The Ocean Carbon Cycle in the Western Arctic Ocean

DISTRIBUTIONS AND AIR-SEA FLUXES OF CARBON DIOXIDE

BY NICHOLAS R. BATES, WEI-JUN CAI, AND JEREMY T. MATHIS

ABSTRACT. The Arctic Ocean is a potentially important sink for atmospheric carbon dioxide (CO₂) with a recent estimate suggesting that the region contributes from 5 to 14% of the global ocean’s net uptake of CO₂. In the western Arctic Ocean, the focus of this paper, the Chukchi Sea is a strong ocean sink for CO₂ that is partially compensated for by outgassing of CO₂ from the East Siberian Sea shelf. The Arctic marine carbon cycle and exchange of CO₂ between the ocean and atmosphere appear particularly sensitive to environmental changes, including sea ice loss, warming, changes in seasonal marine phytoplankton primary production, changes in ocean circulation and freshwater inputs, and even the impacts of ocean acidification. In the near term, further sea ice loss, increases in phytoplankton growth rates, and other environmental and physical changes in the Arctic are expected to cause a limited net increase in the uptake of CO₂ by Arctic surface waters. Recent studies suggest that this enhanced uptake will be short lived, with surface waters rapidly warming and equilibrating with the atmosphere. Furthermore, release of large stores of carbon from the surrounding Arctic landmasses through rivers into the Arctic Ocean and further warming over the next century may alter the Arctic from a CO₂ sink to a source over the next century.
INTRODUCTION
The Arctic plays an important and likely increasing role in the global climate system with complex and poorly understood interactions and feedbacks among sea ice, ocean, and atmosphere, the cryosphere-hydrological cycle, and ocean circulation, leading to significant impacts on the global balance of atmospheric greenhouse gases such as CO₂ and methane. Over the last few decades, numerous studies have shown that there are significant warming (ACIA, 2005; Serreze and Francis, 2006), seasonal sea ice loss (e.g., Maslanik et al., 2007; Wang and Overland, 2009), and other physical and biological transformations in the terrestrial and marine realms of the Arctic (Wu et al., 2005; McGuire et al., 2006, 2009). The Arctic Ocean is also sensitive to atmosphere-ocean-sea ice forcing and feedbacks and ecosystem transitions associated with warming temperatures and sea ice loss (e.g., Arrigo et al., 2008; Pabi et al., 2008). Because of these rapid environmental changes, the Arctic marine carbon cycle will likely enter a highly dynamic state in the coming decades, with large uncertainties in the exchange of atmosphere-ocean CO₂ (Anderson and Kaltin, 2001; Bates et al., 2006a; Bates and Mathis, 2009; Cai et al., 2010; Jutterström and Anderson, 2010) in response to sea ice loss and other climate-change-induced processes.

Furthermore, the Arctic marine carbon cycle and marine ecosystems are also vulnerable to ocean acidification that results from the uptake of anthropogenic CO₂ from the atmosphere (Orr et al., 2005; Steinacher et al., 2009; Bates et al., 2009; Yamamoto-Kawai et al., 2009).

In this article, we review the present state of knowledge about the Arctic marine carbon cycle, exchanges of CO₂ between the atmosphere and the ocean, and the potential physical and biological processes that influence CO₂ sources and sinks in the Pacific-Ocean-influenced Arctic. To illustrate their potential controls on air-sea CO₂ flux in a changing environment, this review also includes a brief treatment of marine ecosystems and organic carbon cycling in the western Arctic; more comprehensive reviews may be found elsewhere, e.g., Stein and Macdonald, (2004) and Macdonald et al., (2010). Our geographic scope is focused primarily on the western Arctic Ocean shelves (e.g., Chukchi, Beaufort, and East Siberian Seas) and the adjacent Canada Basin, which are influenced by the inflow of Pacific Ocean waters through Bering Strait (Figure 1). We discuss marine carbon cycle data collected in the early 2000s during the Shelf-Basin Interactions (SBI) project as well as more recent data collected during the China National Arctic Research Expedition (CHINARE), Russian-American Long-term Census of the Arctic (RUSALCA), and National Aeronautics and Space Administration (NASA) Impacts of Climate change on the Eco-Systems and Chemistry of the Arctic Pacific Environment (ICESCAPE) projects.

PHYSICAL SETTING OF THE WESTERN ARCTIC OCEAN
The relatively small Arctic Ocean, containing 2.6% of the world’s ocean area but < 1% of its volume, is almost completely surrounded by landmasses. It is disproportionately affected by terrestrial fluxes because it receives almost 10% of total global river runoff annually from an extensive system of rivers that drain the watersheds of Siberia and northern North America (McGuire et al., 2006; Cooper et al., 2008). These landmasses contain large stores of freshwater (mostly glacial ice and permafrost) and terrestrial carbon, which, combined with the presence of sea ice in the Arctic Ocean, profoundly influence the hydrological cycle, climate, and biogeochemical dynamics of carbon in the Arctic region.

In wintertime, the Arctic Ocean is almost completely covered by sea ice (except for minor areas of open water associated with polynyas and flaw leads). Physical transformations and seasonal sea ice cover together play a major role in controlling shelf water-mass properties through vertical homogenization of the water column by such physical processes as ventilation, brine rejection, and convective mixing. In summertime, seasonal atmospheric warming and the inflow of Pacific and Atlantic Ocean waters, combined with local warming and sea ice melt, leave the Arctic shelves sea ice-free for a relatively brief period. However, the presence of multiyear ice in the central basin and thinner seasonal sea ice (1 to 2 m) across the Arctic shelves has declined dramatically since the 1990s and in particular since 2007 (Comiso et al., 2008). Thus, sea ice loss reinforces surface warming due to reduced surface reflectivity and increased heat absorption (Perovich et al., 2007), which in turn impact Arctic Ocean chemistry and biology.

The expansive coastal seas of the Arctic Ocean (e.g., Barents, Laptev, Kara, East Siberian, Chukchi, and Beaufort Seas) comprise approximately 53% of its total area (Macdonald et al., 2010).
and completely surround a deep central basin (Eurasian and Canada Basins; Figure 1). The Arctic Ocean has several important gateways that allow exchanges of seawater with the Pacific (through Bering Strait) and Atlantic (through the Canadian Archipelago, Fram Strait, and Barents Sea; Figure 1). In the western Arctic, the wide and shallow Chukchi Sea occupies a particularly extensive portion of the Arctic shelf system. Relatively warm and nutrient-rich Pacific Ocean waters enter the Chukchi Sea, flowing northward through Bering Strait from the Bering Sea (Coachman et al., 1975; Roach et al., 1995; Woodgate et al., 2005). The physics and biogeochemistry of the Chukchi Sea is highly influenced by this inflow, and its shelf can be characterized as an “inflow” shelf (Carmack and Wassmann, 2006; Bates and Mathis, 2009). In contrast to the Chukchi Sea, the East Siberian Sea and Beaufort Seas are more influenced by freshwater inputs, exchanges with adjoining shelves, and internal processes (i.e., “interior shelves”; Figure 1). For example, there is a general flow from the Laptev Sea across the East Siberian Sea shelf, and subsequent export of water offshore into the central basin or through Long Strait into the Chukchi Sea via the Siberian Coastal Current (e.g., Weingartner et al., 1998;
approximately 25 Pg of dissolved inorganic carbon (DIC) in the forms of bicarbonate (HCO$_3$), carbonate (CO$_3^{2-}$), and carbon dioxide (CO$_2$). Inflow of Pacific Ocean water through Bering Strait into the Chukchi Sea constitutes an input of ~ 0.8–1.0 Pg C yr$^{-1}$ of inorganic carbon into the Arctic Ocean (Bates and Mathis, 2009), with outflow from the western Arctic primarily through the Canadian Archipelago. In comparison, rates of primary production (or new and export production) have been estimated at ~ 135 Tg C yr$^{-1}$ (Tg = 10$^{12}$ g) in the entire Arctic Ocean, though there are large uncertainties in these estimates (Macdonald et al., 2010). The Arctic landmasses contain even larger stores of carbon compared to the marine environment, and there are significant river inputs of organic carbon to the Arctic shelves (e.g., Lobbes et al., 2000; Amon, 2004; Rachold et al., 2004; Guo and Macdonald, 2006; Raymond et al., 2007; Holmes et al., 2011). Pan-Arctic river inputs of carbon have been estimated by McGuire et al. (2009) at 33 Tg C yr$^{-1}$ of DOC and 43.2 Tg C yr$^{-1}$ DIC, which are 7.1% and 10.6% of their respective total global river fluxes (Cai, 2011). River inputs of POC and coastal erosion of terrestrial carbon (containing both refractory and labile organic carbon) have been estimated at ~ 12 Tg C yr$^{-1}$ (e.g., Rachold et al., 2004; Macdonald et al., 2010), at least for the present. Rivers thus contribute disproportionately large amounts of freshwater and carbon to the Arctic Ocean compared to river contributions in other ocean basins. Compared to many other open-ocean and coastal environments, relatively few studies of the marine carbon cycle have been conducted in the Arctic. The harsh polar climate and difficult logistical support have limited most studies to opportunistic icebreaker surveys conducted on the Arctic Ocean shelves during the summertime sea ice retreat. Even with transpolar surveys across the deep basin (e.g., Arctic Ocean Section of 1994 [Jutterström and Anderson, 2005; Jones et al., 2008; Tanhua et al., 2009; Jutterström and Anderson, 2010]) and shelf projects such as the Shelf-Basin Interactions (SBI II) program (Grebmeier et al., 2008) and Canadian Arctic Shelf Exchange Study (CASES; Mucci et al., 2008; Fortier and Cochran, 2008), spring and summer observations of the Arctic Ocean marine carbon cycle are highly limited, and observations are virtually absent during winter sea ice cover. Thus, there are considerable uncertainties about physical and biological controls on the marine carbon cycle, natural and human perturbed seasonal and interannual variability, and CO$_2$ sinks and sources in the Arctic Ocean.

**MARINE ECOSYSTEMS AND ORGANIC CARBON OF THE WESTERN ARCTIC**

In the western Arctic, the different physical setting of each shelf strongly influences its biology. The inflow of nutrient-rich seawater from the Pacific Ocean into the Chukchi Sea (Codispoti et al., 2005), coupled with abundant light and the seasonal retreat and melting of sea ice, supports a brief, but intensive, period of marine phytoplankton photosynthesis and growth compared to other Arctic Ocean shelves where nutrients are limited (Cota et al., 1996; Hill and Cota, 2005). As the foundation for supporting the pelagic/benthic food web, rates of phytoplankton primary production on the Chukchi Sea shelf can be
≥ 300 g C m⁻² yr⁻¹ or 0.3–2.8 g C m⁻² d⁻¹ (e.g., Hameedi, 1978; Cota et al., 1996; Gosselin et al., 1997; Hill and Cota, 2005; Bates et al., 2005a; Mathis et al., 2009; Macdonald et al., 2010). Sea ice algal communities also contribute substantively to early season primary production (e.g., Legendre et al., 1992; Gosselin et al., 1997), with springtime production rates in the Chukchi Sea estimated at ~1–2 g C m⁻² d⁻¹ (Gradinger, 2009). Intense seasonal growth of marine phytoplankton supports a large zooplankton (e.g., shrimp, copepods) biomass that in turn supports diverse open-water and seafloor ecosystems (Feder et al., 2005; Grebmeier et al., 2008). Both pelagic and benthic ecosystems on the Chukchi Sea shelf support marine mammal (e.g., gray whale, walrus, polar bear), seabird, and human populations in the region.

In the Chukchi Sea, the brief period of high rates of marine phytoplankton primary production results in the formation of high concentrations of suspended POC (sPOC; Bates et al., 2005b) and export of organic carbon to the subsurface and benthos (Moran et al., 2005; Lepore et al., 2007). During the SBI project in the early 2000s, high concentrations of sPOC were observed (up to 2000 mg C L⁻¹; average of ~200–300 mg C L⁻¹) across the shelf (Figure 2), with considerable export of sPOC off the shelf into the Canada Basin (Bates et al., 2005b; ~2.3–3.5 Tg C yr⁻¹ assuming 0.8 Sv transport during 100 days of active POC production), and relatively high rates of vertical export of organic carbon to shelf, slope, and basin sediments (Moran et al., 2005; Lepore et al., 2007; Belicka and Harvey, 2009). In contrast, little seasonal accumulation of DOC due to phytoplankton primary production has been observed (e.g., Davis and Benner, 2005; Mathis et al., 2007b) from springtime to summertime during sea ice retreat (Figure 3). This marine ecosystem appears dominated by large-sized phytoplankton (e.g., diatoms; Grebmeier et al., 2008) that produce a relatively large-size class of organic matter (i.e., as POC rather than DOC). In contrast, in other marine ecosystems dominated by small phytoplankton (i.e., picoplankton) such as the subtropical North Atlantic Ocean, a much larger fraction of DOC is produced seasonally compared to POC (e.g., Carlson et al., 1994).

Elsewhere in the western Arctic, coastal waters of the East Siberian and

![Figure 2. Distributions of suspended particulate organic carbon (POC) in the Chukchi Sea collected during the 2002 and 2004 Shelf-Basin Interactions (SBI) project in the western Arctic (Bates et al., 2005b, 2006b,c, http://www.eol.ucar.edu/projects/sbi/all_data.shtml). In the left panel, CTD/hydrocast stations are shown with different seas denoted: CS = Chukchi Sea. ESS = East Siberian Sea. BS = Beaufort Sea. CB = Canada Basin. In the right panel, POC data include two sea ice-covered cruises in spring and two sea ice-free cruises conducted in summertime, including: spring 2002 (blue symbols), summer 2002 (green symbols), spring 2004 (yellow symbols), and summer 2004 (red symbols). The data are plotted using Ocean Data View (Schlitzer, 2005).](image-url)
Beaufort Sea have much lower rates of marine phytoplankton photosynthesis and growth due primarily to reduced physical supply of nutrients, briefer periods of sea ice retreat, and more turbid surface waters, which reduces solar penetration (Carmack and Wassmann, 2006; Macdonald et al., 2010). Rates of summertime phytoplankton primary production (compared to other Arctic shelves) in the euphotic zone of the East Siberian Sea and Beaufort Sea shelves have been estimated at ~6–12 g C m⁻² yr⁻¹ (Macdonald et al., 2010; Anderson et al., 2011), which is low compared to the Chukchi Sea and the Barents Sea shelf, for example. Notwithstanding these lower rates of primary production, the Siberian and Beaufort Sea shelves have a dynamic carbon cycle (e.g., Macdonald et al., 1998), with significant marine production of organic matter and proportionately greater (compared to the Chukchi Sea) input of terrestrial derived organic matter (e.g., Lobbes et al., 2000; Rachold et al., 2004; Raymond et al., 2007; Gustafsson et al., 2011). Terrestrial organic carbon constitutes up to 44% of vertical POC export on the Beaufort Sea shelf (e.g., Belicka et al., 2009; Belicka and Harvey, 2009; Sampei et al., 2011), with significant shelf-basin transport of organic matter (e.g., 1.6–5.9 g C m⁻² d⁻¹; Lalande et al., 2009; Forest et al., 2007).

In the central basins of the Arctic, surface waters are mostly covered by sea ice and have very low nutrient concentrations. As a result, surface waters of the Canada Basin have very low rates of marine phytoplankton growth (e.g., English, 1961; Wheeler et al., 1996; Gosselin et al., 1997; Moran et al., 1997; Pomeroy, 1997; Anderson et al., 2003) and relatively low vertical export of organic matter to the deep seafloor (e.g., Moran et al., 1997; Wassmann et al., 2004; Honjo et al., 2010). Differences in the availability of nutrients, productivity, and sources of organic carbon briefly discussed above provide critical links to explain the observed contrasting distribution of surface CO₂ in various subregions of the western Arctic Ocean (see below).

**INORGANIC CARBON IN THE WESTERN ARCTIC OCEAN**

The complete seawater inorganic carbon system (i.e., CO₂, HCO₃⁻, CO₃²⁻, H⁺, and calcium carbonate [CaCO₃] mineral saturation states, Ω) can be calculated from measurements of two carbonate...
parameters such as dissolved inorganic carbon (DIC), total alkalinity (TA), partial pressure ($p_{CO_2}$) or fugacity of carbon dioxide ($f_{CO_2}$), and pH (Dickson et al., 2007).

There are numerous physical and biological controls on the marine carbon cycle with complex interactions between them. Arguably, the most important processes include seasonal cooling and warming of surface waters, exchange of carbon with other basins and shelves, phytoplankton primary production, air-sea transfer of $CO_2$, sea ice processes, and inputs of freshwater and terrestrial carbon (Bates and Mathis, 2009). At the air-sea interface, sea ice cover has generally been thought to be a barrier to gas exchange, although there may be minor exchanges in leads and diffusion through the ice (e.g., Gosink et al., 1976; Semiletov et al., 2004; Delille et al., 2007; Nagurnyi, 2008). Recent studies, however, suggest that the exchange of $CO_2$ through sea ice is much greater than previously thought, with significant release and uptake of $CO_2$ depending on season and sea ice condition (Rysgaard et al., 2007; Miller et al., 2011; Papakyriakou and Miller, 2011). Within the water column, carbon export via brine rejection during sea ice formation, shelf-basin exchanges of carbon, vertical diffusion, entrainment and detrainment through mixing, vertical export of organic carbon, and remineralization of organic matter to $CO_2$ in shelf and subsurface waters and sediments are also important processes.

In early studies of the Chukchi Sea, Semiletov (1999) observed that seawater $p_{CO_2}$ (~ 200–350 µatm) values were lower than those in the atmosphere (~ 365–380 µatm at the time of observation) during the sea ice-free period. Since then, other studies have observed low seawater $p_{CO_2}$ conditions on the Chukchi Sea shelf during summertime (~ 150–350 µatm; Pipko et al., 2002; Murata and Takizawa, 2003; Bates et al., 2005a, 2006a; Bates, 2006; Chen and Gao, 2007; Fransson et al., 2009; Andreev et al., 2010). More recently, similarly low values for seawater $p_{CO_2}$ were observed during the 2008 CHINARE (Figure 4), 2009 RUSALCA (Figure 5), and 2010 ICECAPES projects (Figure 6). In 2010, similar to other years, extremely low summertime $p_{CO_2}$ conditions (< 100 µatm) were observed under sea ice in surface waters of the Northwest Chukchi Sea close to the Canada Basin (Figure 6) similar to previous observations north of Wrangel Island (Fransson et al., 2009).

On the Chukchi Sea shelf, large drawdowns of surface-water DIC have also been observed during summertime open-water conditions (Bates et al., 2005b; Bates, 2006; Cai et al., 2010).
similar to the seasonal changes observed in the Barents Sea, for example (Omar et al., 2003, 2007; Nakaoka et al., 2006). The seasonal changes in DIC have been largely attributed to high rates of summertime phytoplankton primary production or net community production, especially in the vicinity of Barrow Canyon at the northern edge of the Chukchi Sea shelf (Bates et al., 2005a; Hill and Cota, 2005; Mathis et al., 2007b). In summary, seasonal changes in surface $p$CO$_2$ on the Chukchi Sea shelf have been largely attributed to cooling of surface waters during the northward transit of waters across the Chukchi Sea shelf (Murata and Takizawa, 2003) and high rates of summertime phytoplankton primary production that act to decrease seawater DIC and $p$CO$_2$ (Bates, 2006). These processes produce a dynamic shelf-to-basin carbon pump (Bates, 2006; Anderson et al., 2010). The seasonal rebound of seawater $p$CO$_2$ and DIC during wintertime likely results from a continued uptake of CO$_2$ through gas exchange during sea ice formation and brine rejection (Anderson et al., 2004; Omar et al., 2005), continued transport of Pacific Ocean waters into the Chukchi Sea through Bering Strait, and vertical entrainment by mixing with CO$_2$-rich subsurface waters.

In the East Siberian and Beaufort Seas, surface water $p$CO$_2$ conditions appear highly variable during the sea ice-free period. In the East Siberian Sea shelf (~300–500 µatm), surface waters close to or above atmospheric values have been reported (Semiletov et al., 1999, 2007; Pipko et al., 2008), with much higher values near the outflow of the Kolyma River (~500 µatm) that drains into the East Siberian Sea shelf (Semiletov et al., 1999, 2007). Furthermore, very high values (~500 to ~1500 µatm) have been observed in bottom waters of the inner shelf and also in the nearshore bays (e.g., Tiksi Bay) and estuaries of the East Siberian Sea (Semiletov et al., 1999, 2007). We have also observed seawater $p$CO$_2$ values close to equilibrium with the atmosphere in the East Siberian Sea (Figure 5). The high seawater $p$CO$_2$ values can be attributed primarily to the remineralization of organic matter introduced from the Siberian Rivers (e.g., Anderson et al., 1990; Cauwet and Sidorov, 1996; Kattner et al., 1999), given that there are low rates of summertime phytoplankton primary production (~6–12 g C m$^{-2}$ yr$^{-1}$; Macdonald et al., 2010). In the western Chukchi Sea near Long Strait, summertime seawater $p$CO$_2$ conditions were observed to be close to equilibrium with the atmosphere (Fransson et al., 2009; also Figure 5), presumably reflecting outflow of

Figure 5. Surface distributions of seawater partial pressure of CO$_2$ ($p$CO$_2$ in µatm) calculated from dissolved inorganic carbon (DIC) and total alkalinity (TA) data collected during the summer of 2009 as part of the RUSALCA project (recent work of author Bates). Samples were collected from CTD/hydrocast stations occupied by the icebreaker Professor Khromov. DIC and TA sample analysis is described elsewhere in Bates (2007). Seawater $p$CO$_2$ was calculated using CO2calc (Robbins et al., 2010) with dissociation constants of Mehrbach et al. (1973) as refit by Dickson and Millero (1987) and KSO$_4$ of Dickson (1990). The data are plotted using Ocean Data View (Schlitzer, 2005).
higher $pCO_2$ surface waters from the East Siberian Sea with the intermittent Siberian Coastal Current (Weingartner et al., 1999). In the Beaufort Sea, seawater $pCO_2$ conditions appear to be highly variable ($\sim$ 150–350 µatm) in the western parts of the shelf (Murata and Takizawa, 2003; Bates, 2006), with low values (< 100 µatm) observed in areas with high proportions of freshwater (10–20%) and sea ice melt (10–25%) (e.g., Cooper et al., 2005; Bates, 2006). In the eastern Beaufort Sea shelf, summertime surface seawater $pCO_2$ values were generally low (Mucci et al., 2008) or close to equilibrium with the atmosphere, particularly in the vicinity of the Banks Island polynya (Fransson et al., 2009).

In the central basin, which has been poorly sampled for the marine carbon cycle, there is an emerging picture of mixed surface seawater $pCO_2$ conditions. In early studies, such as the Arctic Ocean Section (AOS) expedition in 1994, surface waters under sea ice had seawater $pCO_2$ values of $\sim$ 300–330 µatm (i.e., much lower than the atmosphere; Jutterström and Anderson, 2010). Several repeated sections across the central basin also have shown similar results (Jutterström and Anderson, 2010). In the early 2000s, low seawater $pCO_2$ values of $\sim$ 240–280 µatm were observed in the Canada Basin off the Chukchi Sea shelf (Bates, 2006; Bates et al., 2006a), and there were even lower surface seawater $pCO_2$ values of $\sim$ 150–250 µatm in the Makarov Basin of the Canada Basin (Fransson et al., 2009). However, more recently, Yamamoto-Kawai et al. (2009) showed that some surface areas of the Canada Basin had seawater $pCO_2$ conditions close to equilibrium with the atmosphere, reflecting uptake of CO$_2$ from the atmosphere and warming during exposure of surface waters as well as strong vertical stratification and low biological production. However, areas with heavy ice cover (mostly the northern part) had lower surface water $pCO_2$ (Figure 4). Thus, ongoing rapid sea ice retreat to the northern basin appears to have resulted in a recent increase in seawater $pCO_2$ in the Canada Basin that approaches the atmospheric $pCO_2$.

![Figure 6. Surface distributions of seawater partial pressure of CO$_2$ ($pCO_2$ in µatm) calculated from DIC and TA data collected during the summer of 2010 as part of the NASA ICESCAPE project (recent work of authors Bates and Mathis). Samples were collected from CTD/hydro-cast stations occupied by the icebreaker USCGC Healy. DIC and TA sample analysis is described in Bates (2007). Seawater $pCO_2$ was calculated using CO2calc (Robbins et al., 2010) using pKs of Mehrbach et al. (1973) as refit by Dickson and Millero (1987) and KSO$_4$ of Dickson (1990). The data are plotted using Ocean Data View (Schlitzer, 2005).](image-url)
AIR-SEA CO2 FLUXES IN THE WESTERN ARCTIC OCEAN

The exchange of gases such as CO2 between the atmosphere and the ocean is primarily controlled by gas concentration differences between air and sea (i.e., air-sea CO2 disequilibrium or $\Delta p$CO2) and by turbulence in the lower atmosphere (which is commonly parameterized as a function of wind speed; see Wanninkhof, 1992). In the earliest study of the inorganic carbon cycle in the Arctic Ocean, Kelley (1970) observed that surface waters in the Barents Sea had lower pCO2 values than the atmosphere. In the last two decades, more precise and accurate carbon data have been collected in the Arctic Ocean, allowing better assessments of its sink or source status.

In the Chukchi Sea, early season observations under near complete sea ice cover also indicate that Chukchi Sea shelf “winter” surface waters were not as undersaturated with respect to the atmosphere ($\Delta p$CO2 values of $\sim$20 to –60 µatm, with negative values indicating direction of gas exchange toward the ocean) compared to the summertime sea ice-free period (Bates, 2006). In contrast, summertime $\Delta p$CO2 values are typically in the range of –50 to –200 µatm. Previous estimates of the rates of air-sea CO2 exchange during the sea ice-free period in the summertime have ranged from $\sim$20 to –90 mmol CO2 m$^{-2}$ d$^{-1}$ (Wang et al., 2003; Murata and Takizawa, 2003; Bates, 2006; Fransson et al., 2009), indicating that the surface waters of the Chukchi Sea shelf have the potential to be a strong sink of atmospheric CO2 (Kaltin et al., 2002), similar to the Barents Sea shelf (Kelley, 1970; Fransson et al., 2001; Kaltin and Anderson, 2005). However, in regions of the Chukchi Sea shelf where sea ice cover remained high (>80%) during the summertime, air-sea CO2 exchange rates were estimated to be generally low (i.e., ocean uptake of <1 mmol CO2 m$^{-2}$ d$^{-1}$; Bates, 2006), while wintertime air-sea CO2 exchange rates (during complete sea ice cover) were estimated to be minor (i.e., ocean uptake of <1 mmol CO2 m$^{-2}$ d$^{-1}$; Bates, 2006) as sea ice coverage greatly reduces air-sea gas exchange. The annual ocean CO2 uptake for the Chukchi Sea shelf has been estimated at 2–9 mmol C m$^{-2}$ yr$^{-1}$ (Kaltin and Anderson, 2005; Bates, 2006), or approximately 11–53 Tg C yr$^{-1}$ (Table 1). More recent results from the 2008 CHINARE, 2009 RUSALCA, and 2010 ICESCAPES cruises further demonstrate that much of the Chukchi Sea is highly undersaturated, with a very strong potential for uptake of CO2 from the atmosphere (Figures 4, 5, 6).

In contrast to the Chukchi Sea, the ocean CO2 sink or source terms for the East Siberian Sea shelf remain unclear. Semiletov et al. (2007) suggested that the western area of the shelf is a source of CO2 to the atmosphere (1 ± 1.6 mmol m$^{-2}$ d$^{-1}$ in 2003 and 10.9 ± 12.6 mmol C m$^{-2}$ d$^{-1}$ in 2004), particularly in the nearshore regions and close to river outflows onto the shelf. Nitishinsky et al. (2007) and Anderson et al. (2009) estimated that the East Siberian Sea shelf is a source of CO2 to the atmosphere (0.3 mmol m$^{-2}$ d$^{-1}$), while Semiletov et al. (2007) reported that the Pacific Ocean water influenced eastern area of the East Siberia Sea is a sink for atmospheric CO2. Similarly, in the western Beaufort Sea, Murata and Takizawa (2003) estimated that surface waters were modest sinks for CO2 (~12 mmol CO2 m$^{-2}$ d$^{-1}$) during summertime. In the eastern Beaufort Sea shelf, surface waters are apparently minor sinks for CO2 (Mucci et al., 2008; Fransson et al., 2009, ~6 mmol CO2 m$^{-2}$ d$^{-1}$) or have a neutral status. Fransson et al. (2009) estimated that there is ocean CO2 uptake in the summertime in the eastern Beaufort Sea shelf. However, in areas with high sea ice cover (>80%), air-to-sea CO2 fluxes were generally low (<1–10 mmol CO2 m$^{-2}$ d$^{-1}$; Bates, 2006; Fransson et al., 2009), again due to the physical barrier of sea ice. The annual ocean CO2 uptake for the Beaufort Sea shelf has been estimated at 1.2 g C m$^{-2}$ yr$^{-1}$, low compared to other Arctic Ocean shelves (Table 1; Murata and Takizawa, 2003). In the Canada Basin, the potential uptake or release of CO2 remains uncertain. Prior to 2007, relatively low (~150–350 µatm) surface seawater pCO2 values of the Canada Basin suggested that these waters had the potential to uptake CO2 once exposed to the atmosphere (Fransson et al., 2009). However, the CO2 sink status of the Canada Basin appears to have significantly changed since 2007 given that surface seawater pCO2 values close to atmospheric values have been observed (e.g., Yamamoto-Kawai et al., 2009; Cai et al., 2010).

The above studies suggest that the Chukchi Sea shelf dominates air-sea CO2 fluxes in the western Arctic region, with the strong Chukchi Sea CO2 sink heavily outweighing potential minor sources of CO2 in the East Siberian Sea. Recent studies suggest that surface waters of the Arctic Ocean generally have low to very low CO2 concentrations compared to atmospheric CO2 concentrations (including the Barents Sea, Chukchi Sea, and Beaufort Sea shelves as well as...
the central basin of the Arctic Ocean; Bates and Mathis, 2009). Thus, these surface waters have the ability to absorb relatively large amounts of CO₂ (about 66–175 Tg C yr⁻¹). However, given more recent observations (Cai et al., 2010), the 2007 sea ice loss event in the Arctic Ocean may have tipped it toward being a smaller sink of CO₂. Because nutrients and therefore phytoplankton primary production are limited in the central basin, equilibrium of polar mixed-layer seawater CO₂ with the atmosphere occurs because there are few processes to remove CO₂ from surface waters. Thus, enhanced uptake of CO₂ through sea ice loss (e.g., Bates et al., 2006a; Jutterström and Anderson, 2010) into newly exposed surface waters of the central basin is likely to be a very short-term phenomenon, and surface waters appear to be rapidly equilibrating with the atmosphere (Cai et al., 2010). In addition, it should be noted that the uptake of CO₂ by the Arctic Ocean is small compared to the potential release of land-based carbon to the atmosphere from surrounding Arctic landmasses over the next few centuries as a result of climate change. Finally, potential increases in organic carbon respiration as a result of warming and enhanced terrestrial organic carbon flux due to thawing of permafrost and coastal erosion are difficult to evaluate but will certainly further modify the CO₂ source-sink terms in the Arctic Ocean under future climate change.

### Ocean Acidification Impacts in the Western Arctic Ocean

The decrease in seawater pH due to the uptake of anthropogenic CO₂ (Bindoff et al., 2007; Bates, 2007) has been termed

| Table 1. Areas, depths, residence times, air-sea CO₂ exchange rates expressed in mmoles C m⁻² d⁻¹, and annual air-sea CO₂ exchange rate expressed in Tg C (10¹² g C). Negative air-sea CO₂ exchange rates indicate ocean uptake of CO₂ (i.e., CO₂ sink). Modified from Bates and Mathis (2009) |
| --- | --- | --- | --- | --- |
| **Area** (km²) | **Depth** (m) | **Residence** (years) | **Air-sea CO₂ flux** (mmoles C m⁻² d⁻¹) | **Annual CO₂ flux** (Tg C yr⁻¹) | **Reference** |
| **East Siberian Sea** | 987,000 | 58 | 3.5 ± 2 | −1 to −10.9 | −1.2 to −13 | Semiletov et al. (2007) |
| | | | | +0.3 | +0.3 | Nitishinsky et al. (2007) |
| | | | | n/a | −5.9 | Anderson et al. (1998a,b) |
| **Chukchi Sea** | 620,000 | 80 | 0.2 to 1.2 | −12 | −11 | Murata and Takizawa (2003) |
| | | | | −40 ± 22 | −36 to +6 | Bates et al. (2006a) |
| | | | | n/a | −46 to +6 | Bates et al. (2006a) |
| | | | | n/a | −53 ± 14 | Kaltin and Anderson (2001) |
| **Beaufort Sea** | 178,000 | 124 | 0.5 to 1.0 | n/a | −2.9 | Anderson et al. (1998a,b) |
| | | | | n/a | −12 | −2 | Murata and Takizawa (2003) |
| **Central Basin** | 4,489,000 | 2,748 | 2 to 30 | < −1 to −3 | −6 to −19 | Bates et al. (2006a) |
| | | | | −66 to −199 | −66 | Bates and Mathis (2009) |
| | | | | −129 ± 65 | −70 ± 65 | Anderson et al. (1990) |
| | | | | −70 ± 65 | −110 | Lundberg and Haugen (1996) |
| | | | | −24 ± 17 | −41 ± 18 | Anderson et al. (1998b) |
| | | | | −31 | −31 | Kaltin and Anderson (2005) |
| | | | | −66 to −199 | −66 to −199 | Bates and Mathis (2009) |
ocean acidification. As observed at several open-ocean time series stations, the uptake of anthropogenic CO₂ has already decreased surface water pH by 0.1 units. Intergovernmental Panel on Climate Change (IPCC) scenarios, based on present-day CO₂ emissions, predict a further decrease in seawater pH by 0.3 to 0.5 units over the next century and beyond (Caldeira and Wickett, 2004; Fabry et al., 2008) and increased CaCO₃ dissolution. The Arctic Ocean is particularly vulnerable to ocean acidification due to relatively low pH and low temperature of polar waters compared to other waters (Orr et al., 2005; Steinacher et al., 2009) and low buffer capacity of sea ice meltwaters (Yamamoto-Kawai et al., 2009). In the Arctic Ocean, potentially corrosive waters are found in the subsurface layer of the central basin (Jutterström and Anderson, 2005; Yamamoto-Kawai et al., 2009; Chierici and Fransson, 2009), on the Chukchi Sea shelf (Bates et al., 2009), and in outflow waters of the Arctic found on the Canadian Arctic Archipelago shelf (Azetsu-Scott et al., 2010). On the Chukchi Sea, waters corrosive to CaCO₃ occur seasonally in the bottom waters, with unknown impacts to benthic organisms. The seasonally high rates of summertime phytoplankton primary production in the Chukchi Sea drive a downward export of organic carbon that is remineralized back to CO₂, which in turn increases pCO₂ (and decreases pH) of subsurface waters. Such seasonal biological influence on the pH of subsurface waters amplifies existing impacts of ocean acidification induced by the uptake of anthropogenic CO₂ over the last century (Bates et al., 2009). Given the scenarios for pH changes in the Arctic, the Arctic Ocean, and adjacent Arctic shelves, including the western Arctic, will be increasingly affected by ocean acidification, with potentially negative implications for shelled benthic organisms as well as those animals that rely on the shelf seafloor ecosystem.

CONCLUSIONS
The continental shelves and central basin of the Pacific sector of the Arctic Ocean generally have lower surface CO₂ content than the atmosphere. At present, although seasonal sea ice cover provides a barrier to atmosphere-ocean gas exchange, the Arctic Ocean is a sink for CO₂, taking up about 65 to 175 Tg of carbon per year (Bates and Mathis, 2009), contributing perhaps 5 to 14% to the global balance of CO₂ sinks and sources (Takahashi et al., 2002, 2009). The Chukchi Sea is a large ocean sink for CO₂ during the brief summertime sea ice-free period and contributes nearly one-third to one-half of the CO₂ sink in the Arctic, with the Barents Sea the other dominant shelf region for air-sea CO₂ exchange. There are, however, localized areas of surface seawater that are highly influenced by sea ice melt and river inputs where the opposite is observed, and these areas are potential sources of CO₂ to the atmosphere (e.g., East Siberian Sea). On the Siberian and Beaufort Sea shelves, river inputs of terrestrial organic carbon contribute to net heterotrophy (e.g., Macdonald et al., 1998; Anderson et al., 2010, 2011) and sustained release of CO₂ to the atmosphere on these Arctic “interior” shelves. Arctic Ocean CO₂ chemistry is strongly influenced by physical and biological processes, including seasonal marine phytoplankton photosynthesis and growth during summertime sea ice retreat toward the pole, temperature effects (both cooling and warming), shelf-basin exchanges, formation of dense winter waters, and river inputs of freshwater and land-based carbon. Indeed, terrestrially derived DOC supplied to the Arctic shelves and central basins appears much more labile and susceptible to remineralization back to CO₂ than previously thought (e.g., Hansell et al., 2004; Holmes et al., 2008; Alling et al., 2010; Letscher et al., 2011), with a longer-term potential of contributing to reversing the CO₂ sink status of the Arctic. The Arctic Ocean will likely exert greater influence on the global carbon cycle in the coming decades, with the marine carbon cycle and atmosphere-ocean CO₂ exchanges sensitive to both regional and global climate transitions and feedbacks. The capacity of the Arctic Ocean to uptake CO₂ appears to be changing in response to climate and environmental change such as sea ice loss, Arctic warming, and increased inputs of terrestrially derived organic carbon. Finally, in response to increased marine phytoplankton growth and uptake of human-produced CO₂, the seafloor ecosystem of the Arctic shelves already appears affected by ocean acidification, particularly those species that produce CaCO₃ shells or skeletons.

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