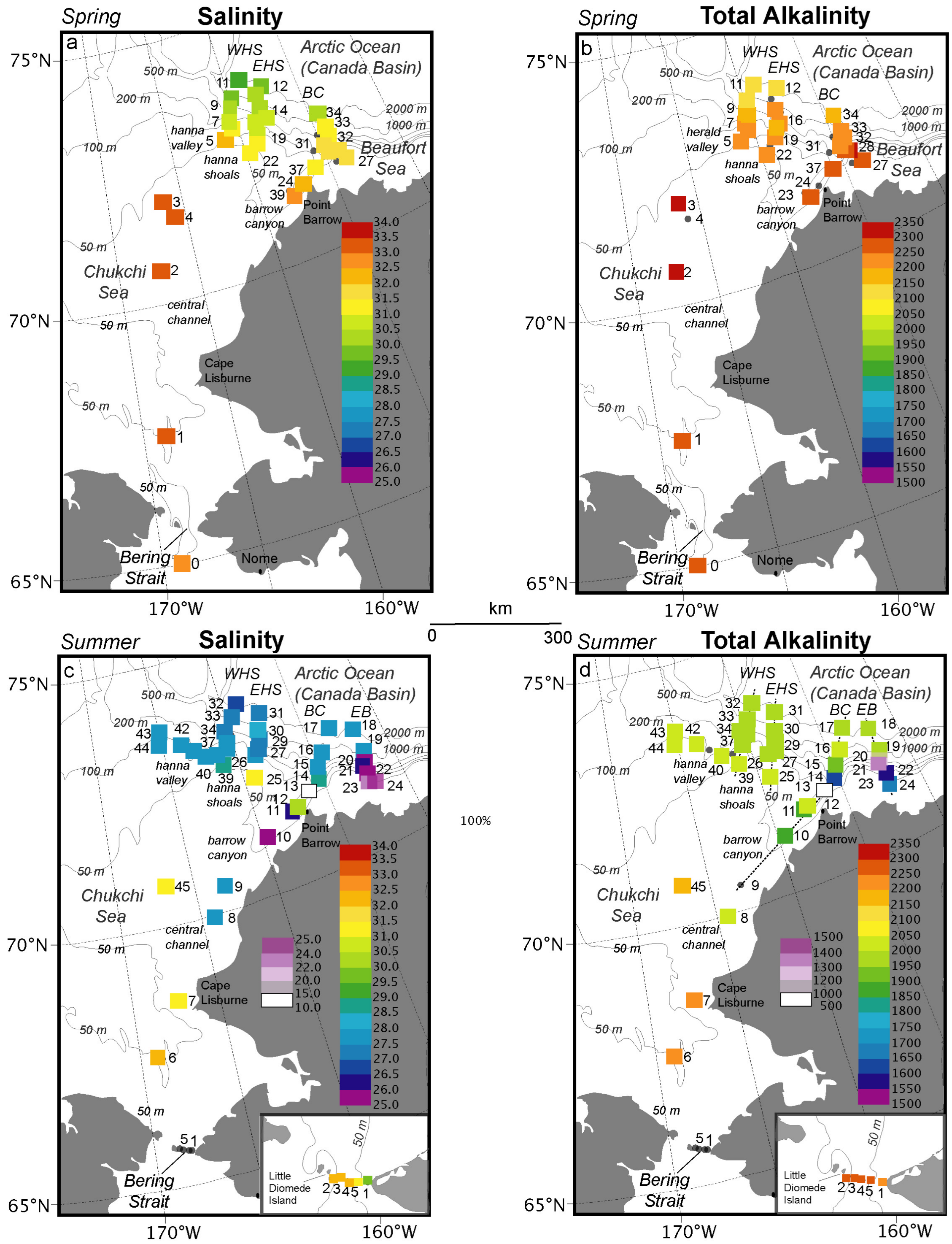

Figure 3. Surface salinity and total alkalinity (μmoles kg^{-1}) distributions in the Chukchi Sea, Bering Strait, and western Beaufort Sea. (a) Springtime surface salinity distributions and (b) summertime surface salinity distributions. (c) Springtime surface total alkalinity distributions and (d) summertime surface total alkalinity distributions. Inset shows surface salinity and alkalinity at Bering Strait.

DIC and nDIC concentrations remained almost constant between spring and summer, with NCP rates estimated to be very low ~0.015 +0.030 g C m^{-2} d^{-1}[*Bates et al.*, 2005a], similar to previous studies [e.g., *English*, 1961; *Moran et al.*, 1997; *Anderson and Kaltin*, 2001].

[25] There were also large changes in seawater pCO_2 conditions on the Chukchi Sea shelf. By summer (July–August), low pCO_2 conditions (<150 μatm) were observed in the surface of the PML in the Barrow Canyon region of the Chukchi Sea shelf and western Beaufort Sea shelf

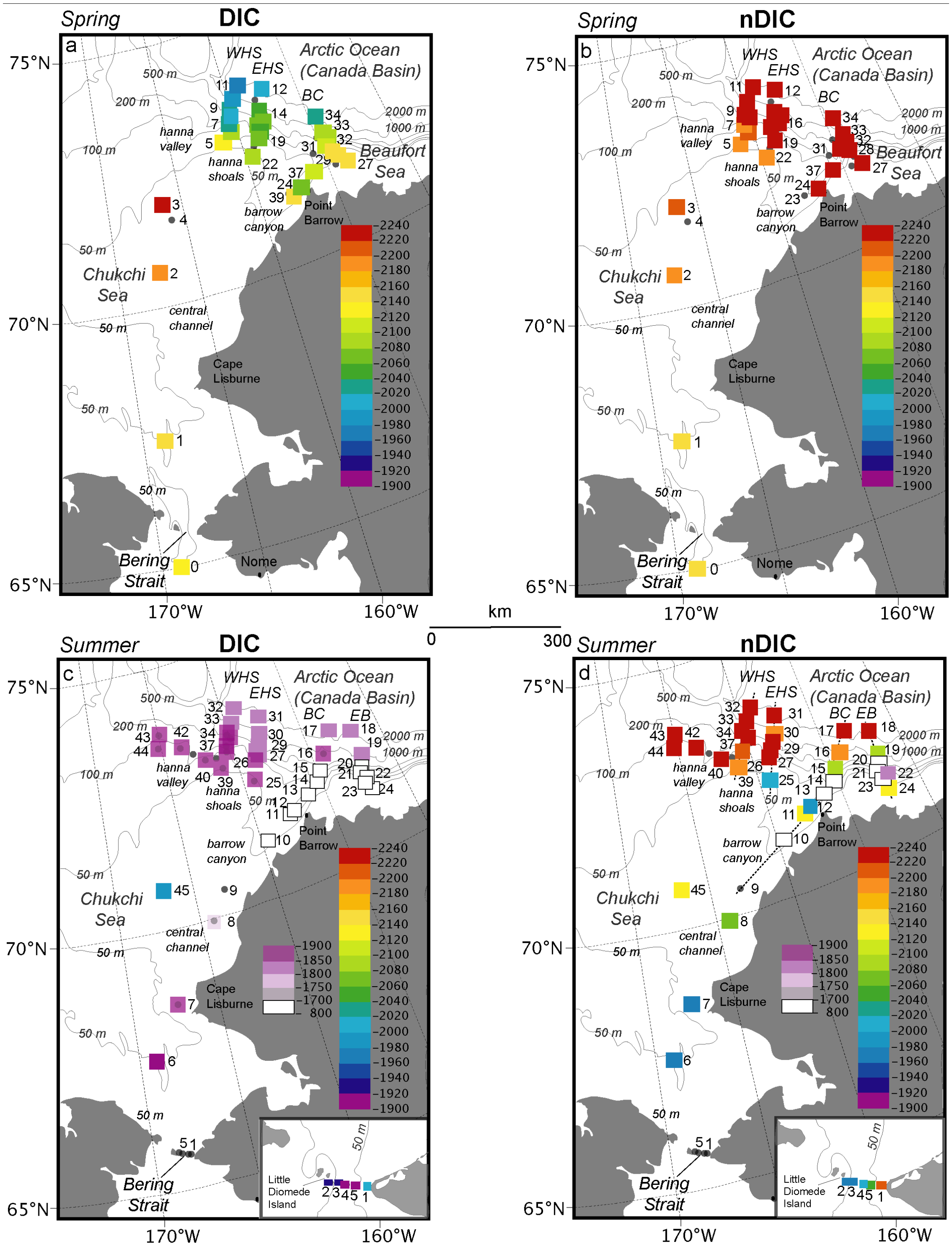

Figure 4. Surface dissolved inorganic carbon (DIC; μmoles kg^{-1}) and salinity normalized DIC (nDIC; μmoles kg^{-1}) distributions in the Chukchi Sea, Bering Strait, and western Beaufort Sea. (a) Springtime surface DIC distributions and (b) summertime surface DIC distributions. (c) Springtime surface nDIC distributions and (d) summertime surface nDIC distributions. The nDIC data were normalized to a salinity of 33.1, the core salinity value of the underlying upper halocline layer (UHL). Inset shows surface DIC and nDIC at Bering Strait.

(Figure 5b). The low pCO_2 conditions occurred in regions where there was, for example: (1) intense pelagic and benthic production [*Hill and Cota*, 2005; *Bates et al.*, 2005a]; (2) complete depletion of inorganic nutrients and large drawdown of DIC (~100–200 μmoles kg^{-1} [*Bates et al.*, 2005a]); (3) production and export of organic matter [*Bates et al.*, 2005b; *Moran et al.*, 2005; *Mathis et al.*, 2006] and, large increases in phytoplankton [*Hill and Cota*, 2005]

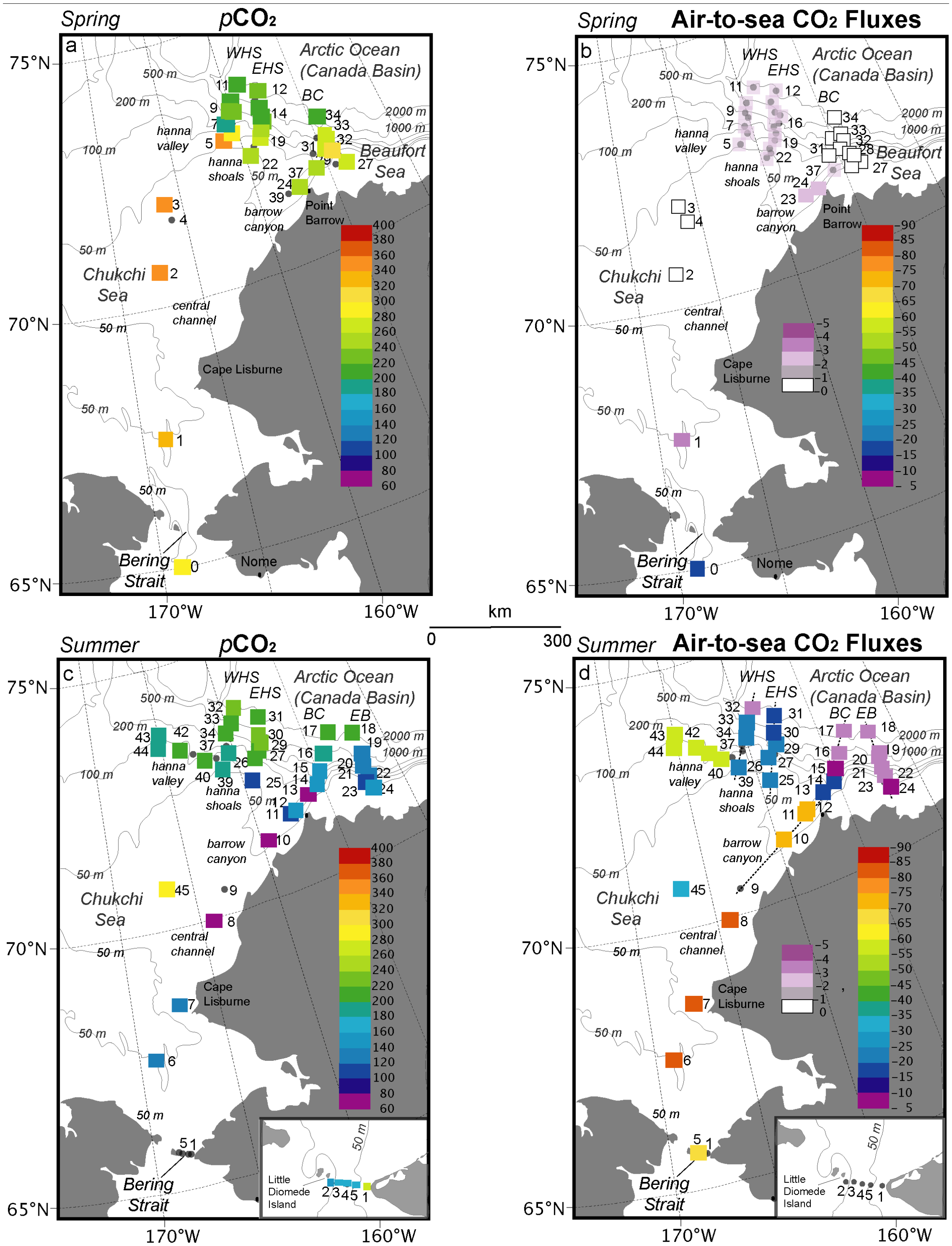

Figure 5. Surface seawater pCO_2 (μatm) and mean air-to-sea CO_2 flux (mmoles CO_2 m^{-2} d^{-1}) distributions in the Chukchi Sea, Bering Strait, and western Beaufort Sea. (a) Springtime surface seawater pCO_2 distributions and (b) summertime surface seawater pCO_2 distributions. (c) Springtime air-to-sea CO_2 flux and (d) summertime air-to-sea CO_2 flux.

and zooplankton biomass [*Ashjian et al.*, 2005]. Extremely low pCO_2 conditions (<100 μatm) were observed in the upper 5 m of the PML in the Beaufort Sea shelf in a region of mixing between Mackenzie River runoff, PML waters and sea-ice melt. Vertically, these regions were highly stratified with seawater pCO_2 increasing with depth.

[26] The data reported here represent the first seawater pCO_2 observations during the early growing season (i.e., May and June) and summer season (July and August).

However, the SBI field survey in 2002 did not sample during the month of September before surface freezing and sea-ice advance in early October. In previous studies, *Pipko et al.* [2002] and *Murata and Takizawa* [2003] surveyed the Chukchi Sea in September, and a composite view of seasonality on the Chukchi Sea emerges. In 1996, *Pipko et al.* [2002] found seawater pCO_2 values (calculated from pH and total alkalinity) of ~280–320 μatm from the Central Channel west of Cape Lisburne to Barrow Canyon. Along the same track, *Murata and Takizawa* [2003] found similar seawater pCO_2 values (~290–350 μatm) in 1998. Subsequently, *Murata and Takizawa* [2003] observed low seawater pCO_2 conditions in 1999 (~240–280 μatm) and 2000 (~180–220 μatm), similar to the 2002 SBI observations. Thus, during period before surface freezing and return of sea-ice cover, seawater pCO_2 conditions remained highly undersaturated with respect to the atmosphere.

[27] The late season increase in seawater pCO_2 conditions from summertime minima likely reflects the net balance of organic matter remineralization (including benthic OM respiration), air to sea CO_2 gas exchange and temperature changes. The first two processes add CO_2 to the surface layer, increasing seawater pCO_2, while temperature changes act to decrease seawater pCO_2. In the fall period (during sea-ice advance), surface layer waters in the Chukchi Sea shelf, slope and Arctic Ocean region would have cooled from summertime values (~−0.5°C to +0.5°C) to wintertime values of ~−1.5–1.7°C. Assuming that the thermodynamic influence of temperature on seawater pCO_2 is ~4.2% °C^{-1} [i.e., *Takahashi et al.*, 1993], the average cooling of surface water by ~2°C would have decreased seawater pCO_2 by ~15 μatm, opposite in direction to the additions from OM remineralization and air to sea CO_2 gas exchange.

[28] In the adjacent slope and Arctic Ocean basin, surface seawater pCO_2 had a small seasonal range (Figure 3a; May to September; ~200–275 μatm). *Pipko et al.* [2002] and *Murata and Takizawa* [2003] also surveyed along the sea-ice edge of the Beaufort Sea during the month of September (~150–160°W, 72–74°N), finding seawater pCO_2 values of ~160–280 μatm, in the same range as observed on the SBI 2002 field survey. Combined, these observations suggest that the sea-ice covered surface waters of the Arctic Ocean (specifically the Canada Basin) remain perennially undersaturated with respect to CO_2 in the atmosphere.

4.3. Air-to-Sea CO_2 Fluxes on the Chukchi Sea and Western Beaufort Sea Shelves

[29] Across the Chukchi Sea and western Beaufort Sea, the ΔpCO_2 values in both seasons were negative (i.e., seawater pCO_2 conditions undersaturated compared to atmospheric pCO_2). Thus, the direction of CO_2 gas exchange in the region was uniformly from air to sea. Distinct spatiotemporal distributions of air-to-sea CO_2 flux were observed on the Chukchi Sea and western Beaufort Sea shelves.

[30] In springtime, sea-ice coverage at each CTD/rosette station was typically 100% and an effective barrier to air-sea CO_2 gas exchange. If minor air-sea gas exchange is allowed for through leads and fractures in the sea-ice, rates of air to sea CO_2 gas exchange in most areas were very low (<0.1 to 1 mmol CO_2 m^{-2} d^{-1}; Figure 5c) despite seawater pCO_2 levels being undersaturated (ΔpCO_2 values of −50 to −150 μatm). Only in the region of Bering Strait were air-to-sea CO_2 fluxes >4 mmol CO_2 m^{-2} d^{-1} due to sea-ice retreat and early break up of sea-ice.

[31] By summertime, much of the Chukchi Sea shelf was sea-ice free and seawater pCO_2 was highly undersaturated with respect to the atmosphere (ΔpCO_2 values of −50 to −150 μatm), particularly in those regions with very low (~80–150 μatm) seawater pCO_2 levels due to intense primary production [e.g., *Hill and Cota*, 2005; *Bates et al.*, 2005a]. In the Central Channel (east of Herald Shoals), Hanna Valley and Barrow Canyon regions, air-to-sea CO_2 fluxes were very high, ranging from ~30–90 mmol CO_2 m^{-2} d^{-1}(Figure 5d). In contrast, air-to-sea CO_2 fluxes remained low (<0.1–2 mmoles CO_2 m^{-2} d^{-1}) in regions of the Chukchi Sea slope, Arctic Ocean basin, and western Beaufort Sea stations where sea-ice coverage remained high (>80%).

5. Discussion

5.1. Comparison of Air-Sea CO_2 Fluxes for the Chukchi Sea and Other Polar Shelves

[32] There have been few studies of the spatiotemporal pCO_2 distributions and air-sea CO_2 fluxes in the Arctic Ocean and adjacent shelves. Early studies focused on the Barents and Kara Seas [*Kelley*, 1970], and the sub-polar Bering Sea [*Kelley and Hood*, 1971; *Park et al.*, 1974; *Codispoti et al.*, 1982, 1986; *Anderson et al.*, 1990; *Chen*, 1993]. These and recent studies of the Laptev, East Siberian and Chukchi Seas [*Semiletov*, 1999; *Pipko et al.*, 2002; *Murata and Takizawa*, 2003; *Bates et al.*, 2005a] have shown large seasonal drawdown of CO_2 associated with seasonal ice retreat across the shelves adjacent to the Arctic Ocean. All these studies imply that the Arctic Ocean and adjacent continental shelves are sinks for atmospheric CO_2.

[33] Previous estimates of the net oceanic CO_2 sink in the Arctic Ocean and adjacent shelves (excluding the Bering Sea) have relied on indirect mass balance considerations rather than direct air-to-sea CO_2 flux considerations. Early estimates of the net oceanic CO_2 sink for the Arctic Ocean (and adjacent shelves) ranged from 70 to 120 Tg C yr^{-1} [*Anderson et al.*, 1990, 1994; *Lundberg and Haugen*, 1996] (note that the latter paper included the Norwegian Sea). More recently, *Anderson et al.* [1998b] revised the flux estimate downward to 24 ± 18 Tg C yr^{-1}. In the Barents Sea, the annual estimate of atmospheric CO_2 uptake into the ocean has been estimated at ~9 Tg C year^{-1} [*Fransson et al.*, 2001; *Kaltin et al.*, 2002], who revised the Arctic Ocean air-to-sea CO_2 flux upwards slightly to ~31 Tg C year^{-1}. All these annual rates of net air-to-sea CO_2 flux have considerable uncertainty due to the mass balance approaches used.

[34] In this study, the mean air-to-sea CO_2 flux at stations on the Chukchi Sea shelf was 40 ± 10 mmol CO_2 m^{-2} d^{-1}. If this flux rate is extrapolated to the entire Chukchi Sea (i.e., 595000 km^2), net air-sea CO_2 flux during the sea-ice free period (~100 d) was 29 ± 8 Tg C. Since sea-ice provides an effective barrier to gas exchange during the rest of the year, this rate is also equivalent to an annual flux. Alternatively, if air-sea CO_2 fluxes are estimated for each

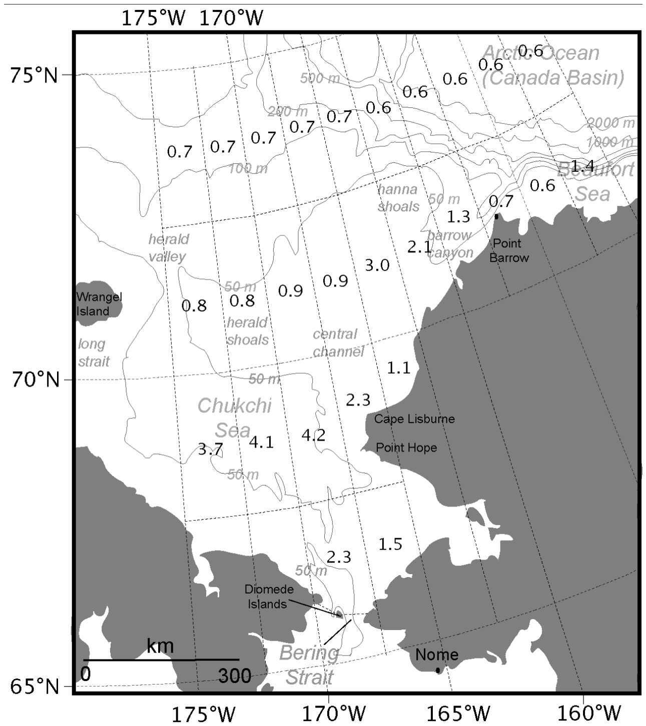

Figure 6. Mean annual air-to-sea CO_2 flux (Tg C yr^{-1}) for each 2.5° by 2.5° areas of the Chukchi Sea within the area 65–75°N, 150–175°W.

2.5° by 2.5° using monthly averaged seawater pCO_2 and daily wind speed data, the net air-to-sea CO_2 flux for the Chukchi Sea (the region bounded by 150°W to 170°W, and 65°N to 75°N) for the May to September period was 27 ± 6 Tg C (Table 1 and Figure 6). The highest net air-to-sea CO_2 flux occurred during August and September during the sea-ice coverage minima and lowest seawater pCO_2 conditions. For example, for the month of September, a net air-to-sea CO_2 flux of 8.6 Tg C is calculated here compared to the *Pipko et al.* [2002] estimate of ~2 Tg C during September 1996. Since then, late season surface pCO_2 conditions appear to have decreased (1998–2000 [*Murata and Takizawa*, 2003]), with areas of lowest undersaturated waters (seawater pCO_2 values of 120–250 μatm) observed during the summertime 2002 SBI field survey.

[35] The annual flux of CO_2 (for 2002) can be calculated for the Chukchi Sea. If wintertime months are included in the estimate of CO_2 flux (i.e., January to April; October–December), the annual net air-to-sea CO_2 flux for the Chukchi Sea was 38 ± 7 Tg C yr^{-1} (Table 2). This compares to the mass balance estimate of net air-to-sea CO_2 flux of 22 and 31 ± 18 Tg C yr^{-1} calculated for the Chukchi Sea [*Kaltin and Anderson*, 2005] and Arctic Ocean basin [*Fransson et al.*, 2001] and adjacent seas [*Anderson et al.*, 1998a]. More recently, mass balance calculations indicate a 9 Tg C yr^{-1} oceanic sink for atmospheric CO_2 in the Barents Sea [*Fransson et al.*, 2001]. Scaling these mass balance estimates to the Arctic Ocean and adjacent seas yields an annual net air-to-sea CO_2 flux estimate of ~31 Tg C yr^{-1} (Table 2). This mass balance approach yields a small oceanic sink for CO_2 in the Chukchi Sea (~3.8 Tg C yr^{-1}) compared to estimates (i.e., 38 ± 7 Tg C yr^{-1}) reported by direct means here. If rates of air-to-sea CO_2 flux for the Chukchi Sea (this study) are combined with mass balance estimates [*Anderson et al.*, 1998a, 1998b; *Fransson et al.*, 2001] for other adjacent Arctic Ocean seas, the annual oceanic sink for CO_2 is ~66 Tg C yr^{-1}(Table 2). Additionally, if minor rates of CO_2 gas exchange (e.g., 0.2 mmoles CO_2 d^{-1}) occur within the perennially sea-ice covered Arctic Ocean basin, the annual rate increases by 5 Tg C yr^{-1}.

Table 2. Annual Net Air-to-Sea CO_2 Fluxes (Tg C) for the Arctic Ocean (Including Adjacent Continental Shelves), Chukchi Sea, and Other Adjacent Continental Shelves (i.e., Barents, Laptev, Kara, East Siberian, and Beaufort Seas)[a]

Region	Area, km^2	Net Air-to-Sea CO_2 Fluxes, Tg C or 10^{12} g C A	B	C	Reference
		Arctic Ocean(Including Adjacent Coastal Seas)			
Arctic Ocean	~10,720,000	24[b]	-	-	*Anderson et al.* [1998b]
Arctic Ocean	~10,720,000	-	31[b,c]	-	Previous studies modified here
Arctic Ocean	~10,720,000	-	-	66[b,d]	This study
		Coastal Seas Adjacent to the Arctic Ocean			
Barents Sea	1,400,000	9[b]	9[b,c]	9[b]	*Fransson et al.* [2001]
Laptev Sea	672,000	-	4.3[b,c]	4.3[b,c]	Previous studies modified here
Kara Sea	880,000	-	5.7[b,c]	5.7[b,c]	Previous studies modified here
East Siberian Sea	924,000	-	5.9[b,c]	5.9[b,c]	Previous studies modified here
Chukchi Sea	595,000	-	22[b]	-	*Kaltin and Anderson* [2005]
Chukchi Sea	595,000	-	3.8[b,c]	38.1[d]	This study
Chukchi Sea	595,000	-	-	34.8[e]	This study
Beaufort Sea	450,000	-	2.9[b,c]	2.9[b,c]	Previous studies modified here

[a]A, Annual Arctic Ocean and adjacent sea CO_2 flux estimates from previous studies are given. B, Annual Arctic Ocean and adjacent sea CO_2 flux estimates are scaled to the Arctic Ocean and adjacent seas using the areas for each coastal sea and fluxes from the previous studies of *Anderson et al.* [1998a, 1998b] and *Fransson et al.* [2001]. C, Annual Arctic Ocean CO_2 flux estimates compiled from direct (this study) and mass balance considerations.

[b]Indirect estimate of net air-to-sea CO_2 fluxes from mass balance considerations.

[c]Indirect estimate of net air-to-sea CO_2 fluxes from mass balance considerations modified in this study from *Anderson et al.* [1998a, 1998b] and *Fransson et al.* [2001].

[d]Direct estimate of CO_2 flux from seawater pCO_2 observations with a spatial resolution of 2.5° by 2.5°.

[e]Direct estimate of CO_2 flux extrapolated from a mean net air-to-sea CO_2 fluxes of 40 ± 10 mmol CO_2 m^{-2} d^{-1} to the entire Chukchi Sea assuming a sea-ice free period of 120 d. If this flux rate is extrapolated to the entire Chukchi Sea (i.e., 595000 km^2), net air-sea CO_2 flux during the sea-ice free period (~120 d) was 29 ± 8 Tg C.

[36] Unlike the Chukchi Sea, which appears to be a perennial ocean CO_2 sink, the adjacent and upstream Bering Sea appears to seasonally oscillate between CO_2 sink and source status. As with the Chukchi Sea, physical processes and seasonal sea ice cover play a major role in shaping the Bering Sea ecosystem [e.g., *McRoy and Goering*, 1974; *Walsh and Dieterle*, 1994; *Walsh et al.*, 1996; *Grebmeier and Whitledge*, 1996; *Wyllie-Echeverria and Ohtani*, 1999; *Stabeno et al.*, 2001, 2002]. During the winter, sea-ice cover covers much of the Bering shelf area, but the advance is constrained by the presence of relatively warm water in the central and southern Bering Sea. The extent of sea-ice cover and ecosystem structure undergoes significant interannual changes or regime shifts [e.g., *Stabeno et al.*, 2001; *Macklin et al.*, 2002; *Hunt et al.*, 2002] that appear related to interannual changes in the low-frequency modes of the atmosphere. There are large gradients in primary production and pelagic (and benthic) biomass between the "Green belt" of the shelf [*Springer et al.*, 1996; *Springer and McRoy*, 1993] and oceanic basin [*Kinder and Coachman*, 1978]. In contrast, the open ocean domain of the Bering Sea has been described as a high nutrient, low chlorophyll (HNLC) region [*Banse and English*, 1999].

[37] Knowledge about the spatiotemporal variability of CO_2 species and air-sea CO_2 fluxes in the Bering Sea (particularly the continental shelf region) are poorly known and contradictory. The high levels of primary production observed in the southeastern Bering Sea result in drawdown of inorganic nutrients and DIC [*Codispoti et al.*, 1982, 1986]. From a very limited pCO_2 data set, the extrapolated seawater pCO_2 climatology (4° by 4° resolution) compiled by *Takahashi et al.* [2002] also shows supersaturated pCO_2 conditions in February in the open-ocean and continental shelf of the Bering Sea. Subsequently, undersaturated pCO_2 conditions (due to biological drawdown) are shown for the summer period and the Bering Sea (open-ocean and coastal ocean) is inferred to be a net sink for atmospheric CO_2. There appears to be a seasonal oscillation in the sink and source conditions in the Bering Sea. *Chen et al.* [2004] suggested that the open ocean of the Bering Sea is a net oceanic sink of CO_2. *Walsh and Dieterle* [1994] calculated a mean invasion of CO_2 of 4.3 mol m^{-2} yr^{-1}. Scaling this value to the Bering Sea yields a net annual oceanic sink of $\sim$57 Tg C yr^{-1}, similar in magnitude to the Chukchi Sea. A further complication to understanding the source-sink status of the Bering Sea is the recent observations by *Murata and Takizawa* [2002] of elevated pCO_2 conditions (>400 μatm) and total alkalinity drawdown in coccolithophore blooms (*E. Huxleyi*) of the Bering Sea in 2000. These widespread coccolithophore blooms have only occurred since 1997 [e.g., *Overland et al.*, 2001; *Napp and Hunt*, 2001] with the implication that the spatiotemporal distributions of CO_2 and possibly the CO_2 sink-source status of the Bering Sea is changing in concert with the observed ecosystem regime shifts.

5.2. A Continental Shelf Pump for CO_2 in the Chukchi Sea

5.2.1. Carbon Dynamics of Coastal Systems

[38] A few other regions of the global coastal ocean have been reasonably well studied for CO_2 dynamics, including the west European shelves [e.g., *Hoppema*, 1991; *Kempe and Peglar*, 1991; *Frankignoulle et al.*, 1998; *Borges and Frankignoulle*, 1999; *Frankignoulle and Borges*, 2001; *Borges and Frankignoulle*, 2002a, 2002b, 2003; *Thomas et al.*, 2004; *Bozec et al.*, 2005], the Middle Atlantic Bight [e.g., *Boehme et al.*, 1998; *Bates and Hansell*, 1999; *DeGrandpre et al.*, 2002] and South Atlantic Bight of the eastern U.S. [*Cai et al.*, 2003], the East China Sea [e.g., *Tsunogai et al.*, 1999; *Liu et al.*, 2000; *Wang et al.*, 2000], upwelling regions (where continental margin processes extend out into the open ocean [e.g., *Goyet et al.*, 1998; *Friederich et al.*, 2002; *Sarma*, 2003; *Torres et al.*, 2003; *Hales et al.*, 2005]), and polar polynyas [e.g., *Yager et al.*, 1995; *Bates et al.*, 1998; *Sweeney et al.*, 2000; *Sweeney*, 2003]. These studies have shown a large range of seawater pCO_2 concentrations (<100–>900 μatm), reflecting the complex biological, physical and climatic factors that influence the seawater pCO_2 in the coastal ocean. These factors include: (1) temperature; (2) balance of precipitation and evaporation (e.g., salinity changes); (3) net balance of photosynthetic CO_2 fixation and respiration of OM; (4) air-sea CO_2 gas exchange; (5) coastal upwelling of remineralized CO_2; (6) riverine inputs of terrestrial OM and alkalinity (7) $CaCO_3$ production, and; (8) horizontal and vertical exchange driven by physical factors operating over a variety of time and space scales. In the polar seas, sea-ice formation [*Anderson et al.*, 2004] and melting, and sea-ice capping of air-sea CO_2 gas exchange also have influence. In the nearshore coastal systems, such as coral reefs and mangroves, $CaCO_3$ precipitation increases pCO_2 [e.g., *Ware et al.*, 1992; *Bates et al.*, 2001; *Bates*, 2002; *Borges et al.*, 2005] and water residence times play an important role in dictating the net metabolism of the ecosystem. The dominance of one or two of the above multitude of factors can drive the metabolism of the coastal ocean either to net autotrophy or net heterotrophy, and either to a sink or source of CO_2.

[39] In upwelling regions, the CO_2 sink or source term can be highly variable. For example, vertical transport of remineralized inorganic nutrients (and CO_2) to the surface can support high levels of primary production and drawdown of pCO_2 significantly below equilibrium with the atmosphere [e.g., *Pérez et al.*, 1999; *van Geen et al.*, 2000; *Borges and Frankignoulle*, 2001; *Friederich et al.*, 2002]. However, in the Arabian Sea, pCO_2 conditions remain above or close to atmospheric values and portions of the coastal and central Arabian Sea are thought to be a perennial source of CO_2 to the atmosphere [*Körtzinger et al.*, 1997; *Goyet et al.*, 1998; *Sarma*, 2003]. In this region, *Ducklow and McAllister* [2005] have suggested that upwelling of remineralized CO_2 is not fully compensated for by primary production (or net community production) thereby driving the system to a CO_2 source. The variability in CO_2 sink or source conditions of upwelling regions may also relate to differences in the carbon, nitrogen and phosphorus stoichiometry of upwelled waters.

[40] In the East China Sea [*Tsunogai et al.*, 1999; *Wang et al.*, 2000; *Liu et al.*, 2000] and parts of west European shelves (e.g., northern North Sea [*Thomas et al.*, 2004; *Bozec et al.*, 2005]), seawater pCO_2 concentrations remain below atmospheric CO_2 values for most of the year. These continental shelves are net sinks for atmospheric CO_2 [e.g., *Tsunogai et al.*, 1999; *Wang et al.*, 2000; *Borges and

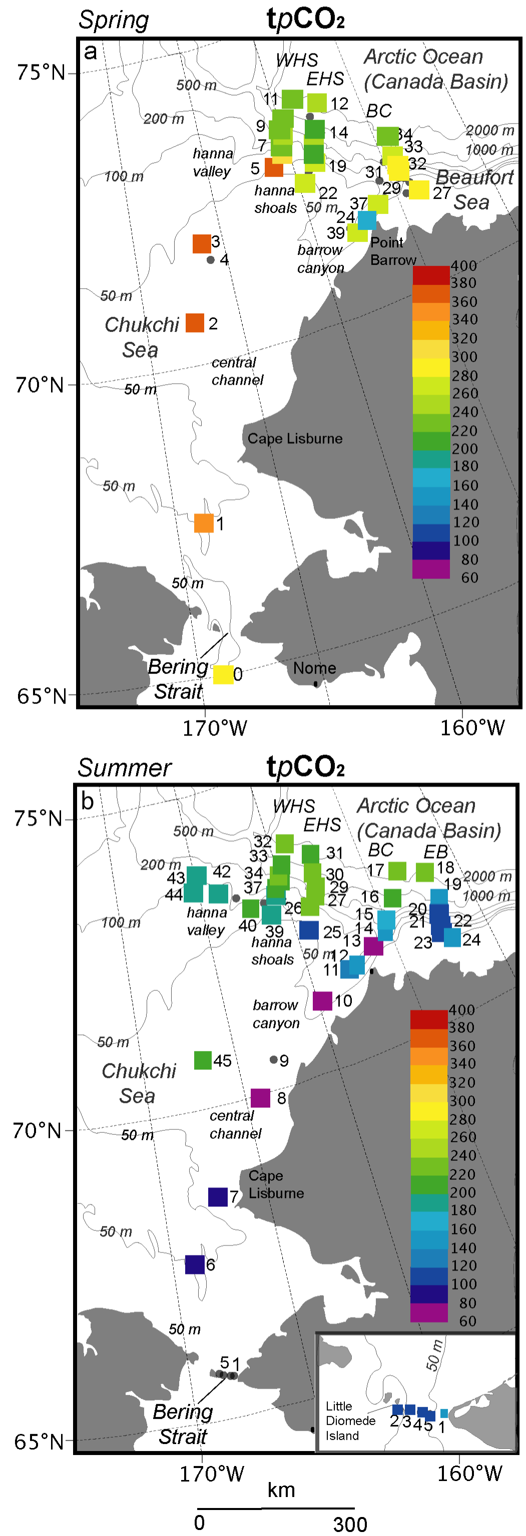

Figure 7. Surface temperature corrected seawater pCO_2 (i.e., $tpCO_2$) in (μatm) and mean air-to-sea CO_2 flux (mmoles CO_2 m^{-2} d^{-1}) distributions in the Chukchi Sea, Bering Strait, and western Beaufort Sea. (a) Springtime surface seawater pCO_2 distributions and (b) summertime surface seawater pCO_2 distributions. Seawater pCO_2 (μatm) was corrected to a temperature of 0°C using a temperature-pCO_2 relationship of 4.21% change in pCO_2 $°C^{-1}$ [*Takahashi et al.*, 1993].

Frankignoulle, 1999; *Thomas et al.*, 2004; *Bozec et al.*, 2005]. *Tsunogai et al.* [1999] suggested that a "continental shelf pump" of carbon from the shelf maintained oceanic CO_2 sink conditions. In this scenario, winter cooling on the shelf depressed seawater pCO_2 below saturation. During the subsequent summertime, inorganic nutrient supply, continued CO_2 drawdown in the summer due to primary production, and the subsequent vertical export of organic matter and lateral export of DIC maintain the CO_2 sink status of the shelf throughout the year. Not all continental shelves act in this manner, for example, in the Middle Atlantic Bight, thermally driven increase in pCO_2 during summertime appears not to be compensated for by sufficient nutrient input and primary production [*DeGrandpre et al.*, 2002]. This continental shelf region acts as a weak sink for CO_2 due to the seasonal oscillation driven by winter cooling (undersaturated pCO_2 conditions) and summertime heating (oversaturated pCO_2 conditions) rather than primary production and remineralization.

[41] In the polar seas, *Yager et al.* [1995] put forward the "seasonal rectification hypothesis" to explain seasonal pCO_2 variability in the North East Water (NEW) polynya. There is a brief but large pCO_2 drawdown in the NEW polynya in response to local primary production during the ice-free periods of summertime. During the remainder of the year, *Yager et al.* [1995] suggested that the sea-ice cover prevented gas exchange, thereby allowing wintertime rectification of seawater pCO_2 to near equilibrium values through remineralization of OM produced earlier in the season. Air-sea CO_2 gas exchange may, however, contribute to rectification since there is the potential for CO_2 gas exchange through leads, fractures, and brine channels within sea-ice [*Semiletov*, 1999].

5.2.2. Carbon Dynamics of the Chukchi Sea

[42] In the Chukchi Sea, surface waters are undersaturated with respect to CO_2 in the atmosphere during sea-ice cover and the brief seasonal sea-ice free period (Figure 5). The dominant processes maintaining the Chukchi Sea shelf as a perennial oceanic CO_2 sink relate to factors such as the northward transport of water, seasonal cooling, warming and sea-ice cover, and very high rates of seasonal primary and net community production during the brief, summertime exposure of nutrient-laden surface waters of Pacific Ocean origin.

[43] The northward transport (~0.8 Sv) of Pacific Ocean water from the Bering Sea through Bering Strait clearly acts to precondition the Chukchi Sea by providing inorganic nutrients that the pelagic plankton communities utilize during seasonally suitable light and sea-ice free conditions. Water mass transit times from Bering Strait to the northern margins of the Chukchi Sea are approximately 3–6 months [*Woodgate et al.*, 2005a, 2005b], with waters of the Chukchi Sea shelf renewed and replenished from the Bering Sea each year (note that there are minor exchanges with the East Siberian Sea and Canada Basin). Limited knowledge about CO_2 dynamics in the Bering Sea makes it difficult to assess how the Bering Sea preconditions the Chukchi Sea. The SBI data from Bering Strait suggests that surface waters transiting into the Chukchi Sea are undersaturated with respect to the atmosphere. The seawater pCO_2 climatology maps of *Takahashi et al.* [2002] also suggest that surface waters in the northern Bering Sea are undersaturated with

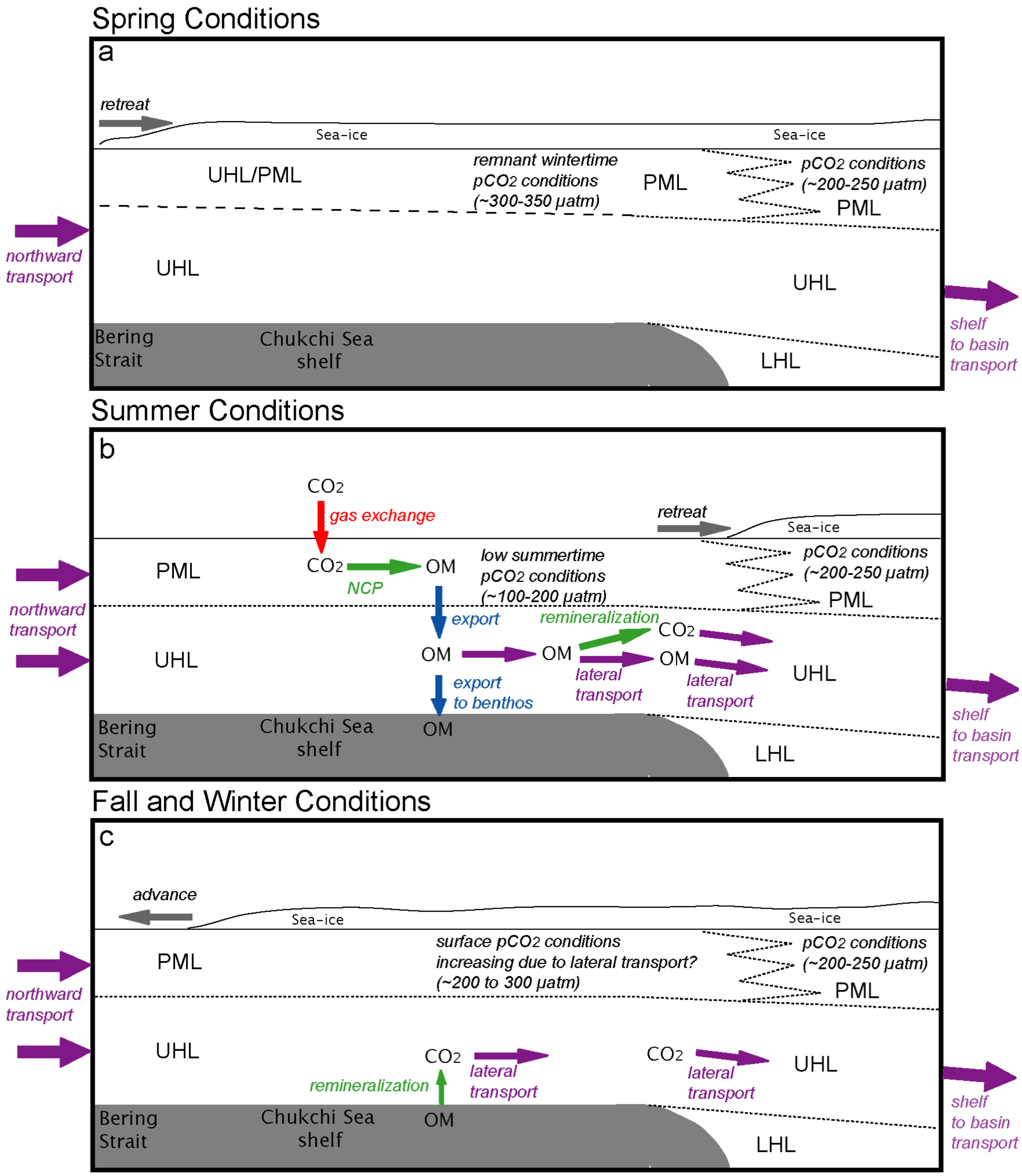

Figure 8. Schematic diagram of hypothesized continental shelf pump of carbon operating on the Chukchi Sea shelf. (a) Springtime conditions. Surface seawater pCO_2 of water remnant from winter is undersaturated with respect to the atmosphere.pCO_2 gas exchange is suppressed by sea-ice cover. (b) Summertime conditions. Surface seawater pCO_2 on the shelf is drawdown by photosynthesis and fixation of CO_2 into organic matter (OM). Primary production enhances air-to-sea CO_2 flux during sea-ice free conditions. Much of the OM is exported from the PML into the UHL, where a part of the export reaches the benthos or is exported laterally off the shelf as suspended POM. (c) Fall to wintertime conditions. Surface seawater pCO_2 on the shelf is partially restored by mixing and lateral transport through Bering Strait. There may also be some respiratory CO_2 released from the benthos.

respect to atmospheric pCO_2 in summertime (August), and neutral in the wintertime (February).

[44] Surface water cooling during the continual northward transport of surface water across the Chukchi Sea from Bering Strait partly contributes to seawater pCO_2 undersaturation on the shelf. During the summertime seasonal sea-ice minima (e.g., June to September), relatively warm waters from the Bering Sea (particularly Alaskan Coastal Current waters) can cool by $\sim$5–7°C as they transit northward across the shelf. Given the thermodynamic seawater pCO_2 change of $\sim$4.2% per °C [*Takahashi et al.*, 1993], seawater pCO_2 could potentially decrease by 8–12 μatm per °C (or $\sim$40–80 μatm) during the transit northward. Previously, the northward shelf to slope decrease

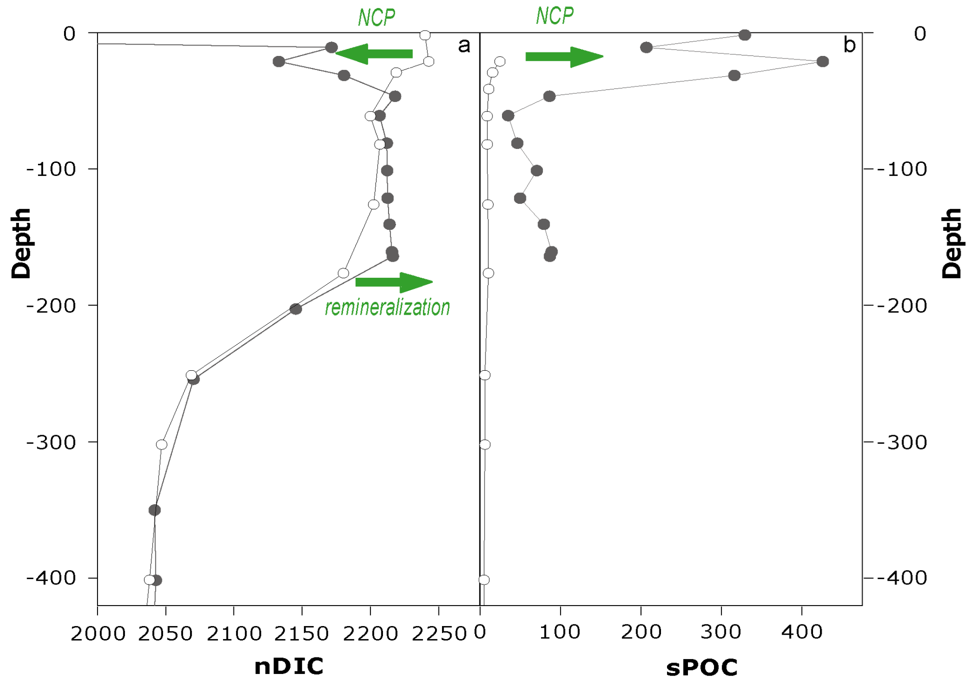

Figure 9. Distributions of dissolved inorganic carbon (DIC) and suspended particulate organic carbon (sPOC), in the Chukchi Sea. (a) Comparison of springtime (open circles; station 34 not listed on map) and summertime (solid circles; station 13) vertical distributions of DIC (normalized to a constant salinity of 33.1) at the edge of the Chukchi Sea in the Barrow Canyon region. By summertime, DIC is drawdown in the surface layer due to productivity, while DIC has increased in the UHL due to remineralization of OM to CO_2. There may also be some respiratory CO_2 released from the benthos that contributes to this increase in DIC. (b) Comparison of springtime (open circles; station 34 not listed on map) and summertime (solid circles; station 13) vertical distributions of sPOC.

in pCO_2 observed in September was primarily attributed to the effect of temperature rather than production or other effects [*Pipko et al.*, 2002; *Murata and Takizawa*, 2003]. *Murata and Takizawa* [2003] suggested that the net air-to-sea CO_2 flux on the Chukchi Sea shelf was driven primarily by an enhancement of the solubility pump (i.e., temperature decrease northward) rather than primary production. At other times (e.g., ~October to May), during sea-ice advance and wintertime sea-ice cover, the latitudinal gradients in temperature across the Chukchi Sea shelf are small (<2°C), and cooling has less impact on seawater pCO_2.

[45] The major determinant of seawater pCO_2 undersaturation and strong air-to-sea CO_2 flux on the Chukchi Sea shelf is summertime primary (and net community) production. The strong oceanic sink for atmospheric CO_2 on the Chukchi Sea results from the biogeochemical modification of seawater CO_2 conditions (rather than temperature) and enhancement of the capacity of surface waters to absorb CO_2.

[46] Observations from the seasonal SBI cruises indicate that temperature changes have a smaller impact on seawater pCO_2 compared to the impact of primary or net community production. Seawater pCO_2 can be corrected for the thermodynamic effect of temperature (e.g., ~4.2% per °C [*Takahashi et al.*, 1993]). On the Chukchi Sea shelf, the largest changes occur between the spring and summertime, when temperature corrected seawater pCO_2 decreased by ~100–220 μatm (Figure 7), particularly in those regions with high rates of primary and net community production [e.g., *Hill and Cota*, 2005; *Bates et al.*, 2005a]. In the regions of high net community production, summertime surface water temperatures were only slightly warmer (<1°C) than wintertime conditions, and the thermodynamic impact of cooling had minor influence on the large seawater pCO_2 (and DIC) drawdown.

[47] In the region of highest primary (and net community) production, the removal of inorganic and organic carbon from surface waters lead to very low seawater pCO_2 conditions (<100–150 μatm) (Figure 8). As a consequence, primary or net community production drives the Chukchi Sea shelf to be a very strong oceanic sink for atmospheric CO_2 (Figure 8). In the surface layer, the summertime shelf outflow of water from the Chukchi Sea shelf exports warm, primary production-modified surface water with a DIC deficit, a suspended POM load, and low seawater pCO_2 (<200 μatm) content that merges with polar mixed layer waters of the Arctic Ocean (Figure 9). Furthermore, much of the summertime primary production on the Chukchi Sea shelf is vertical exported as organic matter from the surface layer to the underlying waters of the Upper Halocline Layer and to the shelf floor (e.g., export production rates were ~20–40 mmol C $m^{-2}d^{-1}$ [*Moran et al.*, 2005]). Subsequently, lateral water transport advects suspended POM off the Chukchi Sea shelf into the Arctic Ocean (Figure 9). At Barrow Canyon, high concentrations of suspended POM (~60 μM) were found

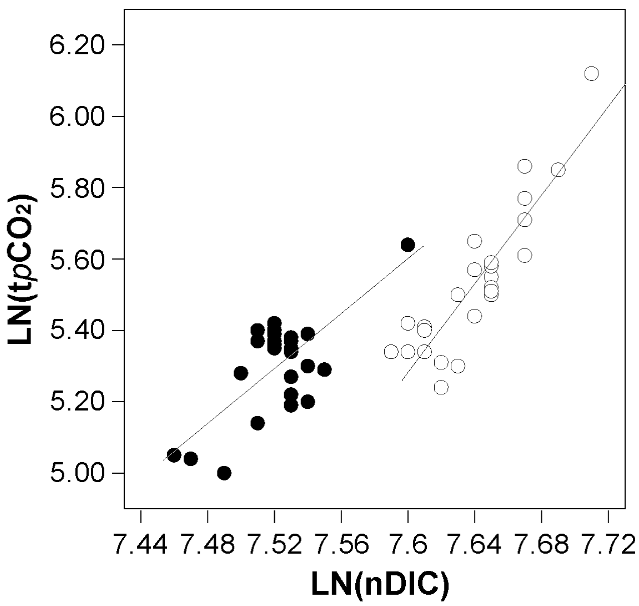

Figure 10. The Revelle factor (i.e., LNt$p$$CO_2$/LNnDIC) of surface waters of the Chukchi Sea shelf slope and adjacent Canada Basin. Springtime (solid circles) Revelle Factor of 6.6 and summertime (open circle) Revelle Factor of 3.8 were determined from 2002 pCO_2 and DIC data. Seawater pCO_2 data were normalized to a constant temperature, tpCO_2 (in this study 0°C) using the thermodynamic rate of ~4.2% change in pCO_2 per °C change. DIC data were also normalized to a salinity of 33.1 (the core salinity of the UHL).

in the upper part of the Upper Halocline Layer extending northward from the shelf into the Arctic Ocean basin [*Bates et al.*, 2005b]. Similar features were observed in the outflow of Hanna Valley [*Bates et al.*, 2005b] and the Herald Valley [*Weingartner et al.*, 2006]. The lateral export of Upper Halocline Layer water from the Chukchi Sea shelf also exports DIC to the Arctic Ocean (in contrast to the surface layer).

[48] Summertime primary (and net community) production also enhances the capacity of Chukchi Sea surface layer water to absorb CO_2 and act as a strong oceanic sink for atmospheric CO_2. The capacity of seawater to absorb CO_2 depends primarily on the buffer capacity or Revelle Factor of seawater [*Takahashi et al.*, 1993; *Sabine et al.*, 2004]. The Revelle Factor quantifies the rate of change of pCO_2 to dissolved inorganic carbon (DIC) in water masses and reflects the underlying seawater charge balance and ratios of DIC to total alkalinity. Tropical and subtropical waters typically have low Revelle Factors (e.g., 8–10) [*Takahashi et al.*, 1993; *Sabine et al.*, 2004], with a greater potential capacity to absorb atmospheric CO_2 than temperate and sub-polar waters with high Revelle Factors (e.g., 11–14). Here, the Revelle Factor (i.e., LNtpCO_2/LNnDIC) was calculated for surface waters of the Chukchi Sea shelf and slope waters. In accordance with other studies, seawater pCO_2 was normalized to a constant temperature (in this study 0°C) using the thermodynamic rate of ~4.2% change in pCO_2 per °C change. DIC data were also normalized to a salinity of 33.1 (the core salinity of the upper halocline layer). Previous observations of polar surface waters from other polar and sub-polar seas, suggest that surface waters of the Chukchi Sea should have high Revelle Factors and low capacity to absorb CO_2. However, SBI data from 2002 indicate that the surface waters of the Chukchi Sea shelf and slope have unusually low Revelle Factors (~3.5–6.5; Figure 10) and a high capacity to absorb CO_2. This results primarily from a decrease in the DIC to total alkalinity ratios of surface waters of the Chukchi Sea due to the removal of DIC by primary production while total alkalinity remains constant (due to the absence of pelagic calcification in the Chukchi Sea). This in turn, reduces the Revelle Factor and consequently enhances the capacity of Chukchi Sea surface waters to absorb CO_2 during summertime.

[49] Do the carbon dynamics on the Chukchi Sea shelf have the attributes of either the "continental shelf pump" [*Tsunogai et al.*, 1999] or the "seasonal rectification hypothesis" [*Yager et al.*, 1995]. The "seasonal rectification hypothesis" of *Yager et al.* [1995] requires that all of the CO_2 fixed into organic matter during a period of brief primary production is retained on the shelf and subsequently remineralized back to CO_2 during the wintertime. The strength of the continental shelf pump as a weak or strong CO_2 sinks is thus dependent on whether organic matter is preferentially retained and remineralized to CO_2 (weaker sink) or organic matter is preferentially export to the open ocean (stronger CO_2 sink) during the sea-ice covered period. On the Chukchi Sea shelf, carbon (either as suspended POM or remineralized CO_2) is lost from the shelf to the Arctic Ocean basin during summertime. As such, during the subsequent sea-ice covered period, the depression of seawater pCO_2 conditions cannot be fully rectified or recharged by CO_2 through organic matter remineralization, and shelf seawater pCO_2 conditions remain undersaturated.

[50] The "continental shelf carbon pump" mechanism hypothesized for the East China Sea [*Tsunogai et al.*, 1999] and other coastal systems requires wintertime cooling to depress seawater pCO_2 conditions, summertime production, vertical export of OM, and lateral export of remineralized CO_2 as DIC from the shelf. Although there are similarities to this general process, Chukchi Sea carbon dynamics have some unique attributes. In the Chukchi Sea, it is the depression of seawater pCO_2 by primary production, facilitated by seasonal conditions of light availability and sea-ice retreat, combined with cooling and uncertain preconditioning of waters in the Bering Sea that drives surface waters to be a strong oceanic sink for atmospheric CO_2 during their one-way transit northward across the Chukchi Sea. The removal of DIC from brief and intense primary production occurring during the summertime increases the capacity of surface waters to absorb CO_2, and subsequent lateral export of DIC and suspended particulate organic carbon from the shelf to the Arctic Ocean basin maintains the Chukchi Sea as a perennial ocean CO_2 sink. Furthermore, during sea-ice cover in the wintertime, water transport into the Chukchi Sea from the Bering Sea, and release of CO_2 from the benthic community [*Grebmeier and Harvey*, 2005] and shallow sediments of the Chukchi Sea shelf (~50–100 m deep) must partially rectify seawater pCO_2 conditions toward atmospheric pCO_2 values. Finally, the Chukchi Sea shelf is also strongly net autotrophic on annual time-

scales since the output of OM from the shelf to the Arctic Ocean is greater than the OM input through Bering Strait.

[51] How potentially important is the Chukchi Sea sink for atmospheric CO_2 compared to the global coastal ocean. Overall, global marginal coastal seas are thought to be a sink of CO_2 of ~450 Tg C yr^{-1} [*Borges et al.*, 2005]. This may be compensated for by nearshore coastal systems acting as sources of CO_2 of ~400 Tg C yr^{-1}[*Borges et al.*, 2005]. The Chukchi Sea and Arctic Ocean CO_2 sinks of 38 ± 7 and 66 ± 7 Tg C yr^{-1} estimated here are ~8% and 15%, respectively, of the global marginal coastal sea sink for CO_2 estimated by *Borges et al.* [2005]. In the Arctic Ocean, sea-ice extent and volume has decreased over the last few decades[e.g., *Cavalieri et al.*, 2003; *Rothrock and Zhang*, 2005; *Stroeve et al.*, 2005], with complex interactions and feedbacks between the atmosphere, oceans and sea-ice that influence heat and freshwater budgets and exchanges within the Arctic Ocean region. The inputs of freshwater and organic carbon inputs to the Arctic Ocean [e.g., *Peterson et al.*, 2002; *Hansell et al.*, 2004; *Frey and Smith*, 2005] are likely to change in the future with hard to predict changes in the Arctic Ocean carbon cycle. Thus, the relatively large contribution of the Chukchi Sea and Arctic Ocean to the global marginal coastal CO_2 sink may change significantly, with implications for the global carbon cycle.

6. Conclusions

[52] In springtime (May–June) of 2002, surface water properties on the Chukchi Sea shelf were characteristic of remnant winter water. Surface layer DIC (and nDIC) had a small concentration range and seawater $p\mathrm{CO}_2$ contents on the Chukchi Sea shelf and slope regions were undersaturated with respect to atmospheric $p\mathrm{CO}_2$. Two months later, in response to high rates of localized primary production, low seawater $p\mathrm{CO}_2$ conditions (<150 μatm) were observed in the surface layer in the Central Channel and Barrow Canyon region of the Chukchi Sea shelf and western Beaufort Sea shelf. At some stations, very low $p\mathrm{CO}_2$ conditions (<150 μatm) were observed. In the Arctic Ocean basin, spring and summertime surface layer DIC (and nDIC) had a small concentration range and seawater $p\mathrm{CO}_2$ contents (~200–250 μatm) were highly undersaturated with respect to atmospheric $p\mathrm{CO}_2$.

[53] In the seasonally sea-ice free regions of the Chukchi Sea shelf, rates of air-to-sea CO_2 fluxes were high, ranging from ~50–90 mmoles CO_2 m^{-2} d^{-1}. Air-to-sea CO_2 fluxes decreased to <5 mmoles CO_2 m^{-2} d^{-1}, in slope, Arctic Ocean basin, and western Beaufort Sea stations where sea-ice cover remained very high (>80%). The Arctic Ocean basin region appears to act as a potential oceanic sink for atmospheric CO_2 through this is suppressed by perennial sea-ice conditions. Annually and during the May to September period, the net air-to-sea CO_2 flux from the Chukchi Sea shelf was estimated at ~38 ± 7 and ~27 ± 7 Tg C, respectively. An active continental shelf pump of carbon, driven by the northward transport of nutrient-rich water of Pacific Ocean origin, high rates of primary and net community production during the sea-ice free period, and lateral export of organic carbon from the shelf maintains the Chukchi Sea shelf and slope as a perennial ocean CO_2 sink.

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