Carbon Biogeochemistry of the Western Arctic: Primary Production, Carbon Export and the Controls on Ocean Acidification

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Introduction

The Pacific sector of the western Arctic Ocean (**Figure 1**) is now in a state of rapid transition, with potentially significant economic, social and environmental consequences. These changes are best exemplified by the marked warming and reduction in the thickness, extent, and seasonal persistence of ice cover witnessed in instrumental records over the last 30 years (e.g., Serreze et al., 2007; Maslanik et al. 2007; Serreze et al., 2009). Sea-ice reduction is occurring more rapidly than predicted by global climate models (Stroeve et al., 2007; IPCC, 2007; Polyak et al., 2010; Holland et al., 2010). The mismatch between observations and models requires better synthesis to forecast variability in sea ice cover under future carbon dioxide (CO_2) emission/warming scenarios, and feedbacks on and with regional and global carbon cycle budgets. For example, observed changes in sea-ice cover impact the physical, chemical, and biological environments of established ecosystems as well as the terrestrial and atmospheric boundary conditions (e.g., via coastal erosion and ocean-atmosphere CO_2 flux). There is a growing consensus that the Arctic is passing 'tipping' points and exceeding ecological thresholds (Grebmeier et al., 2006; Wassmann et al., 2008; Andersen et al 2009; Sommerkorn and Hassol, 2009). In this new state, physical, chemical, and biological linkages and feedbacks within the ocean-ice-atmosphere system are to a large extent unknown. Therefore, it is now more critical than ever to synthesize existing emerging datasets to provide context for the regional carbon system as the environment transitions to a new state.

The Arctic Ocean and adjacent polar continental shelf seas (**Figure 1**) play an important role in the cycling of carbon, nutrients, and radiatively-important gases such as CO_2 and methane (CH_4) (e.g. McGuire et al., 2010). Due to complex interactions and feedbacks (**Figure 2**), this region is particularly sensitive to atmosphere-ocean-sea-ice physical forcing (Overland and Wang, 2005; Wang et al., 2005), and ocean ecosystem changes such as the "greening" of the Arctic (Arrigo et al., 2008) associated with warming temperatures (e.g. Serreze et al., 2009) and sea-ice loss (Moritz and Perovich, 1996; Grebmeier and Whitledge, 1996; Manabe and Stouffer, 2000). For example, average temperatures in the Arctic have increased over the last century at nearly twice the global average (IPCC 2007), while sea ice extent has decreased on average by 2.7% per decade (Cavalieri et al., 2003; Rothrock and Zhang, 2005; Stroeve et al., 2005). However, since 2007, the pace of sea-ice decline has accelerated beyond model predictions

(Stroeve et al., 2007; Overland and Wang, 2007; Holland et al., 2006; Winton, 2006; Maslanik et al., 2007; Shimada et al., 2007) with sea-ice extent declining by more than 20-25% (an additional loss of ~1.2 million km2) and predictions of summertime ice free conditions within a few years to a couple of decades (e.g., Wang and Overland, 2009).

The potential responses and feedbacks of the regional carbon cycle (**Figure 2**) to climate change is a critically important component of past (e.g., Sarmiento and Wofsy, 1999; Wofsy and Harriss, 2002; Doney et al. 2004; Denning et al. 2005) and new (Michalak et al., 2011) carbon cycle science plans as well as regional efforts such as the North American Carbon Project (NACP). This importance stems from the vast reservoirs of terrestrial and marine carbon in the Pacific-Arctic Region (PAR) (McGuire et al., 2006; 2009; 2010). Freshwater inputs(Peterson et al., 2002; Wu et al., 2005; Serreze et al. 2006; Waddington and Roulet, 1997), fluxes of dissolved organic carbon (DOC) (Dittmar and Kattner, 2003; Benner et al. 2003), particulate organic carbon (POC) (Guo et al., 2004) and dissolved inorganic carbon (DIC) to the PAR shelves are disproportionately large (Opsahl et al., 1999) compared to other basins (McGuire et al., 2009), and the responses of these carbon stocks and fluxes to projected climate change is highly uncertain under projected rapid changes in sea-ice cover and increased fluxes of glacial and fluvial source waters. Warming, sea-ice loss, "greening" of the Arctic and changes in physical circulation, stratification and freshwater inputs are arguably the most important potential drivers on the carbon cycle but there are multiple synergistic processes at play (Bates and Mathis, 2009; see **Figure 2**). The loss of sea-ice has the potential to increase the CO_2 sink in the region (e.g. Jutterstrom and Anderson, 2010; Bates et al., 2010) to globally significant rates (~5-12% of global; Bates and Mathis, 2009). However, these shelves are highly variable in their CO_2 sink or source status. Adding complexity to such assessments is that the 2007 sea-ice loss event may have reset the Arctic's capacity to absorb CO_2 (Cai et al., 2010) and that "greening" of the Arctic, and warming/other physical changes have opposite impacts on CO_2 sink or source potential of the Arctic Ocean (Bates and Mathis, 2009). Furthermore, the uptake of anthropogenic CO_2, river/glacial inputs and sea-ice melt also appear to be amplifying the impact of ocean acidification on the saturation states of calcium carbonate ($CaCO_3$) minerals in the Pacific-Arctic region (e.g., Steinacher et al., 2008; Bates and Mathis, 2009; Yamamoto-Kawai et al., 2009; Mathis et al., in press; Mathis et al., in review). It is thus critical to gain a better understanding of the interactions and feedbacks of the ocean carbon cycle to freshwater, sea-ice

dynamics, climate and environmental change in this region. But significant gaps and uncertainties remain that limit our understanding of the PAR carbon sources and sinks and the linkages and feedbacks between carbon and climate.

The gateway fluxes of carbon as well as the atmosphere-terrestrial-ocean exchanges are discussed in the previous chapter (Cai et al., this book). Here, the focus will be on the internal water column processes that impact the distribution and cycling of carbon in the PAR. The discussion starts with primary production and its contribution to the dissolved and particulate pools of carbon as well as the associated fluxes and fate of each. This is followed by a discussion of microbial remineralization of organic carbon in the water column and the role that sediments play in processing and storing carbon. Finally, we discuss the controls and potential impacts of ocean acidification in the PAR.

Primary Production

Over the past several decades, higher temperatures have decreased the extent of sea-ice cover as well as its thickness in the Arctic Ocean. Because of this, the overall amount of perennial sea ice, especially in the western Arctic Ocean, has been reduced (Perovich et al., 2009). The reduction of seasonal ice and reduced ice cover has altered several important processes, such as the depth of mixing, stratification, light penetration, nutrient supply, temperature-related processes, and possibly photochemical reactions (Tremblay et al., 2008; Codispoti et al., 2009; Lee et al., 2010). These recent changes in climate and ice conditions could change the patterns and the total amount of carbon production from phytoplankton (**Figure 2**), with unknown consequences to higher trophic levels. However, there is some controversy as to whether changing climate conditions enhance or reduce the overall production in the Arctic Ocean. Since the responses of phytoplankton production to current environmental conditions are variable in different regions, three main regions of the western Arctic Ocean – the northern Bering Sea, Chukchi Sea, and the deep Canada Basin - were separated by their geographical locations.

Northern Bering Sea

The northern Bering Sea (**Figure 1**) is a seasonally ice-covered shelf that is strongly influenced by the advection of cold, nutrient-rich Pacific water from the edge of the deep Bering

Sea basin (Springer 1988; Grebmeier et al. 2006a). Recently measured inorganic carbon uptake rates ranged from 0.1 to 3.9 g C m^{-2} d^{-1} (mean ± S.D. = 1.1 ± 1.2 g C m^{-2} d^{-1}) and from 0.2 to 2.0 g C m^{-2} (mean ± S.D. = 0.9 ± 0.6 g C m^{-2} d^{-1}) (south and north of St. Lawrence Island), respectively. These data were recorded in 2007 (**Figure 3**; Lee et al., 2011), based on a 15-h photoperiod (Hansell and Goering 1990) and hourly uptake rates. For comparative purposes, the annual primary production was estimated assuming a 120-day growing season in this region (Hansell et al. 1993; Sambrotto et al. 1984; Mathis et al., 2010). The estimated annual phytoplankton production based on the average daily rate was only 120 g C m^{-2} (based on an average daily production rate of about 1.0 g C m^{-2} d^{-1} considering the whole cruise period in 2007). These estimated annual rates are two to three times lower than those in previous studies in the northern Bering Sea done more than a decade ago (250-470 g C m^{-2} - see Hansell and Goering 1990; Springer and McRoy 1993; Springer et al. 1996). Recently, Grebmeier et al. (2006b) found that geographic displacement of marine mammal populations coincided with a reduction of benthic prey populations in the region from 1988-2004. They hypothesized that ecosystem change and declining productivity are reducing food supply to benthic prey, thus affecting apex predators (Grebmeier et al. 2006b). The recent lower phytoplankton production and subsequent decline of benthic biomass might partly be due to a decrease in the phytoplankton biomass transported from lower latitudes, because the amount of phytoplankton production largely depends on the carbon biomass (Lee et al., 2011). Since northward flowing waters in the northern Bering Sea originate from the Pacific Ocean (Danielson et al. 2006), a decline of phytoplankton biomass transport from lower latitudes in the Bering Sea could cause a decrease in phytoplankton production in the higher latitudes of the Bering Sea (Lee et al., 2011).

Chukchi Sea

Northward flow of water through the narrow, shallow (< 50 m) Bering Strait results in characteristic water mass distributions of the shelf regions of the southern Chukchi Sea (Coachman et al. 1975; Walsh et al. 1989). The inflow carries three water masses or branches, into the Chukchi Sea (Coachman et al., 1975): Anadyr Water (AW) in the west, Bering Shelf (BS) water in the central system and the Alaska Coastal Current (ACC) in the east. AW supplies the Chukchi continental shelf with high nutrients that promote abundant phytoplankton growth throughout the summer and transports oceanic zooplankton onto the northern shelf (Sambrotto et

al. 1984; Springer et al. 1989; Springer and McRoy 1993). The location and direction of the three water masses moving through the Bering Strait have a strong influence on the physical conditions, nutrient concentrations, and phytoplankton communities observed in this important gateway to the Arctic Ocean (Springer and McRoy 1993; Lee et al. 2007). For example, Lee et al. (2007) found two distinctly different size compositions of phytoplankton communities in the different water masses in the Chukchi Sea. Large phytoplankton (> 20 μm) contributed about 42 % of total phytoplankton biomass in the ACW, whereas they are dominant (about 94 %) in AW (Lee et al. 2007).

In previous studies, Sambrotto et al. (1984) estimated an annual production of 324 g C m^{-2}, based on the nitrate utilization rate, while Hansell et al. (1993) calculated 576-720 g C m^{-2} for annual production in the western Anadyr flow north of the Bering Strait based on new production in the region. Based on ^{14}C uptake and chlorophyll-a concentrations in the region, Springer and McRoy (1993) estimated an annual production of 470 g C m^{-2}. These rates are unusually large considering the high latitude Arctic location (Sambrotto et al. 1984). However, Lee et al (2007) recently found much lower rates in the region (**Figure 3**), based on data from 2002 to 2004. The daily carbon uptake rates in these years ranged from 0.1 g C m^{-2} d^{-1} to 3.6 g C m^{-2} d^{-1} with a mean of 0.7 g C m^{-2} d^{-1} (S.D. = ± 0.9 g C m^{-2} d^{-1}) (Lee et al. 2007). The estimates of production in the southern part of the Chukchi Sea during late July to August from previous studies were 1.7 g C m^{-2} d^{-1} with a range from 0.4 to 4.7 g C m^{-2} d^{-1} (Korsak 1992) and 1.6 g C m^{-2} d^{-1} with a range from 0.2 to 5.5 g C m^{-2} d^{-1} (Zeeman 1992). Only in the southern part of the Chukchi Sea did, Lee et al. (2007) find 0.6 g C m^{-2} d^{-1} with a range from 0.1 to 1.5 g C m^{-2} d^{-1}, which is less than half of the values from the previous studies. The daily production in the southern Chukchi Sea measured by this study was somewhat lower than the rate (0.8 g C m^{-2} d^{-1}) on the northeastern shelf region reported by Hill and Cota (2005). Although the production range (0.1-1.0 g C m^{-2} d^{-1}) from Hameedi (1978) is similar to the range of Lee et al., (2007), production was measured in the marginal ice zone of the northern Chukchi Sea during summer, rather than open water. The physical and chemical structures and thus production could be different in the water column of these two contrasting environments.

Based on a 100-day growing season, the recent annual production of phytoplankton was between 10 to 150 g C m^{-2} with a mean of 73 g C m^{-2} for the southern Chukchi Sea, while the mean annual production for the whole Chukchi Sea including the northwestern part was

somewhat lower (55 g C m^{-2}) (Lee et al. 2007). In comparison, the estimated averages of annual primary production rates for the whole Chukchi Sea are 148 and 170 g C m^{-2} from Zeeman (1992) and Korsak (1992), respectively. Although the average values of their production rates are comparable to the highest values in the study of Lee et al. (2007), the recent average annual production is 2 or 3 times lower than the previous estimates. The average production based on an interval of 120 days is estimated at 144 g C m^{-2} y^{-1} by Lee et al. (2007) which is still lower than that estimated by Hansell et al. (1993) (576-720 g C m^{-2} y^{-1}) or Sambrotto et al. (1984) (324 g C m^{-2} y^{-1}). The recent lower rates might be the result of seasonal, annual, and/or geographical variations in primary productivity in the Chukchi Sea. Those variations are well known in this area and are mostly attributed to different water masses and thus nutrient concentrations (Springer and McRoy 1993; Springer 1988; Hansell and Goering 1990). The lower production might be an indication of the recent decline in primary production of lower latitude regions in the Bering Sea. Gregg and Conkright (2002) found that chlorophyll-a concentrations decreased in the North Pacific from 1979-1986 to 1997-2000 period, suggesting that the decline in productivity may be a region-wide occurrence. However, more seasonal and annual measurements will be necessary to determine whether the recently detected decrease in phytoplankton productivity provides a common seasonal or intraannual variation or an overall trend in the northern Bering Sea and the Chukchi Sea.

Deep Canada Basin

The Canada Basin (**Figure 1**) represents one of the deepest parts of the Arctic Ocean and is covered with sea ice for most of the year. Pelagic primary production has been estimated rarely in this region (Cota et al. 1996; Gosselin et al. 1997; Chen et al. 2003; Lee and Whitledge 2005; **Figure 3** - Lee et al., 2010). As in the Bering and Chukchi Sea, recent rates of primary production in the Canada Basin are higher than those previously measured (Apollonio 1959; English 1961; Pautzke 1979).

In general, chlorophyll-a at surface is very low (<0.2 mg Chl a m^{-3}), whereas the relatively higher concentrations (<1 mg Chl a m^{-3}) of the deep chlorophyll maximum layer is prominent between 40 to 60 m water depths depending on season (Lee and Whitledge 2005; Lee et al. 2010). The maximum photosynthetic rates were co-located with the chlorophyll maximum (Lee and Whitledge 2005). Primary production rates in the open water ranged from 79 to 145 mg

C m^{-2} d^{-1}, with a mean of 106 mg C m^{-2} from mid-August to early September 2002. These rates are much lower than those estimated in the eastern Canadian Arctic. which were 227-450 mg C m^{-2} (Grainger 1975; Harrison et al. 1982), but comparable to those from a recent study in the Canada Basin (Cota et al. 1996). The rates below snow covered sea ice are much lower than those in open waters due to low light intensity. Production below sea ice of 2.3 m thickness ranged from 2.6 to 26.8 mg C m^{-2} d^{-1}, with a mean of 11.3 mg C m^{-2} in a study by Lee and Whitledge (2005). In comparison, the rates under thinner sea ice (1.5 m) ranged from 20.4 to 178.3 mg C m^{-2} d^{-1} in the Canada Basin from 27 June to 26 July 2005, with a mean of 59.5 mg C m^{-2} d^{-1} (Lee et al. 2010). This was significantly higher than found under thicker sea ice in 2002 (Lee and Whitledge 2005). Higher averaged particulate organic carbon and chlorophyll-a (POC/Chl-a) and particulate organic nitrogen (PON/Chl-a) of phytoplankton in 2005 compared to 2002 indicate that phytoplankton were less light limited in 2005 (Lee et al. 2010). In fact, Gosselin et al. (1997) found that the mean daily carbon uptake rate of phytoplankton was 35 mg C m^{-2} d^{-1} under a sea ice thickness of about 2.0-m in the Canada Basin from 26 July to 26 August 1994.

Since there are seasonal and interannual changes in the photosynthetic rates in the Arctic Ocean (English 1961; Pautzke 1979), annual primary production must be estimated with caution. However, for a comparison purpose, the annual carbon production can be roughly estimated with the assumption of a 120-day growing season in the Arctic (Subba Rao and Platt 1984; Gosselin et al. 1997; Lee and Whitledge 2005). The annual carbon production rate of phytoplankton under a mean sea-ice thickness of 1.5 m can range from 2.5 to 21.4 g C m^{-2}, with a mean of 7.1 g C m^{-2} in the Canada Basin in 2005 (Lee et al. 2010). This mean rate under sea ice is comparable with that in the open water column (8.9 g C m^{-2}) (Cota et al. 1996). Compared with a previous study, the under-ice productivity in 2005 is about one order of magnitude greater than that estimated by English (1961) (about 0.6 g C m^{-2}) under 2.5–3.0 m pack ice in the central Arctic Ocean several decades ago. If portions of ice algal production and the release of extracellular carbon are added to the total (Gosselin et al. 1997), the annual rates of primary production under-ice in the Canada Basin will be higher than the estimation of Lee et al. (2010).

The decreasing sea-ice thickness in the Canada Basin (Rothrock et al. 2003; Nghiem et al. 2007; Perovich and Richter-Menge 2009) might be favorable for increased phytoplankton

growth under the sea ice because light intensity governed by different sea-ice thicknesses is one of the most important factor affecting phytoplankton production in the Canada Basin (Lee and Whitledge 2005; Lee et al., 2010). However, phytoplankton adapted to low-light conditions under sea ice would show different effects if the sea ice cover melted away in the Arctic Ocean. In fact, nutrients were shown to be the main limiting factors for phytoplankton production rates at the surface in open waters, whereas light was the major limiting factor at the chlorophyll maximum layer just above the pycnocline in the Canada Basin (Lee and Whitledge 2005). Codispoti (2009) also found the biological production rates to be low because of limited availability of nutrients in their SBI (Western Arctic Shelf-Basin Interaction) studies. More seasonal and annual data under a variety of environmental conditions in different regions should be obtained to improve the understanding of primary production processes in the Arctic and marine ecosystem responses to recent ongoing changes in sea-ice conditions in the Arctic Ocean.

The varying degree and spatial distribution of primary production in the Pacific-Arctic Region plays a strong role in determining the concentrations of organic matter and export of particles from the surface. Each of these processes and their impact on carbon distribution in the water column will be discussed independently.

DOC Production

An estimated 9 Pg of carbon reside in the Arctic Ocean as DOC (McGuire et al., 2009), or <2% of the 662 Pg global DOC inventory (Hansell et al., 2009). An interesting feature in the system, however, is that DOC in the surface ocean has a very strong terrigenous signature (Wheeler et al., 1997; Opsahl et al., 1999), due to the Arctic Ocean being a relatively small basin receiving disproportionate fractions of global river runoff (~10%) and terrigenous DOC (tDOC) export (~13%) (Stein and Macdonald, 2004). Ten to 20% of global vegetative carbon, and up to half the global inventory of upper-soil organic carbon, resides in the Arctic watersheds (Dixon et al., 1994; Zhulidov, 1997; McGuire et al., 2009). Because of Arctic water entrainment into the deep North Atlantic, a potential (but unquantified) route exists for this terrigenous DOC to be transported to and sequestered in the ocean interior (Benner et al., 2005), unlike other regions of the global ocean. Hence, consideration of the terrigenous pool is included in most studies of Arctic DOC.

This section briefly considers controls on DOC concentrations in the western Arctic Ocean. Emphasis is on the allochthonous (terrigenous) inputs and marine consumption of tDOC. Excellent reviews of DOC in the Arctic carbon cycle, including fluvial and marine influences, can be found in Anderson (2002), Dittmar and Kattner (2003), and Amon (2004). Those works include consideration of organic composition, colored dissolved organic matter (CDOM), and the eastern Arctic, issues not addressed here.

Spatial Variability

The distribution of DOC in the surface layer of the Arctic Ocean is shown in **Figure 4**. DOC concentrations are low in marine waters entering the Arctic: <60 μmol kg^{-1} in surface North Atlantic waters (**Figure 4**) and similar values in the far North Pacific (Hansell et al., 2009). DOC is added to these marine waters as they invade the Arctic Ocean shelves, both by autochthonous and allochthonous processes (Shin and Tanaka, 2004; Amon, 2004; Mathis et al., 2007). The DOC concentrations are highest near the outflows of the major rivers on the shelves of the Eastern Arctic, with concentrations >300 μmol kg^{-1} observed over relatively large areas, having been enriched with DOC of a terrigenous source (tDOC). Remnants of those tDOC-enriched waters leave the shelf to form the Transpolar Drift (Letscher et al., 2011), thus delivering elevated DOC waters to the central Arctic basins; note the elevated DOC (>100 um/kg) aligned with the dateline in **Figure 4**. These high concentrations, and the responsible shelf-to-basin export of tDOC, were noted by Wheeler et al. (1997) and Bussmann and Kattner (2000). Similar enrichments occur on the western shelves, but to a lesser degree due to lower initial tDOC concentrations in the western rivers and lower flow (Cooper et al., 2008). Concentrations can be >100 μmol kg^{-1} in the interior of Norton Sound, reflecting drainage of the Yukon River. Similar concentrations exist near the mouth of the Mackenzie River. Note, though, that DOC concentrations are much more elevated further into the mouths of all rivers, relative to concentrations shown in **Figure 4** (e.g., DOC >300 μmol kg^{-1} near the mouth of the Mackenzie River; Guéguen et al., 2005). Based on these distributions, it appears that the tDOC surviving shelf circulation of 2-5 years in the east is exported to the deep Arctic, with eventual export (after another 2-5 years; refs) via Fram Strait as the East Greenland Current (DOC > 80 μmol kg^{-1} along the east coast of Greenland). Western tDOC, in contrast, is largely transported along-shelf for eventual export through the Canadian Archipelago. Some of the western tDOC is mixed into

the Beaufort Gyre for decadal circulation and mineralization (Hansell et al., 2004), resulting in concentrations of <60 μmol kg^{-1}, the lowest observed in the surface Arctic Ocean.

As can be inferred from the distributions in **Figure 4** and as suggested by Opsahl et al. (1999), the fraction of bulk DOC present as tDOC varies widely throughout the system. For example, at the shelf break in the Chukchi sea during spring 2002 (prior to major sea ice melt), DOC concentrations (normalized to a salinity of 33, indicative of Pacific water) reached ~90 μmol kg^{-1} at a salinity of 29. If there was no tDOC present, the normalized DOC concentration would equal that in the marine fraction alone (the Pacific waters had ~65 μmol kg^{-1}). The difference in concentrations is the tDOC present; in this case, 90 – 65 = 25 μmol kg^{-1}, or ~38% of the total DOC was tDOC. In contrast, in higher salinity (essentially purely marine) surface waters, where measured DOC was ~65 μmol kg^{-1}, none of the DOC was terrigenous. All waters sampled in the Chukchi system fell within this range (0-38%). Kattner et al. (1999) estimated that ~60% of the DOC in the surface layer of the Laptev Sea is of terrigenous origin. As these systems are constantly mixing low salinity, high tDOC fluvial waters with high salinity, low tDOC marine waters, the contribution of tDOC will vary as a function of salinity and time elapsed since the tDOC entered the marine system.

The Use of DOC/salinity Relationships

Because of this constant mixing of distinct waters, DOC-salinity relationships are commonly employed in studying DOC dynamics of the system. The apparent linearity in the correlation between the two variables led a number of studies to conclude that tDOC is highly conserved as it is mixed into the Arctic Ocean. In fact, tDOC does appear to be well conserved upon initial mixing with marine waters, showing neither quick removal by biological mineralization nor by flocculation (Amon, 2004). Once tDOC is delivered to the shelf system though, and enough time passes (a few years), then the non-conservative nature of tDOC becomes evident (Hansell et al., 2004; Cooper et al., 2005). The use of salinity/DOC relationships is fraught with difficulties (complicating signals from sea ice formation and melt, as well as brine formation and export), so these must be recognized in order to consider the associated uncertainties.

Salinity-DOC regressions observed in the western Arctic are shown in **Figure 5**. During late spring, prior to major sea ice melt, the negative correlation demonstrates a clear linearity (**Figure 5a**). The marine end member is Pacific water of salinity near 33 and DOC ~65 μmol kg^{-1} (waters at higher salinity are subsurface Atlantic waters, which are not involved in the mixing discussed here), while the freshwater end member is river water (effective salinity of ~0). The western Arctic rivers, particularly the Mackenzie and the Yukon, drive the low salinity end of the regression (relevant river end member characterizations available in Cooper et al., 2008). Note that unlike coastal systems in the lower latitudes, where the low salinity/high DOC meteoric waters are present along the coast and marine waters are offshore, in the western Arctic the low salinity waters (in this regression) are in the Beaufort Gyre (over the deep Canada Basin) and the higher salinity waters are over the shelf. While the low salinity waters hold the most tDOC, they are also (in these data) the oldest waters (time since entering the shelf system).

Interpretation of the data in **Figure 5** is demonstrated in **Figure 6**. The immediate (initial) mixing of river and marine end members results in a linear and negative correlation. The zero-salinity intercept indicates the tDOC concentrations in the source river. As tDOC is removed, the relationship depicted by the dashed curve emerges. The entirety of the dashed curve can never be observed though because the river water, as it ages, is continuously mixed with marine water, thereby constantly diluting the riverine signal while surface currents carry it away. The remnant of the regression (i.e., the observable portion of the theoretical dashed line is labeled "observed" in **Figure 6a**) is what we observe in nature (**Figure 5a**). It is only over a short salinity range that the regression survives. Extrapolation of that short line back to the zero-salinity intercept (arrowed, dotted line in **Figure 6**) estimates the tDOC (normalized to zero salinity) still present in the riverine fraction. The difference between the initial river value and the final observed value (determined by extrapolation) is the amount of tDOC that has been removed. Transient tracers of time, such as the $^{228}Ra/^{226}Ra$ ratio (Kadko and Muench, 2005), are employed to determine the rates of tDOC removal (Hansell et al., 2004; Letscher et al., 2011).

The relationship shown in **Figure 5a** exists during winter and spring, when the system is relatively simple. As summer develops, other processes can dominate the signal. High river runoff, high primary production, and strong sea ice melt make the system much more complex. Some of these impacts are shown in **Figure 5b**, which is the DOC-salinity relationship in the

same western Arctic system as in **Figure 5a**, but during summer. Some parts of the regression in **Figure 5a** are evident (such as at salinity >32), but lower salinity waters are highly impacted by the large input of river water associated with seasonal thawing of the watershed and by sea ice melt. The newly added river water is evident as elevated DOC (>100 μmol kg^{-1} in **Figure 5b**), the regression of which against salinity would intercept zero-salinity at very high DOC concentrations. The melting of sea ice similarly lowers the salinity, but as its DOC concentrations are low (Mathis et al., 2005), the DOC concentrations are lowered, such that a regression against salinity has a very low zero-salinity intercept. Evaluating regressions between DOC and salinity must be done with full understanding of the conflicting processes impacting the relationships.

The impacts described above focus on those occurring at the low salinity end of the regressions. Impacts from variations within the marine end member need to be considered as well. One important consideration is the impact on the regressions of the *in situ* production of marine DOC within marine waters. Net DOC production occurs at ~10% of net community production (NCP) in the western Arctic (Mathis et al., 2007), consistent with findings elsewhere (Hansell and Carlson, 1998). NCP, in turn, is dependent on the amount of new nutrients in a system. In the western Arctic, new nutrients are at very low concentrations in low salinity waters (such as in the surface layer of the Beaufort Gyre), so *in situ* production probably has the least impact there (where tDOC is still a large signal). The highest concentrations of new nutrients are in the Pacific water, so to the extent those nutrients are consumed, seasonal DOC accumulation will result. This situation is depicted in **Figure 6b**, where the DOC/salinity relationship should be taken as that observed in the system (i.e., as in **Figure 5a**, but not as in the full salinity scale, depicted in **Figure 6a**). Nitrate is very low at the low salinity end, but elevated in the marine end. *In situ* production occurs during spring and summer when light is adequate, giving another reason for using the early spring data (**Figure 5a**) rather than summer data (**Figure 5b**). One further unknown is the extent to which the DOC produced *in situ* each summer resists degradation through the succeeding winter, such that there is a long term accumulation of the material. If there is interannual accumulation, then the marine end of the regression (depicted in **Figure 6b**) will be elevated relative to its true initial condition. This will reduce the slope of the regression, giving a lowered estimate for tDOC in the riverine fraction.

A final process that may impact the regressions is sea ice formation. Amon (2004) covered this topic well, so it will only be touched on here. As sea ice forms, high density brine is formed from the extruded salt. The brine is enriched with DOC as well, so the fate of the brine solution is important in considering the impact of this DOC on the system. If the brine sinks below the pycnocline, the process removes DOC from the surface layer. If it sinks only into the mixed layer, but not below or into the pycnocline, then the DOC is retained and the initial conditions are perhaps re-established with subsequent ice melt and vertical overturn of the surface layer. Both Schaure (1997) and Amon (2004) estimated that the salinity increase in brine produced in the eastern Arctic was inadequate for raising the density such that those waters break through the pycnocline. If brine impacted waters become decoupled from the region of ice melt, then a more unidirectional impact is expected. This issue needs to be further investigated.

Dynamical Characterization of tDOC – Inputs & Sinks

Large standing stocks of organic carbon in high-latitude soils and peatlands account for as much as 50% of global soil carbon (Dixon et al., 1994; Zhulidov, 1997). Total input of tDOC to the Arctic Ocean is 25–36x10^{12} gC/yr, with the Mackenzie (1.4x10^{12} gC/yr) and Yukon (1.7x10^{12} gC/yr) Rivers dominating input to the western Arctic (Raymond et al., 2007), together adding ~10% of the total tDOC input to the Arctic Ocean. The tDOC yield of a watershed (gC m^{-2} yr^{-1}) is dependent on the water yield (m^3 m^{-2} yr^{-1}) (Raymond et al., 2007), such that an increase in the hydrologic cycle over Arctic watersheds (Savelieva et al., 2000; Peterson et al., 2002) may well increase the tDOC export from those systems (Walvoord and Striegl, 2007). Interannual variability in watershed runoff, then, will largely control variability in DOC export. The highest DOC concentrations in Arctic rivers coincide with the spring freshet (**Figure 7**), when highest discharge occurs (Finlay et al, 2006; Holmes et al., 2008; Spencer et al., 2008). Compositional changes occur in the DOC pool of high latitude rivers over the seasonal cycle (Neff et al., 2006; Guo et al., 2007; Striegl et al., 2007), reflecting the changing magnitude of sources.

The material that is exported is very young compared to marine DOC (Benner et al., 2004; Guo et al., 2007; Raymond et al., 2007). Approximately 50% of DOC exported during the arctic spring thaw is 1–5 years old, ~25% is 6–10 years in age, and 15% is 11–20 years old (Raymond et al., 2007). As lability (or reactivity) negatively correlates with age (Raymond and

Bauer, 2001), each DOC age cohort should exhibit a unique removal constant, with the youngest material being removed most rapidly upon export to the coastal system. That multiple fractions of varying lability comprise tDOC in rivers and coastal systems has been suggested (Hopkinson et al., 2002; Moran et al., 1999; Raymond and Bauer, 2000). Holmes et al. (2008) found in Alaskan rivers that DOC exported during the spring freshet was readily removed, while DOC present during lower flow summer periods was more resistant. These distinct labilities suggest that tDOC removal in the ocean may best be described by a multi-compartment model (Letscher et al., 2011), rather than by a reactivity continuum model.

Lignins, a class of macromolecules indicating terrestrial plant residue, is a commonly employed tracer of tDOC in the Arctic Ocean. Opsahl et al. (1999) reported gymnosperm vegetation as its major source in the Arctic. Its concentration correlates well with riverine CDOM (Spencer et al., 2009), its lifetime is such that it is found throughout the surface Arctic (refs), and it has been located in deep North Atlantic waters (Benner et al., 2005), though at very low concentrations. The extent to which lignins conservatively trace tDOC once in the ocean is unknown. The sources of tDOC are wider than gymnosperms, and the degree to which lignins represent each age class of tDOC has not been evaluated.

The marine removal of tDOC has only recently been considered (Hansell et al., 2004; Cooper et al., 2005; Letscher et al., 2011), but its reactivity makes the pool relevant to the ocean carbon cycle. Hansell et al. (2004) reported an approximate carbon mass balance in the removal of tDOC, such that its removal resulted in a like amount of inorganic carbon production in the system. Anderson et al. (2009) interpreted elevated pCO_2 over the Siberian shelf as due to the mineralization of terrigenous organic matter. The surface Arctic Ocean is presently a sink to atmospheric CO_2 (Bates et al., 2006), so an acceleration of tDOC export (and mineralization) in the future could work to partially neutralize that sink.

Export Flux of Particulate Organic Carbon

Wassmann et al. (2003) reported a comprehensive review of the vertical flux of POC in the Arctic Ocean. The major points from their work were that the vertical export of biogenic carbon is poorly resolved based on existing measurements in the Arctic Ocean, and that POC export is derived primarily from the adjacent margins that undergo seasonal decreases in sea-ice extent. They reported that the vertical export POC in the upper Arctic Ocean is highly variable,

ranging from 1.5 – 14 g C m^{-2} y^{-1} at ~200 m water depth. Vertical POC export is typically episodic, depending upon shelf production that surround the Arctic Ocean and in polynyas. Variations in sea-ice extent, light and stratification all impose constraints on the vertical export of biogenic matter, while remineralization of POC flux due to zooplankton grazing results in extensive attenuation of the total vertical POC export.

Wassman et al. (2003) further reported that the deeper regions of the Arctic Ocean are characterized by a greater retention of carbon in the twilight zone, however marginal ice zones (MIZ) can also show this tendency. Over-wintering of large, long-lived zooplankton such as copepods and appendicularians appear to play an important role in vertical flux attenuation. In the decades to come, the dramatic northwards retreat of the MIZ due to global warming will result in a profound widening of the MIZ, represented by an extensive, stratified area that stretches from the shelves far into the deep Arctic Ocean. As a consequence, primary production and vertical export of biogenic matter will increase in the peripheral band of the contemporary permanent ice cover.

Since the review by Wassman et al. (2003), publications appeared that reported results from major field studies of POC export in the upper Arctic Ocean, including the Shelf Basin Interaction II (SBI-II) study in the Chukchi Sea (Lalande et al. 2007; Lepore et al. 2007; Moran et al. 2005), the CABANERA project in the Northern Barents Sea (Lalande et al. 2008), the Canadian Arctic Shelf Exchange Study (CASES) over the Mackenzie Shelf (Amiel and Cochran 2008), the comparative study of POC export in the Laptev, northern Baffin Bay and Beaufort Seas (Lalande et al. 2009) and the recent eastern Arctic expedition ARK-XXII/2 (Cai et al. 2010). These studies are summarized in the following sections and the results illustrated in **Figure 8**.

Regional Case Studies

Chukchi Sea: The Shelf Basin Interaction Study (SBI-II)

As part of the 2002 Shelf-Basin Interaction (SBI) process study, measurements of the seasonal variations in the export flux of POC were reported for the upper waters of the Chukchi Sea (Moran et al. 2005). POC fluxes were quantified by determination of $^{234}Th/^{238}U$ disequilibrium and $POC/^{234}Th$ ratios in large (>53 μm) aggregates collected using in-situ pumps.

Samples were collected at 35 stations on two cruises, one in predominantly ice-coved conditions during the spring (May 6-June 15) and the other in predominantly open water during the summer (July 17-August 26). Enhanced particle export was observed in the shelf and slope waters, particularly within Barrow Canyon, and there was a marked increase in particle export at all stations during the summer (July-August) relative to the spring (May-June). ^{234}Th-derived POC fluxes exhibit significant seasonal and spatial variability, averaging 2.9 ± 5.3 mmol C m^{-2} d^{-1} (range = 0.031-22 C mmol m^{-2} d^{-1}) in the spring and increasing ~4-fold in the summer to an average value of 10.5 ± 9.3 mmol C m^{-2} d^{-1} (range = 0.79-39 mmol C m^{-2} d^{-1}). The fraction of primary production exported from the upper waters increases from ~15% in the spring to ~32% in the summer. By comparison, DOC accumulation associated with net community production represented ~6% of primary production (~2 mmol C m^{-2} d^{-1}). The majority of shelf and slope stations indicate a close agreement between POC export and benthic C respiration in the spring, whereas there is an imbalance between POC export and benthic respiration in the summer. An implication of this study is that up to ~20% of summer production (~6 ± 7 mmol C m^{-2} d^{-1}) may be seasonally exported off-shelf in this productive shelf/slope region of the Arctic Ocean.

In 2004, seasonal and interannual changes in POC export and deposition were estimated in the shelf-slope region of the Chukchi Sea using measurements of ^{234}Th-^{238}U disequilibria and the POC/^{234}Th ratio in large (>53-μm) particles (Lepore et al. 2007). These export fluxes were used in conjunction with rates of primary productivity and benthic carbon respiration to construct a POC budget for this shelf-slope region. Samples were collected along a series of shelf-basin transects in the spring (May–June) and summer (July–August) of 2004. These stations were previously occupied during the ice covered (spring) and open water (summer) seasons of 2002, allowing for an interannual comparison of export flux. In contrast to 2002, when open water POC fluxes were significantly higher than in the ice-covered period, POC export fluxes in 2004 were similar during the spring (average = 19.7 ± 24.8 mmol C m^{-2} d^{-1}) and summer (average = 20.0 ± 14.5 mmol C m^{-2} d^{-1}). The high POC fluxes measured during the spring are attributed to a plankton bloom, as evidenced by exceptionally high primary productivity (average = 124.4 ± 88.1 mmol C m^{-2} d^{-1}). The shelf-slope budget of particulate organic carbon indicates that 10–20% of primary productivity was exported below 50 m but was not consumed during benthic carbon respiration or burial and oxidation in underlying sediments. A water column-sediment

budget of ^{234}Th indicates that particulate material accumulates in shelf sediments on a seasonal basis.

A comparative study of POC export flux was conducted in 2004 using both ^{234}Th distributions and drifting sediment traps to quantify POC export in the spring (May 15-June 23) and summer (July 17-August 26) (Lalande et al. 2007). Measurements were obtained at five stations in the Chukchi Sea during the spring cruise and four stations during the summer cruise along Barrow Canyon (BC) and along a parallel shelf-to-basin transect from East Hanna Shoal (EHS) to the Canada Basin. ^{234}Th and POC fluxes obtained with *in situ* pumps and drifting sediments traps agreed to within a factor of 2 for 70% of the measurements. POC fluxes were also measured with sediment traps at 50 m along BC were also similar in both seasons (31.3 ± 9.3 mmol C m^{-2} d^{-1} and 29.1 ± 14.2 mmol C m^{-2} d^{-1}, respectively), but were approximately twice as high as POC fluxes measured with *in situ* pumps. Sediment trap POC fluxes measured along the EHS transect also increased from spring to summer (3.0 ± 1.9 mmol C m^{-2} d^{-1} and 13.0 ± 6.4 mmol C m^{-2} d^{-1}, respectively), and these fluxes were similar to the POC fluxes obtained with *in situ* pumps. Discrepancies in POC export fluxes measured using *in situ* pumps and sediment traps may be reasonably explained by differences in the estimated POC/^{234}Th ratios that arise from differences between the techniques, such as time-scale of measurement and size and composition of the collected particles. Despite this variability, *in situ* pump and sediment trap-derived POC fluxes were only significantly different at a highly productive station in BC during the spring.

Mackenzie Shelf: Canadian Arctic Shelf Exchange Study (CASES)

Amiel and Cochran (2008) assessed both terrestrial and marine POC fluxes in the Mackenzie Shelf as part of the CASES study. Water column deficits of ^{234}Th relative to ^{238}U in the Mackenzie Shelf, Cape Bathurst Polynya, and Amundsen Gulf were used to estimate sinking fluxes of POC. The ^{234}Th fluxes were converted to marine and terrestrial POC fluxes using the POC/Th ratio of filterable particles >70 μm and δ^{13}C measurements to estimate the fraction of marine and terrestrial POC. In June/July 2004, the largest ^{234}Th deficits (0-100 m: 56-95 dpm m^{-2}) were observed in the Mackenize outer shelf. Deficits in the upper 100 m ranged 3 to 59 dpm m^{-2} in the Cape Bathurst Polynya. The d13C values of POC in the >70 μm particles filtered

using in situ pumps ranged from -25.1% to -28%. A two-end member mixing model with marine POC = -21.4% (%) and terrestrial POC = -28% indicates that terrestrial POC is most evident at the Mackenzie Shelf stations but is present throughout the region. The fraction of marine POC ranged from 0 to 59% in the area in June/July 2004, with highest values in the Cape Bathurst Polynya. Fluxes of marine POC in the polynya averaged ~5 mmol C m^{-2} d^{-1} at 50 m in June 2004 and increased to ~ 12 mmol C m^{-2} d^{-1} in July. Comparable fluxes were observed at 100 m in June but values decreased to ~ 6 mmol C m^{-2} d^{-1} at 100 m in July. These fluxes are greater than estimates of organic carbon remineralization and burial in sediments of the polynya (~ 3 mmol C m^{-2} d^{-1}). Amiel and Cochran (2008) suggested that POC may be exported out of the area, effectively remineralized by microbial activity in the twilight zone, or incorporated into biomass.

Laptev Sea, Northern Baffin Bay and the Beaufort Sea Shelves

Lalande et al. (2009) deployed moored sediment traps in 2005-2006 in the Beaufort Sea, Northern Baffin Bay, and the Laptev Sea to compare the annual variability in POC export flux and to evaluate the factors regulating the annual cycle of POC export over these continental shelves. Annual POC fluxes at 200 m ranged from 1.6 to 5.9 g C m^{-2} y^{-1} with the highest export in Northern Baffin Bay and the lowest export over the Mackenzie Shelf in the Beaufort Sea. Each annual cycle exhibited an increase in POC export a few weeks prior to, during, or immediately following sea-ice melt, though varying temporal patterns in export were observed over the remainder of the annual cycle. Enhanced primary production, discharge of the Lena River, and resuspension events contributed to periods of elevated POC export over the Laptev Sea slope. Greater POC fluxes in Northern Baffin Bay reflected periods of elevated primary production in the North Water polynya. In the Beaufort Sea, sediment resuspension contributed to most of the large export events. Lalande et al. (2009) suggested that the outer shelf of the Laptev Sea may sustain the largest increase in POC export in the coming years, due to the large reduction in ice cover and the possible increase in the Lena River discharge. Moreover, the large difference in forcing among the regions investigated reinforces the importance of monitoring POC fluxes in the different oceanographic regimes that characterize the Arctic shelves to assess the response of the Arctic Ocean carbon cycle to interannual variability and climate change.

Eastern and Central Arctic Ocean: *Polarstern* ARK-XXII/2 Expedition

There are still very few direct measurements of POC export under the permanently ice-covered central Arctic Ocean (Moran et al. 1997). During the *Polarstern* ARK-XXII/2 expedition to the eastern and central Arctic Ocean (28 July to 7 October in 2007), a high-resolution study of POC export was conducted using $^{234}Th/^{238}U$ disequilibrium (Cai et al. 2010). Depth profiles of total ^{234}Th in the upper 100-200 m were collected at 36 stations in the eastern and central Arctic Ocean and the Barents, Kara and Laptev Seas. Samples were processed using a small volume MnO_2 co-precipitation method with addition of a yield tracer. The ^{234}Th deficit with respect to ^{238}U was found to be evident throughout the upper 100 m over the Arctic shelves. In comparison, the deficit was confined to the upper 25 m in the central Arctic Ocean. Below 25 m, secular equilibrium was approached between ^{234}Th and ^{238}U. Moreover, in association with the surface ^{234}Th deficit, the total chlorophyll concentration was generally found to be enhanced, indicating that *in-situ* production and export of biogenic particles are the main mechanism for upper ocean ^{234}Th removal in the central Arctic Ocean. ^{234}Th-derived POC fluxes were determined with a steady state model and pump-normalized $POC/^{234}Th$ ratios on total suspended particles collected at 100 m. Results showed enhanced POC export over the Arctic shelves. On average, POC export fluxes over the various Arctic shelves were 2.7±1.7 mmol m^{-2} d^{-1} (the Barents Sea), 0.5±0.8 mmol m^{-2} d^{-1} (the Kara Sea) and 2.9±1.8 mmol m^{-2} d^{-1} (the Laptev Sea), respectively. In comparison, the central Arctic Ocean was characterized by the lowest POC export flux ever reported, 0.2±1.0 mmol m^{-2} d^{-1} (1SD, n=26). This value is very low compared to prior estimates, and is also about one order of magnitude lower than the POC export fluxes reported in other oligotrophic oceans. A ThE ratio (^{234}Th-derived POC export/primary production) of 2% or 6% in the central Arctic Ocean was estimated, depending on the definition of primary production. The low ThE ratio indicates that like other oligotrophic regimes, the central Arctic Ocean is characterized by low POC export relative to primary production, i.e., a tightly coupled food web. This recent study implies that the current role of the central Arctic Ocean in C sequestration is still very limited.

Conclusions

Several field programs conducted in the Arctic Ocean over the past decade have reported new measurements of POC export fluxes based on the determination of $^{234}Th/^{238}U$ disequilibria in the upper waters of the permanently ice-covered interior basins, the seasonally ice-covered

shelf and slope waters, and polynya regimes. These studies consistently indicate particle export from the upper few hundred meters of the water column occurring on a time-scale of days to months. $^{234}Th/^{238}U$ disequilibria observed in the interior basin and shelf-slope environments are attributed primarily to particle settling associated with variations in local primary and secondary productivity. In shelf regimes, resuspension of abiogenic bottom sediments also contributes to $^{234}Th/^{238}U$ disequilibria. As is the case with sediment traps, such processes may lead to biased estimates of the vertical POC export flux.

Taken as a whole, these recent Arctic studies indicate a marked regional variability in upper ocean POC export flux, ranging from 0.3-7 mmol C m^{-2} d^{-1} in the central Arctic Ocean to 0.7-45 mmol C m^{-2} d^{-1} in shelf and polynya regimes. A key issue for future studies is to determine the extent of seasonal variability in POC export, which is likely to be significant when considering the high nutrient concentrations and strong seasonal gradients in light and ice-cover that characterizes the Arctic Ocean. These observations provide the basis for what is likely to be a considerable increase in understanding the factors controlling the temporal and spatial variability in POC export flux in the Arctic Ocean and adjacent seas in the future.

Grazing

As in other oceans, both protists and metazoans are believed to be important grazers of both phytoplankton and heterotrophic microbes in the PAR domain. In general, our impressions of the relative importance of different taxonomic groups is based on extrapolation of their importance in similar ecosystems, modeling exercises, or better-known information such aspects of community composition and biomass (e.g. Carmack & Wassmann, 2006; Carmack et al. 2006). One of the difficulties in extrapolating results from other studies to the PAR is the mosaic of habits it encompasses (Hopcroft et al. 2008): the northern Bering Sea and much of the Chukchi operates as a cold extension of the Pacific Ocean fauna (Hopcroft et al 2010), while other parts of the Chukchi and Beaufort Seas have a fauna of more Arctic character (Darnis et al. 2008; Hopcroft et al. 2010), and the Canada Basin itself has a decidedly oceanic Arctic fauna (Ashjian et al. 2003; Lane et al. 2008; Kosobokova et al. 2010). Interwoven with these is a patchwork of polynas with enhanced productivity and grazing rates (Diebel and Daly 2007).

The actual number of studies directly measuring grazing in the PAR domain is limited for both the protisan microzooplankton (Sherr et al. 1997; Sherr et al. 2008) and metazoans (Diebel et al. 2005; Campbell et al. 2009), although several indirect measurements of community grazing (as vertical flux) exist (i.e. Forest et al., 2007; Seuthe et al. 2007). Additional grazing work was been conducted at the southern PAG fringe during PROBES (i.e. Dagg et al. 1982), but this work - like that in BEST/BSIERP (E. Lessard, RG Campbell, unpublished) - has concentrated primarily on Pacific oceanic species.

Near the shelf break, of the Chukchi Sea, the dominant four copepod taxa (*Calanus glacialis, Calanus hyperboreus, Metridia longa, and Pseudocalanus spp*) remove ~13% d^{-1} of the primary production in spring and 28% d-1 in summer, with wide confidence intervals (Campbell et al. 2009). These copepods removed mostly phytoplankton during the spring bloom, but preyed preferentially on the microzooplankton community at all times (Campbell et al. 2009). The microzooplankton themselves were dominated by aloricate ciliates and heterotrophics dinoflagelllates, both with relatively low growth rates, that consumed on average 22% of primary production, much less than typical for other oceanographic environments, including the Barents Sea (Sherr et al. 2009). Although the bulk of the imbalance must be exported to the benthos, or advected further into the basins (Grebmeier et al. 2009), the grazing impact of larvaceans was not considered.

Larvaceans are important filter-feeders in the PAR communities (Lane et al. 2008), as well as elsewhere in the Chukchi Sea (Hopcroft et al. 2010), especially in the marginal ice zone of both the shelf and basins (Hopcroft, unpublished data). The high grazing rate of larvaceans allows them to consume as much as 20% of the daily primary production in the St Lawrence Island polyna (Diebel et al. 2005) much greater than estimated for the copepods in this case as well as in other Arctic polynas they considered (Diebel and Daly, 2007). While food concentration does typically increase the rates of copepod reproduction (Plourde et al. 2005) and development (Ringuete et al. 2002) in Arctic habitats, larvacean growth rates are typically high compared to copepods (Hopcroft et al. 1998). This is true even for arctic species (Choe & Deibel 2009), proving advantageous in exploiting ephemeral habitats of high-food concentration.

The quantitative impact of other planktonic metazoans – grazers, scavengers and predators – in the transfer and cycling of carbon in the PAR region is largely unknown. A

significant amount of carbon must be lost as it is moved to higher planktonic trophic levels. Nonetheless, the cold temperatures characteristic of the Arctic result in relatively low rates of respiration (e.g. Ikeda et al. 2001) at all planktonic trophic levels, resulting in relatively high biomass given the relatively low annual rates of primary production. Although the period of high primary production may be limited, many of these animals accumulate relatively large stores of lipids during such times that carry them through the winter (often in diapause) and to fuel subsequent reproduction (e.g. Hirche & Kattner 1993). In contrast, the more predatory species may have relatively less seasonality in their prey supply and feeding strategy.

Benthic Carbon

Ice algae and open water production in the spring are key components of the seasonal phytoplankton bloom and the timing of the export of this material to the underlying benthos is critical to growth properties of the infaunal organisms. Zooplankton populations have a limited impact early in the spring, allowing most of the ice edge production to settle ungrazed to the sediment. However, with continued sea ice retreat and seawater warming in the Arctic, seasonal phytoplankton blooms may develop more slowly, allowing zooplankton populations to grow fast enough to graze a large fraction of the new production (Coyle and Pinchuk 2002). Currently early season phytoplankton blooms are more typical in the northern Bering Sea and into the Chukchi Sea, both under the influence of high nutrient Anadyr Water, and zooplankton populations are only weakly coupled to water column production, resulting in low recycling in the water column and the fraction of primary production exported to the underlying sediments is high (Grebmeier and Barry 2007). Comparatively, areas of the Alaska Coastal system have a stronger coupling between primary production and the timing of production and subsequent micro- and meso-zooplankton growth and microbial transformations, thus reducing the fraction of primary production exported to the sediments, thereby limiting benthic populations and benthic carbon cycling (Grebmeier et al. 2006).

Sediment trap studies over the last two decades in the Pacific Arctic sector indicate a high carbon export in regions under the influence of Anadyr water in the Bering and Chukchi Seas, including Barrow Canyon, that are coincident with regions of high sediment community oxygen consumption (SCOC) (Grebmeier et al. 2006). Spatial patterns of SCOC identify regions of

organic carbon deposition throughout the Pacific-influenced shelf region and can be used as a surrogate for variations of export production in the region (Grebmeier and Barry, 2007). Looking just at the last decade (2000 onward), we continue to observe specific ‘‘hot-spots’’ of high SCOC in regions southwest of St. Lawrence Island, in the Chirikov Basin north of St. Lawrence Island, in the southern Chukchi Sea and at the head of Barrow Canyon (**Figure 9**). SCOC ranges from 1 to 40 mmol O_2 m-$^{-2}$ d^{-1} (84–335 mg C m^{-2} d^{-1}) in the northern Bering Sea just south and north of St. Lawrence Island to 20–50 mmol O_2 m^{-2} d^{-1} (167–418 mg C m^{-2} d^{-1}) in the southern Chukchi Sea and upper Barrow Canyon. SCOC declines to 1–10 mmol O_2 m-$^{-2}$ d^{-1} (8–84 mg C m^{-2} d^{-1}) on the outer Chukchi and western Beaufort shelves, with the lowest values from 0.1 to 5 mmol O_2 m-$^{-2}$ d^{-1} (<1–42 mg C m^{-2} d^{-1}) on the northern Chukchi and western Beaufort slope and Arctic basin regions (see Grebmeier et al. 2006 for methodology).

The lower SCOC rates nearshore in the northern Bering, Chukchi, East Siberian, and western Beaufort Seas, except Barrow Canyon, indicate reduced organic carbon export and deposition to the benthos (Grebmeier and Barry 2007). These values of SCOC are comparable in range to export production determined from both the thorium method and sediment traps (Lalande et al. 2007, Lepore et al. 2007; this chapter). For example, high SCOC in the southern Chukchi Sea and upper Barrow Canyon ‘‘hotspots’’ is consistent with elevated export flux rates determined by the thorium method (Lepore et al. 2007), although lower than those measured using the floating sediment trap method in the summer period only (Lalande et al. 2007). When SCOC is greater than the water column export production, the import of organic carbon from upstream productive zones is suggested.

A three-fold increase in POC export was observed between the spring and summer of 2002 (spring = 2.9 ± 5.3 mmol C m-2 d^{-1}; summer = 10.5 ± 9.3 mmol C m^{-2} d^{-1}) (Moran et al. 2005), indicative of summer production events and subsequent carbon settlement to the benthos. However, Lepore et al. 2007 found little difference in the POC export fluxes in 2004 between spring and summer, with rates averaging 19.7 ± 24.8 mmol C m^{-2} d-^{1} in the spring and 20.0 ± 14.5 mmol C m^{-2} d^{-1} in the summer. This higher POC export observed in the spring 2004 was attributed to a plankton bloom.

Past studies also indicate that sediment respiration in the productive area of the PAR is dominated by benthic macrofauna and that rates of microbial anoxic respiration are low by comparison (Grebmeier and McRoy 1989, Henriksen et al. 1993, Devol et al. 1997, Clough et al. 2005, Grebmeier and Barry 2007). The dominance of macrofauna in community respiration is assumed for the shelf and upper slope of the Pacific-influenced waters, though the deep slope and basin meiofauna and microfauna become proportionally more important as benthic macrofauna diminish (Clough et al. 2005, Pirtle-Levy, 2006). Clough et al. (2005) found that the role of macrofauna was more important than meiofauna in sediment respiration at depths shallower than 500 m in the Chukchi Sea during the summer. They also noted that benthic macrofaunal biomass explained 75% of the variability in benthic respiration rates, similar to the >50% influence of benthic fauna observed by Grebmeier and McRoy (1989) under the high export areas of the northern Bering and Chukchi Seas. Recent data also indicate that epifaunal animals can increase overall benthic community oxygen consumption and should be considered within total organic carbon budget analyses (Ambrose et al. 2001, Piepenburg et al. 1995, Piepenburg 2005, Renaud 2007a). Thus, whole core SCOC rates, indicative of carbon supply to the benthos, are considered minimal values since they do not include either megafaunal animal impacts or anaerobic processes, both of which would increase total sediment carbon mineralization.

Similarly, macrobenthos was a dominant driver for higher sediment oxygen consumption in the Beaufort Sea during studies undertaken during the CASES program. Studies of Renaud et al. 2007a found that most of the oxygen demand during the productive spring period in 2005 was driven by macrobenthic activity, with only a minor portion through microbial and meiofaunal activities. This study estimated that the benthic carbon demand during the period of highest sediment oxygen demand was around 210 mg m^{-2} d^{-1}, about half the benthic carbon demand of the "hotspot" areas in the southern Chukchi Sea and head of Barrow Canyon (see previous paragraphs). This study also found that although sediment chlorophyll increased during the high sediment oxygen demand, not enough *in situ* carbon was present to support the rates, indicating an outside source of carbon was needed. They also found epibenthos (primarily echinoderms) were important drivers of sediment respiration.

Benthic macroinfaunal biomass from 30-60 g C m^{-2} has been reported in the southern Chukchi Sea productive regions (Grebmeier et al. 2006). Integrated over a 100 d growing season, 30–60 g C m^{-2} corresponds to a carbon export of 25–50 mmol C m^{-2} d^{-1}. While this flux is an upper estimate due to the uncertainty associated with extrapolation of limited measurements to the entire shelf region, the implication is that carbon storage in benthic infaunal biomass is likely an important component of the carbon budget in this region. Additionally, rates of high benthic carbon respiration up to 30 mmol C m^{-2} d^{-1} at the head of Barrow Canyon indicate enhanced consumption of organic carbon during the summer period (Lepore et al. 2007). The increase in sediment focusing in Barrow Canyon during the summer could be due to both observed high levels of primary production and transport of particulate material from upstream production sites in the south, which would make Barrow Canyon an important region of carbon transport from the Chukchi Sea to the Arctic Basin.

Sediment Nutrient Efflux

Evaluation of ammonium and silicate efflux from 2000 onwards (encompassing the 2007-2009 International Polar Year) indicate a direct relationship between regions of high export production as indicated by SCOC (**Figure 10**) and nutrient efflux (**Figures 10 and 11**). Highest levels of ammonium (Figure 10) and silicate (Figure 11) efflux occur under the influence of Anadyr water in the western regions of the northern Bering and Chukchi Seas, indicative of the high pelagic-benthic coupling and carbon export in these regions The high ammonium fluxes (negative efflux values of -2 to -3 mmol NH_4 m^{-2} d^{-1}) occur in regions of high carbon export, as indicated by high SCOC (positive influx of 24-36 mmol O_2 m^{-2} d^{-1}) just SW of St. Lawrence Island (SLI), in central Chirikiov Basin north of SLI, in the southern Chukchi Sea, and at the head of Barrow Canyon (Figure 9), all areas also containing high populations of infaunal bivalves and amphipods (see Lower Trophic section). High silicate fluxes (negative efflux values of -4 to -8 mmol SiO_2 m^{-2} d^{-1}, Figure 10) also occur at high efflux regions as described for ammonium efflux. In particular, silicate efflux is greatest in the SE Chukchi Sea and Barrow Canyon benthic "hotspot" areas where SCOC is also the greatest, indicative of the high carbon supply to the sediments and carbon recycling processes in this region. Notable is that the highest silicate efflux occurs in the upstream region of Herald Valley in the SE Chukchi Sea along the pathway of the Anadyr water and its associated high POC loading, as well as in the region at the

head of Barrow Canyon, a downstream location for transport of this water after passing NW in the Chukchi and eastward at the outer continental shelf (Weingartner et al. 2005).

Differences in nutrient efflux are evident spatially in the Pacific Arctic sector and it is important to evaluate the biological processes influencing benthic carbon cycling rates. Ammonium is recycled via microbial activity as well as excreted by infaunal organisms. By comparison, recycling of silicate from diatoms occurs via bacterial processing of material. In addition, bioturbation by infaunal organisms can influence the rates of oxygen uptake and nutrient regeneration, thus the location of "hotspots" of benthic carbon cycling are directly related to infaunal biomass and population structure. The overall biomass of infaunal populations is significantly related to sediment oxygen uptake and nutrient recycling in the Pacific sector. The high benthic biological infaunal population levels and their influence via bioturbation on benthic carbon cycling processes are likely critical for maintaining ecosystem structure and function on the productive northern Bering and Chukchi shelves. Any changes in physical forcing that influences upper water column biological processes (nutrient availability, primary production, nutrient zooplankton production, export production) will directly influence sediment oxygen uptake, nutrient release and overall benthic carbon cycling that can feed back to both upper water column and higher trophic level productivity.

Contribution of Heterotrophic Bacteria to Carbon Cycling

Heterotrophic bacteria and the rest of the microbial loop usually process a large fraction of primary production and thus contribute substantially to the carbon cycle of the oceans. Bacterially-mediated carbon fluxes through dissolved organic material (DOM) account for half or more of primary production as measured by the ^{14}C method in most aquatic ecosystems (Ducklow 2000), based on data from biomass production estimates and size fractionation experiments that examine respiration or DOC consumption by the bacteria-size fraction. Since bacteria are the main users of DOC, data on bacterial activity can be used to estimate DOC fluxes, especially of the labile components of the DOC pool with turnover times on the scales of days to weeks. In some oceanic regions, these fluxes and respiration by bacteria and other heterotrophic organisms appear to exceed primary production rates over substantial time and

space scales, raising questions about balancing carbon fluxes in these regions (Duarte and Regaudie-De-Gioux 2009; Robinson 2008).

Early studies suggested that bacterial activity would be low in perennially-cold waters like the Arctic Ocean (Pomeroy and Deibel 1986). This low activity was thought to allow more carbon to be channeled to higher trophic levels and to be exported to benthic communities. Studies in the Ross Sea, Antarctica supported the cold temperature hypothesis and found that ratios of bacterial biomass production to ^{14}C-primary production were low (Ducklow et al. 2001; Ducklow 1999), suggesting low fluxes through the DOM pool. In the Arctic Ocean, however, one study found variable but often high ratios of bacterial to primary production (Rich et al. 1997).

The SBI program provided an opportunity to examine bacterial properties and DOC fluxes in the Chukchi Sea and nearby regions of the Canada Basin (Grebmeier and Harvey 2005). The review here will focus on two related questions: i) what fraction of total respiration can be attributed to heterotrophic bacteria?; ii) what fraction of primary production is processed by heterotrophic bacteria, as estimated from biomass production and growth efficiencies estimates? The term "heterotrophic bacteria" accurately describes the microbes involved in the processes discussed in this review because the abundances of autotrophic Archaea and cyanobacteria are low in these surface waters (Cottrell and Kirchman 2009; Garneau et al. 2009; Kirchman et al. 2007).

Respiration by heterotrophic bacteria

The standard size fractionation approach was used to examine respiration by the bacterial size fraction (<0.8 μm) in the summer of 2004 in the Chukchi Sea and Canada Basin (Kirchman et al. 2009a). The small size fraction usually includes a large part (>80%) of total bacterial abundance, but excludes particle-bound microbes, which can be abundant and active in low salinity coastal waters impacted by river inputs (Garneau et al. 2009).

The size fractionation experiments indicated that heterotrophic bacteria accounted for a highly variable fraction of total respiration in the Chukchi Sea and Canada Basin (Kirchman et

al. 2009a). The percentage was 40-60% in shallow shelf waters of the Chukchi Sea and decreased to 3-26% in slope waters. Respiration by the bacterial size fraction exceeded total respiration at two stations in the Canada Basin. The overall average of all experiments indicated that heterotrophic bacteria account for about 25% of total respiration in these Arctic waters. This fraction is smaller than typically seen in low-latitude oceans, supporting the original hypothesis of Pomeroy and colleagues.

Biomass production by heterotrophic bacteria and phytoplankton

Estimates of biomass production by heterotrophic bacteria can be used to explore the transfer of carbon, other elements and energy from DOM, through heterotrophic bacteria and the rest of the microbial loop, and onto higher trophic levels. Since bacterial abundance and biomass is constant on short time scales, bacterial production is roughly equal to transfer of carbon to higher trophic levels after viral lysis is accounted for; the few available estimates indicate that lysis is low in the Arctic for unknown reasons (Steward et al. 1996). The production estimates also can be used to examine community growth rates and generation times, a fundamental property of biological populations. In the Arctic, growth rates range from 0.03 to 0.15 d^{-1}, equivalent to generation times of 5 days to over 3 weeks (Kirchman et al. 2009a). These growth parameters are slower and longer than those estimated in low latitude oceans (Kirchman et al. 2009b).

Biomass production rates also can be used to examine the fraction of primary production processed by heterotrophic bacteria. This approach has many well-known problems. Criticism has focused on bacterial production estimates, but ^{14}C-based estimates of primary production have also been questioned (Quay et al. 2010) and are difficult to interpret for the Arctic (see below). Still, it is technically much easier to measure biomass production than total respiration and respiration by the bacteria-size fraction, especially in cold waters where rates are low and oxygen concentrations are high. Consequently, the data set on production estimates is much larger than that on respiration. These estimates suggest high variability over time and space in relationships between bacterial biomass production and ^{14}C- primary production and by implication, the routing of carbon through the DOM pool from phytoplankton.

In general, bacterial production correlated with ^{14}C-primary production ($r = 0.53$; $p<0.001$; $n=89$) for rates integrated over the euphotic zone (Kirchman et al. 2009a), but the ratio of the two production estimates (BP:PP) varied substantially during the SBI expeditions. It was significantly higher in 2002 than in 2004 and higher in May-June than in July-August of both years. Both bacterial production and primary production tended to decrease in transects from shelf waters to the basin, but since primary production decreased more so, the BP:PP ratio tended to be highest in the basin. In waters such as on the shelf with high rates of primary production (>100 mgC m^{-2} d^{-1}), the BP:PP ratio was low (0.06 ± 0.01; $n=55$) whereas it was high (0.79 ± 0.21; $n=34$) in waters such as the basin with low rates of primary production (<100 mgC m^{-2} d^{-1}). The implication of these data for shelf-basin exchange is discussed below.

Growth efficiency in the Arctic Ocean

The BP:PP ratios do not include respiration and thus cannot be used alone to explore questions about how much primary production is routed through DOC, bacteria and the microbial loop. The bacterial growth efficiency (BGE) is also needed. We can calculate bacterial respiration (BR) from bacterial production (BP) estimates using the equation:

$$BR = BP(1-BGE)/BGE$$

The few estimates of BGE for Arctic waters vary greatly (see references in (Kirchman et al. 2009a)) with an overall average of 6.9% for the SBI data set. This average does not differ statistically from the oceanic average of 15% (Del Giorgio and Cole 2000). There was no significant effect of temperature on BGE in experiments conducted during the SBI expeditions, consistent with the lack of a clear temperature effect on BGE in previous studies (see references in (Kirchman et al. 2009a)).

Implications for shelf-basin exchange

The BGE values can be combined with the biomass production data to provide another estimate for how much of total respiration and of total primary production consumption can be attributed to heterotrophic bacteria. Assuming BGE to be 6.9%, the production data suggest that about 80% of ^{14}C-primary production in the western Arctic is consumed by heterotrophic bacteria in waters with high rates of primary production (Kirchman et al. 2009a). When ice effects on ^{14}C primary production are ignored, consumption by heterotrophic bacteria amounts to

<50% of ^{14}C primary production, significantly less than see in low-latitude oceans (Kirchman et al. 2009b). In contrast, bacterial respiration estimated by this approach exceeds 100% in waters with low primary production rates. This does seem possible in some Arctic regions (e.g. ice-covered waters), but there are known problems with the data. In a discussion of possible errors, Kirchman et al. (2009a) concludes that the ^{14}C method probably underestimates true rates of both net and gross primary production. A recent study also found that ^{14}C-based estimates of primary production were much lower than estimates from other approaches (Quay et al. 2010).

The data still can be used to explore the possible export of organic carbon from productive shelf waters to less productive waters such as those in the basin. The high rates of bacterial production, bacterial respiration and total respiration in waters with low primary production can be sustained only by organic carbon exported from waters with high primary production. In addition to general shelf-basin exchange, organic carbon could be exchanged between ice-free and ice-covered shelf regions with high and low rates of primary production, respectively. These regions could have adequate nutrients but be light limited if covered by ice. The production data can be used to identify these regions.

The organic carbon most likely exported is that in the DOC pool. The amount is too large to be accounted for by particulate organic carbon, whereas it is small compared to the total integrated DOC pool; the daily rate given by Kirchman et al. (2009a) is <10% of total DOC. Exported DOC helps to explain the spatial and temporal variability in net and community production as measured by light-dark incubations in the Arctic (Cottrell et al. 2006).

Ocean Acidification

It has been widely shown that the uptake of anthropogenic CO_2 by the oceans (e.g. Sabine et al., 2004; Sabine et al., 2007) has a significant effect on marine biogeochemistry by reducing seawater pH (Feely et al., 2009; Caldiera et al., 2003) and the saturation states ( ) of important calcium carbonate ($CaCO_3$) minerals (Feely et al., 2004; Orr et al., 2005; Caldiera and Wickett, 2005) through a process termed “ocean acidification”. Seawater exhibiting undersaturated conditions (i.e., <1) are potentially corrosive for biogenic $CaCO_3$ minerals such as aragonite, calcite and high-Mg calcite. The reduction of $CaCO_3$ mineral saturation states in the

surface ocean and along continental margins could have potentially negative consequences for benthic and pelagic calcifying organisms, and entire marine ecosystems (Fabry et al., 2008). Of even greater concern is the rate at which ocean acidification and $CaCO_3$ mineral saturation state suppression are progressing, particularly in the high latitude PAR (Byrne et al., 2010; Fabry et al., 2009) where mixing processes and colder temperatures naturally precondition the water column to have lower pH and Ω values compared to more temperate ocean environments.

Recent observations in the sub-arctic North Pacific Ocean (Mathis et al., 2011) have already revealed areas of seasonal $CaCO_3$ mineral Ω suppression. Aragonite undersaturation has been observed throughout the water column, while models project widening areas of aragonite undersaturation in the region during the next several decades (Steinacher et al., 2009). Undersaturation has potentially negative consequences for the region because the expansive continental shelf of the eastern Bering Sea sustains a commercially valuable fishery (Cooley and Doney, 2009; Cooley et al., 2009) that produces approximately 47% of the US fish catch by weight. This marine ecosystem is critical to both the regional and national economy as well as subsistence communities in Alaska who rely heavily on the seasonal fish catch as their primary source of protein. These new findings show that the eastern Bering Sea will likely be one of the first ocean acidification impact zones for US national interests. Therefore, it is critical to gain a better understanding of both the natural and anthropogenic controls on $CaCO_3$ mineral suppression in the region.

As observed at several open-ocean time-series, the uptake of anthropogenic CO_2 has already decreased surface water pH by 0.1 units. IPCC scenarios, based on present-day CO_2 emissions, predict a further decrease in seawater pH by 0.3 to 0.5 units over the next century and beyond (Caldeira and Wickett, 2003). Ocean acidification and decreased pH reduces the saturation states of calcium carbonate minerals such as aragonite and calcite, with many studies showing decreased $CaCO_3$ production by calcifying fauna (Buddemeier et al., 2004; Fabry et al., 2008) and increased $CaCO_3$ dissolution. The PAR 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 melt waters (Yamamoto-Kawai et al., 2009).

In the high latitude PAR, the uncoupling of primary production and grazing leads to high export rates of organic matter to the bottom waters and the sediments. When this organic matter

is remineralized back into CO_2, it naturally decreases pH and suppresses carbonate mineral saturation states. However, the presence of anthropogenic CO_2 in the water column has caused bottom waters over some parts of the PAR shelves to become undersaturated in carbonate minerasl (mostly aragonite, but in some locations calcite undersaturations have been observed).

The Bering Sea

The eastern shelf of the Bering Sea (**Figure 1**) is a highly dynamic area that is influenced by a number of terrestrial and marine processes (**Figure 12**) that impact seawater carbonate chemistry with considerable spatial, seasonal and interannual variability in the saturation states of the two most biogenically important $CaCO_3$ minerals, aragonite ($\Omega_{aragonite}$) and calcite ($\Omega_{calcite}$) (Mathis et al., 2011). The springtime retreat of sea ice, coupled with warming and seasonally high rates of freshwater discharge create distinctive horizontal and vertical zones over the shelf, each with their own unique characteristics (Stabeno et al., 1999). The onset of stratification in surface waters stimulates an intense period of phytoplankton primary production (PP), particularly over the middle region of the shelf where the confluence of macronutrient-rich Bering Sea water and coastal water replete in micronutrients is highest (Agular-Islas et al., 2007). In this region, historically referred to as the "*green belt*", rates of PP or net community production (NCP) can exceed 480 mg C m^{-2} d^{-1} (see PP section in this chapter) while average rates across the shelf are ~330 mg C m^{-2} d^{-1}, making the eastern Bering Sea shelf one the most productive regions in the global ocean (Sambrotto et al., 2008; Mathis et al., 2010).

On the eastern Bering Sea shelf, a seasonal divergence in pH and Ω is observed between surface and subsurface waters, driven primarily by the biology of the system (Mathis et al., 2010). During the spring phytoplankton bloom, high rates of NCP effectively remove CO_2 from the surface waters creating a strong seasonal disequilibrium with the atmosphere (Bates et al., 2010), but also increasing pH and Ω values by ~0.1 and ~1 respectively (Mathis et al., 2011). However, in subsurface waters the opposite is observed, with pH and Ω values decreasing significantly (~0.3 and ~0.2, respectively) (Mathis et al., 2011). Much of the organic matter that is produced during the spring phytoplankton bloom is exported vertically out of the mixed layer. By mid-summer, the water-column becomes highly stratified and bottom waters are effectively isolated from surface waters over much of the shelf. The vertical export of organic matter and its subsequent seasonal remineralization at depth, induces a significant build-up of CO_2 in bottom

waters (i.e. pCO_2 increases) and concurrent suppression of $CaCO_3$ mineral Ω values (Mathis et al., 2010; Mathis et al., 2011). The seasonal divergence of pH and Ω in surface and subsurface waters has been described in terms of a "Phytoplankton-Carbonate Saturation State" (PhyCaSS) (Bates et al., 2009). In 2008, subsurface waters of the eastern Bering Sea shelf became undersaturated with respect to aragonite (but not calcite) (Mathis et al., 2011). It has also been shown that the addition of anthropogenic CO_2 to the ocean augments this natural seasonal interaction between ocean biology and seawater carbonate chemistry, tipping subsurface waters below the saturation state threshold ($\Omega_{aragonite} = 1$) for aragonite. Increasing levels of atmospheric CO_2 could push the Bering Sea closer to a tipping point that could be detrimental for calcifying organisms.

The Western Arctic Ocean

In the Arctic Ocean, potentially corrosive waters are found in the subsurface layer of the central basin (Jutterstrom and Anderson, 2005; Yamamoto-Kawai et al., 2009; Cheirici 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 $CaCO_3$ 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 drives a downward export of organic carbon, which is remineralized back to CO_2 which in turn increases seawater pCO_2 (and decreasing pH) of subsurface waters. Such a seasonal biological influence on the pH of subsurface waters amplifies existing impacts of ocean acidification induced by the uptake of anthropogenic CO_2 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.

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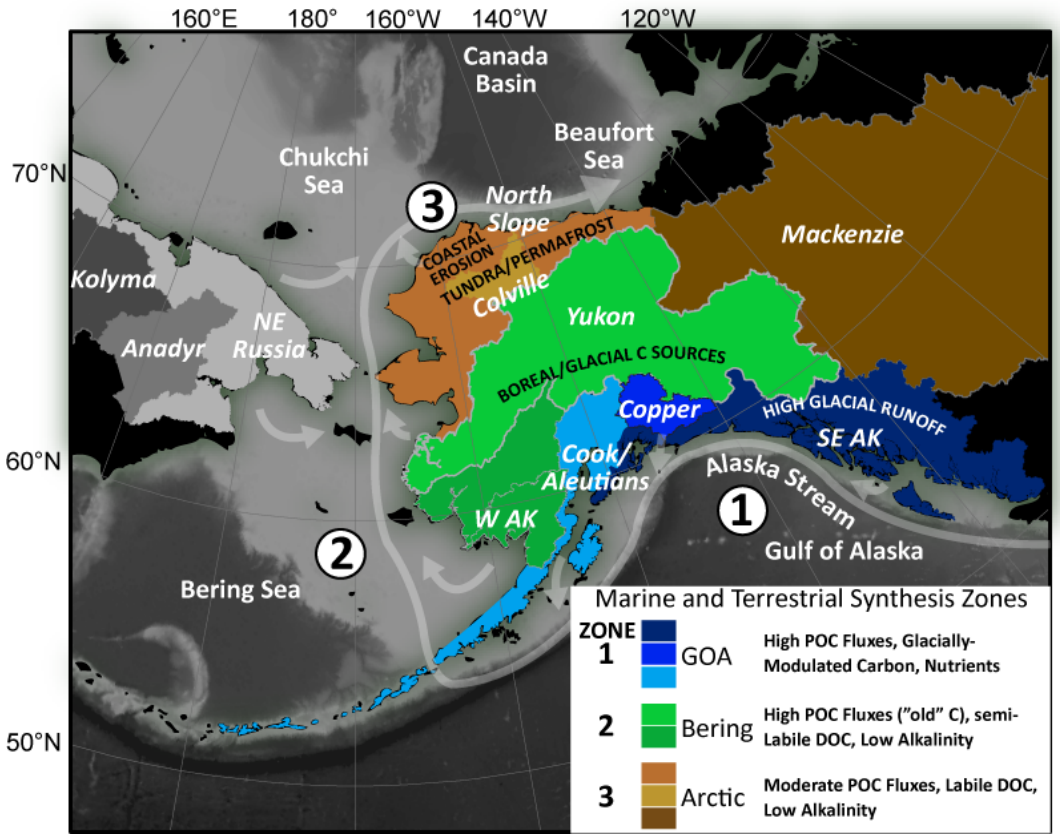

Figure 1 – Map of the Pacific Arctic Region (PAR) showing the major drainage basins and the associated biogeochemical properties that impact the carbon cycle. (1) Gulf of Alaska; (2) Bering Sea; and (3) Chukchi Sea. The color bars in the inset illustrate the various terrestrial drainage basins around North America and their predominant biogeochemical characteristics.

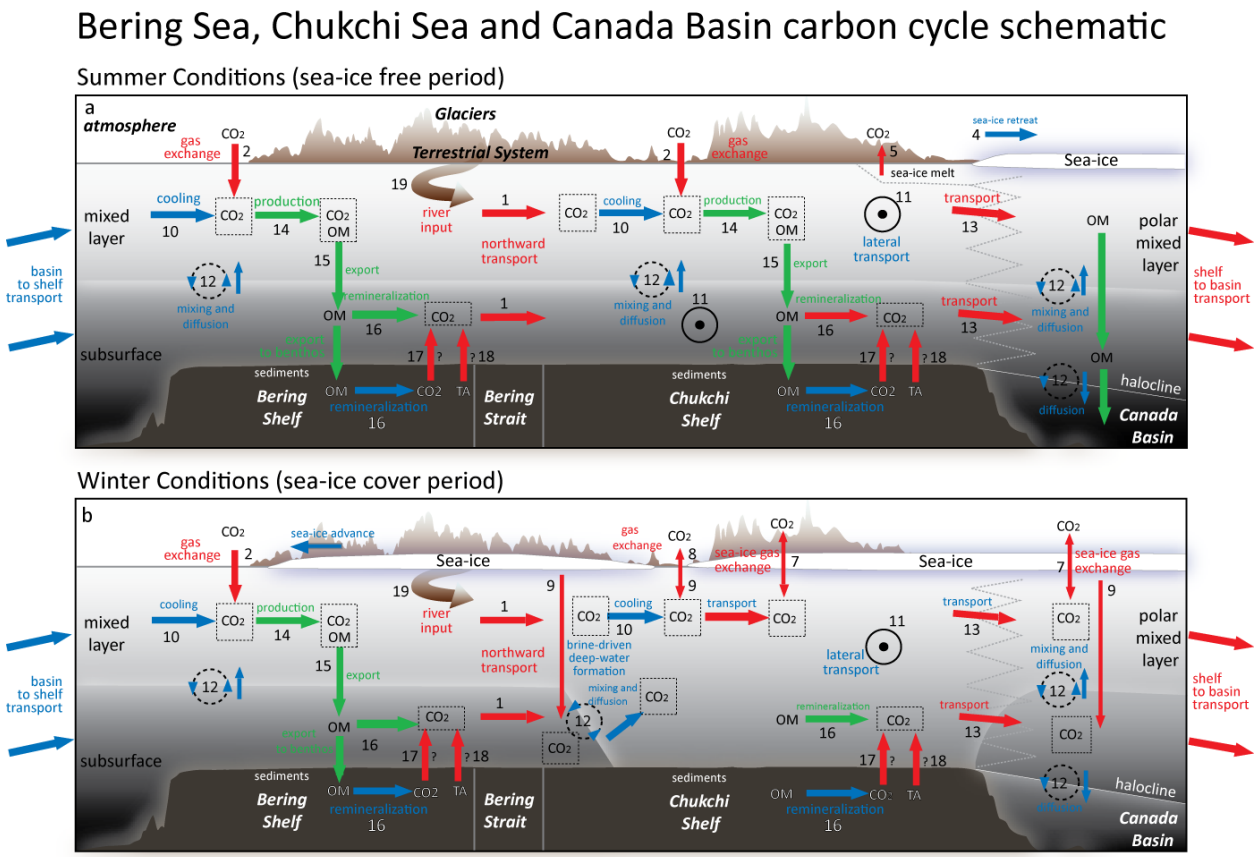

Figure 2 - Schematic of processes potentially influencing the inorganic carbon cycle and air-sea CO_2 gas exchange in the western Arctic Ocean from the Bering Sea shelf through the Bering Strait, across the Chukchi Sea and northwards into the Canada Basin (left to right on Figure) on "inflow" shelves of the Arctic (e.g., Barents and Chukchi Seas). The two panels represent physical and biological processes likely operating during the summertime sea-ice free period (Panel a), and during the wintertime sea-ice covered period (Panel b). The processes are denoted by numeral with the caveat that the size of arrow does not necessarily reflect magnitude of flux, transport or transformation of CO_2. The processes include: 1. northward transport of DIC; 2. air-sea gas exchange; 3. warming; 4. exposure of surface water to the atmosphere due to sea-ice retreat and melting; 5. localized air-sea gas exchange from surface water highly influenced by sea-ice melt; 7. air-sea gas exchange through sea-ice; 8. winter air-sea gas exchange in leads and Polynyas; 9. inorganic carbon flux due to brine-rejection during deep-water formation in fall and winter. 10. cooling of surface waters during northward transport on Atlantic or Pacific Ocean waters into the Arctic Ocean; 11. between shelf transport of water and carbon; 12. redistribution of inorganic carbon between mixed layer and subsurface due to vertical diffusion and vertical entrainment/detrainment due to mixing; 13. shelf-basin exchanges of inorganic carbon (i.e., DIC) and organic carbon due to generalized circulation and eddy mediated transport; 14. net uptake of CO_2 due to phytoplankton photosynthesis or new production; 15. export flux of organic matter (OM) or export production; 16. remineralization of organic matter back to CO_2 either in subsurface waters or in sediments; 17. release of CO_2 from sediments; 18. release of alkalinity from sediments due to anaerobic processes in sediments, and; 19. river runoff input. Adapted from Bates and Mathis, 2009.

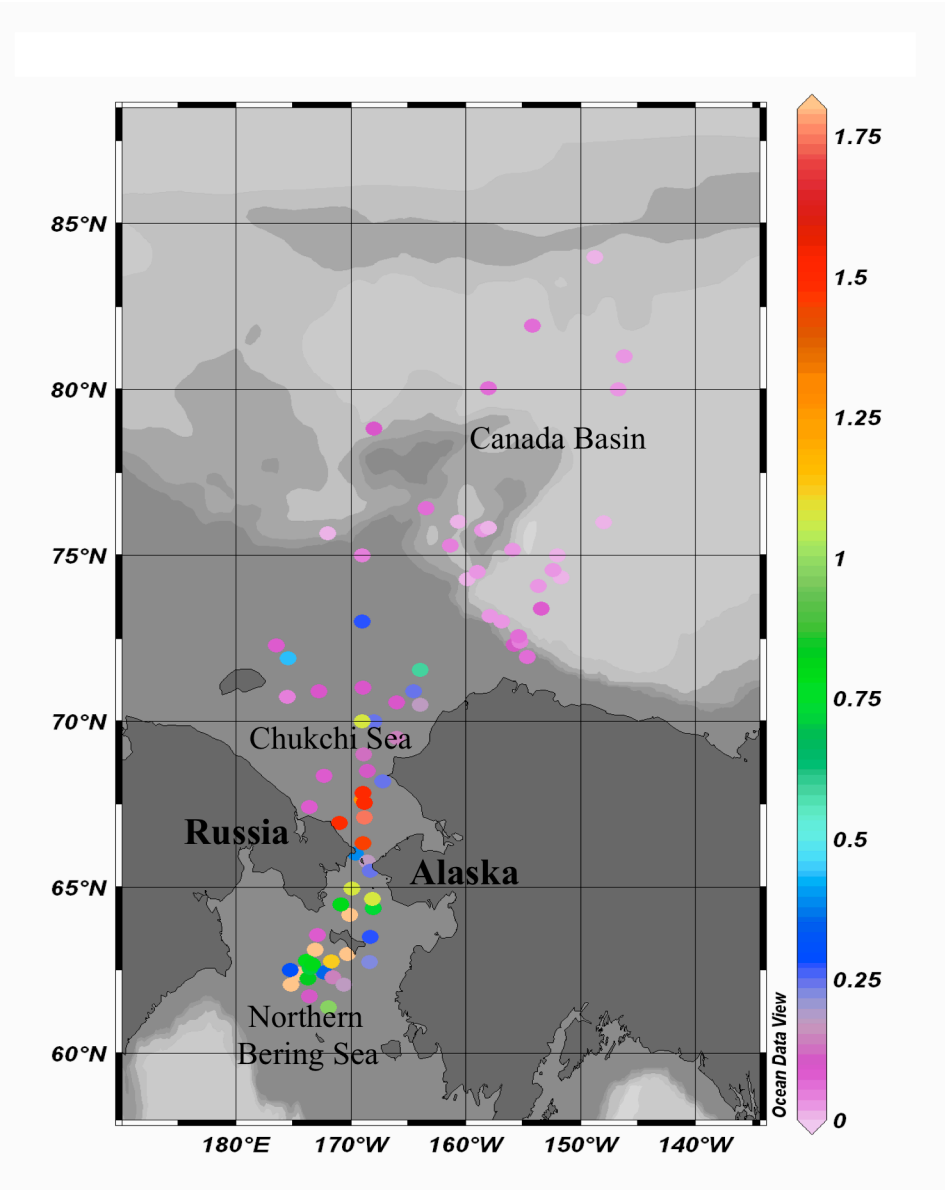

Figure 3 - Carbon uptake rates (g C m^{-2} d^{-1}) integrated to the 1 % light depth in the PAR. Data from Lee and Whitledge (2005), Lee et al (2007), Lee et al (2010), Lee et al (submitted)a, and Lee et al (submitted)b.

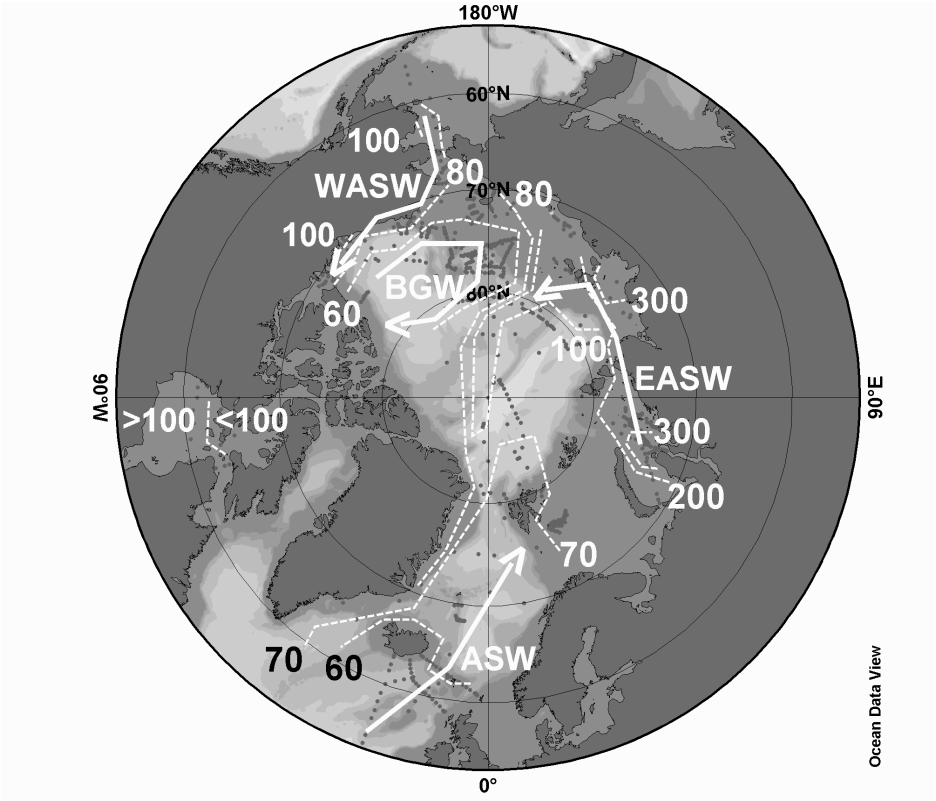

Figure 4 - Contoured distributions of DOC concentrations in the surface layer of the Arctic Ocean (measurement locations are indicated with filled marks). Also shown are water masses and circulations of particular relevance to DOC distributions, including Beaufort Gyre Water (BGW), Western Arctic Shelf Water (WASW), Eastern Arctic Shelf Water (EASW), and Atlantic Surface Water (ASW).

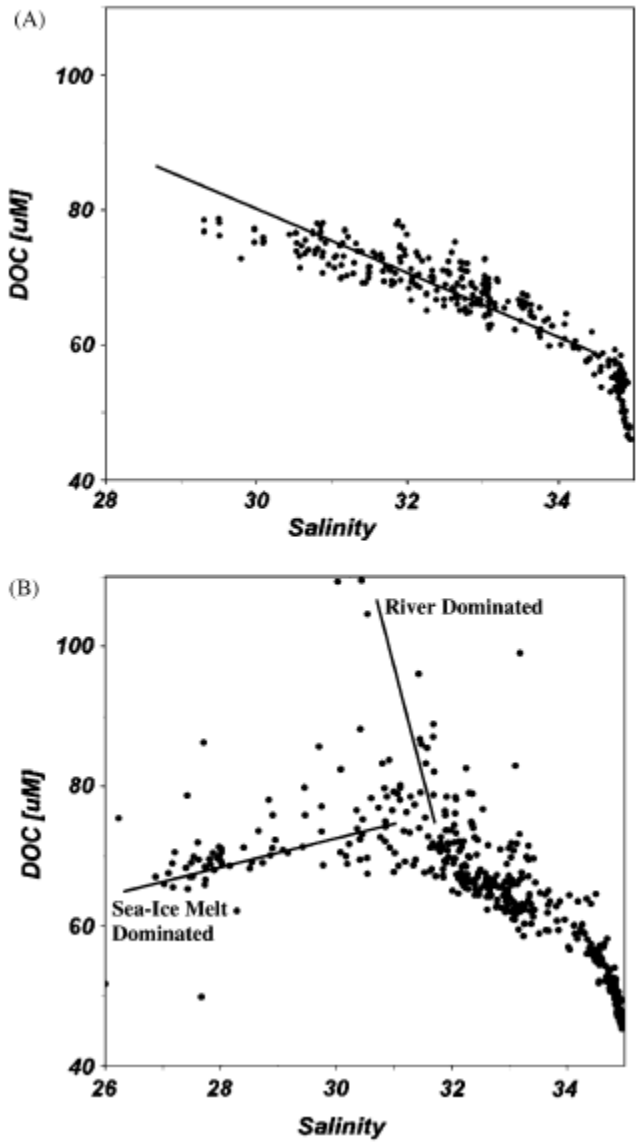

Figure 5 - Scatter plots of salinity and DOC (μmoles kg^{-1}) identifying mixing curves: (A) spring 2002; and (B) summer 2002. Shown with apparent mixing lines.

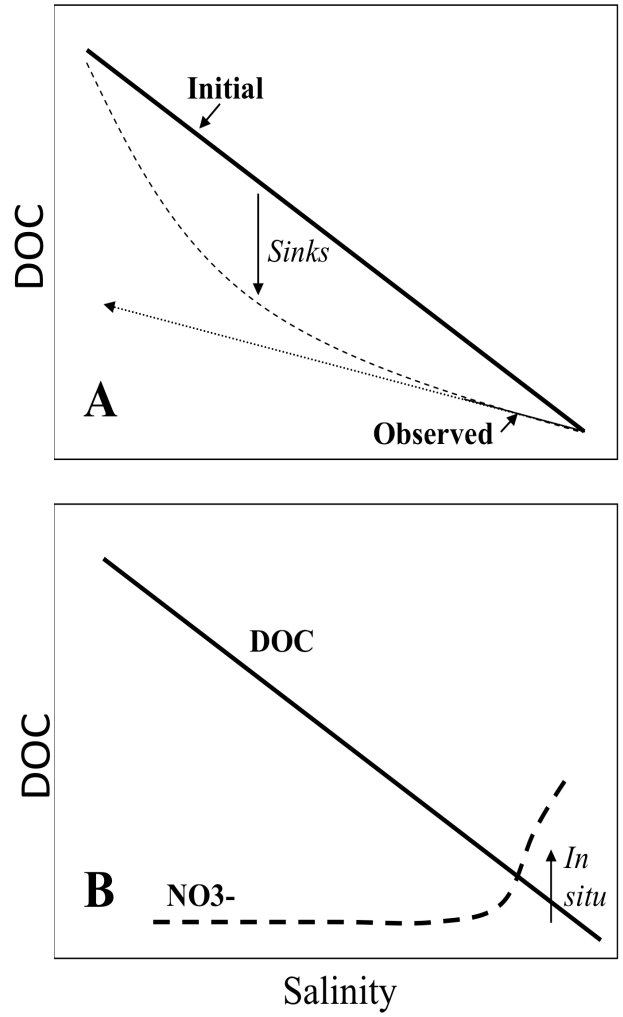

Figure 6 - Diagrammatic rendering of the relationship between western Arctic DOC concentrations and salinity in the surface layer as a function of a) time since introduction of tDOC to the ocean system and b) marine nutrient abundance. In (a) the initial relationship, when tDOC is first introduced to the ocean, is linear over the full salinity range. With time, tDOC is removed and the correlation (which is not actually observable in nature over the full salinity range due to rapid mixing) becomes curvilinear (dashed line). The observable portion of this curve (i.e., Fig. 5a), including the full marine end member and some minor dilution with freshwater, is labeled "observed". The zero intercept of the linear regression of the observed correlation (dotted line) provides an estimate for the tDOC concentration remaining in the freshwater fraction. In (b), the potential impact of marine nutrients on the "observed" correlation is demonstrated. Nutrients are enriched in the marine end of the salinity range (associated with Pacific water) and impoverished in the freshwater end. As such, net community production and net marine DOC production can only impact the DOC/salinity relationship in the high salinity water, increasing DOC at a given high salinity (upward arrow).

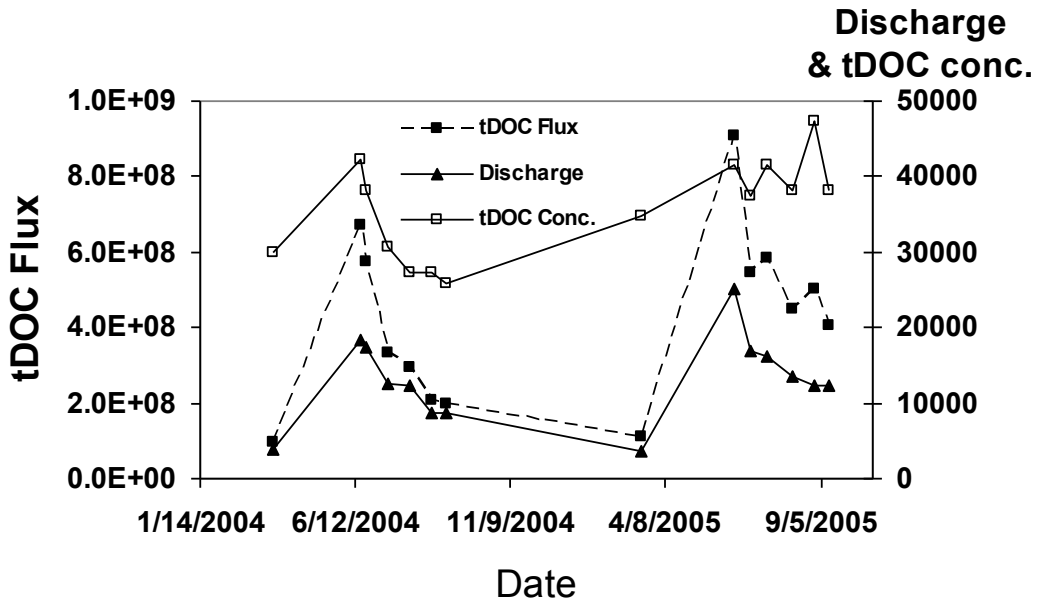

Figure 7 - Mackenzie River discharge (m^3 s^{-1}), tDOC concentration (µmol kg^{-1} x 100), and tDOC flux (molC day^{-1}) during summer seasons of 2004 and 2005 (data taken from Raymond et al., 2007).

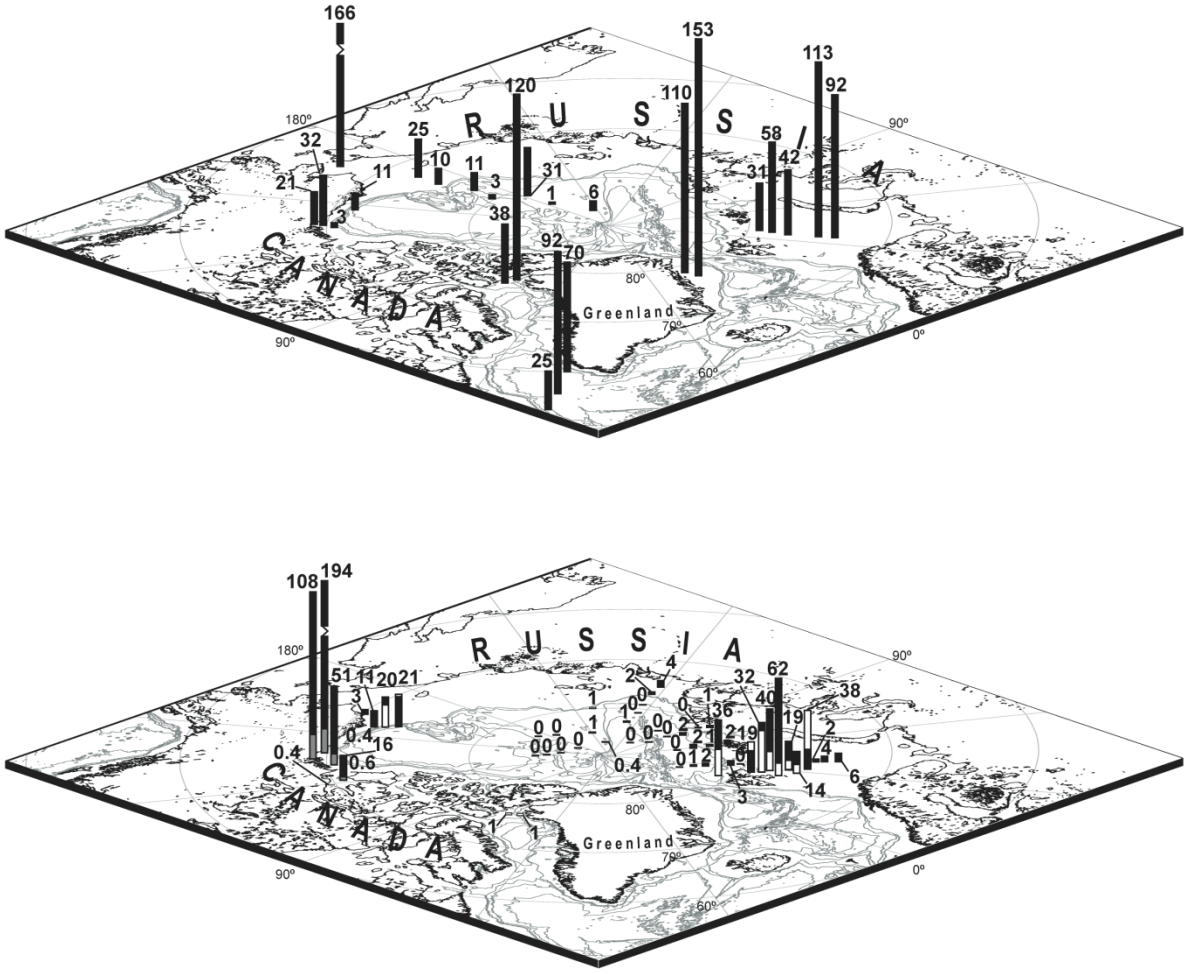

Figure 8 - Regional distribution of POC export fluxes (mmol C m^{-2} d^{-1}) in the Arctic Ocean and sub-polar Labrador Sea determined using sediment traps and $^{234}Th/^{238}U$ disequilibrium in the Chukchi Sea (Lalande et al. 2007; Lepore et al. 2007; Moran et al. 2005), the northern Barents Sea (Lalande et al. 2008), the Mackenzie shelf (Amiel and Cochran 2008), the Laptev, northern Baffin Bay and Beaufort Seas (Lalande et al. 2009), and the eastern Arctic (Cai et al. 2010). These results represent the major field programs of POC export flux in the upper Arctic Ocean since summarized by Wassmann et al. (2003). Black bars indicate POC fluxes calculated from $^{234}Th/^{238}U$ disequilibrium; white bars results from free-floating sediment traps; grey bars represent POC fluxes calculated for the marine component of the total POC flux in the Mackenzie shelf (Amiel and Cochran, 2008). Seasonally averaged fluxes are plotted for the Chukchi Sea (Lalande et al., 2007; Lepore et al., 2007; Moran et al., 2005), and regionally averaged POC fluxes are indicated for the Mackenzie shelf (Amiel and Cochran, 2008).

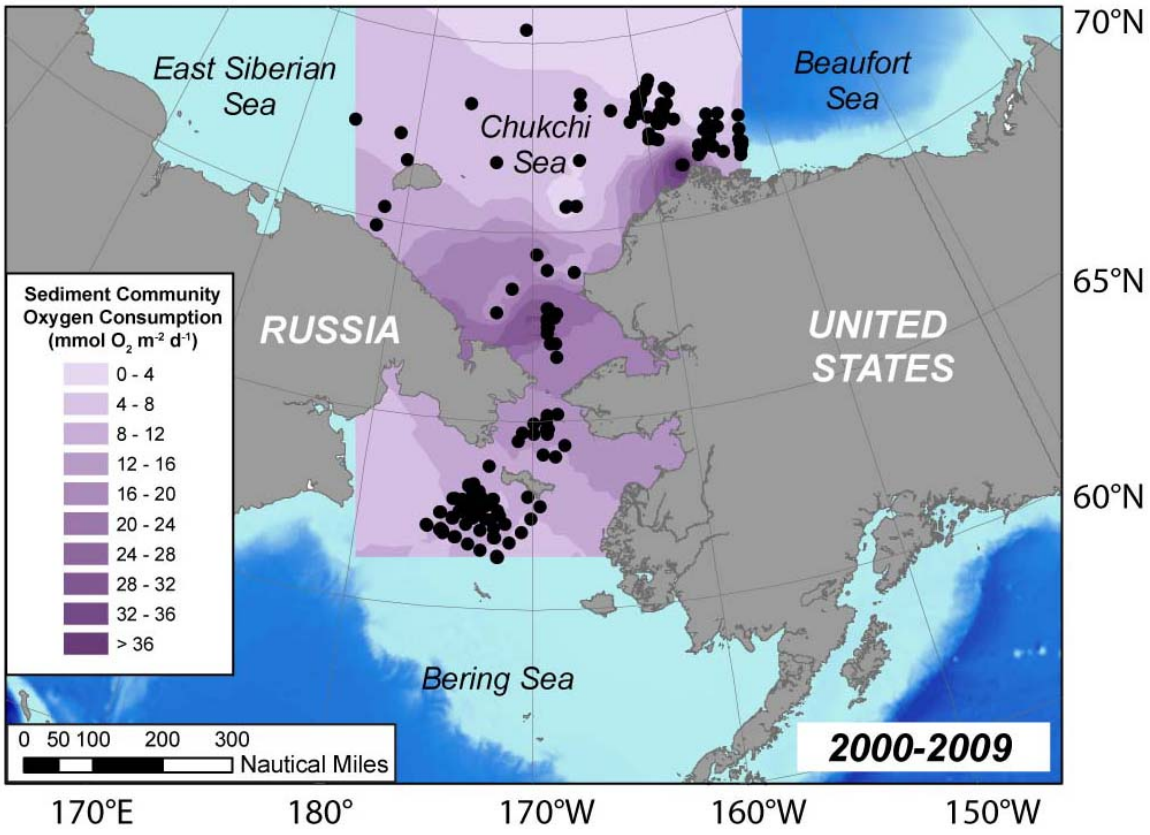

Figure 9 - Distribution of sediment community oxygen consumption (positive influx values) in the Bering and Chukchi seas from 2000-2009.

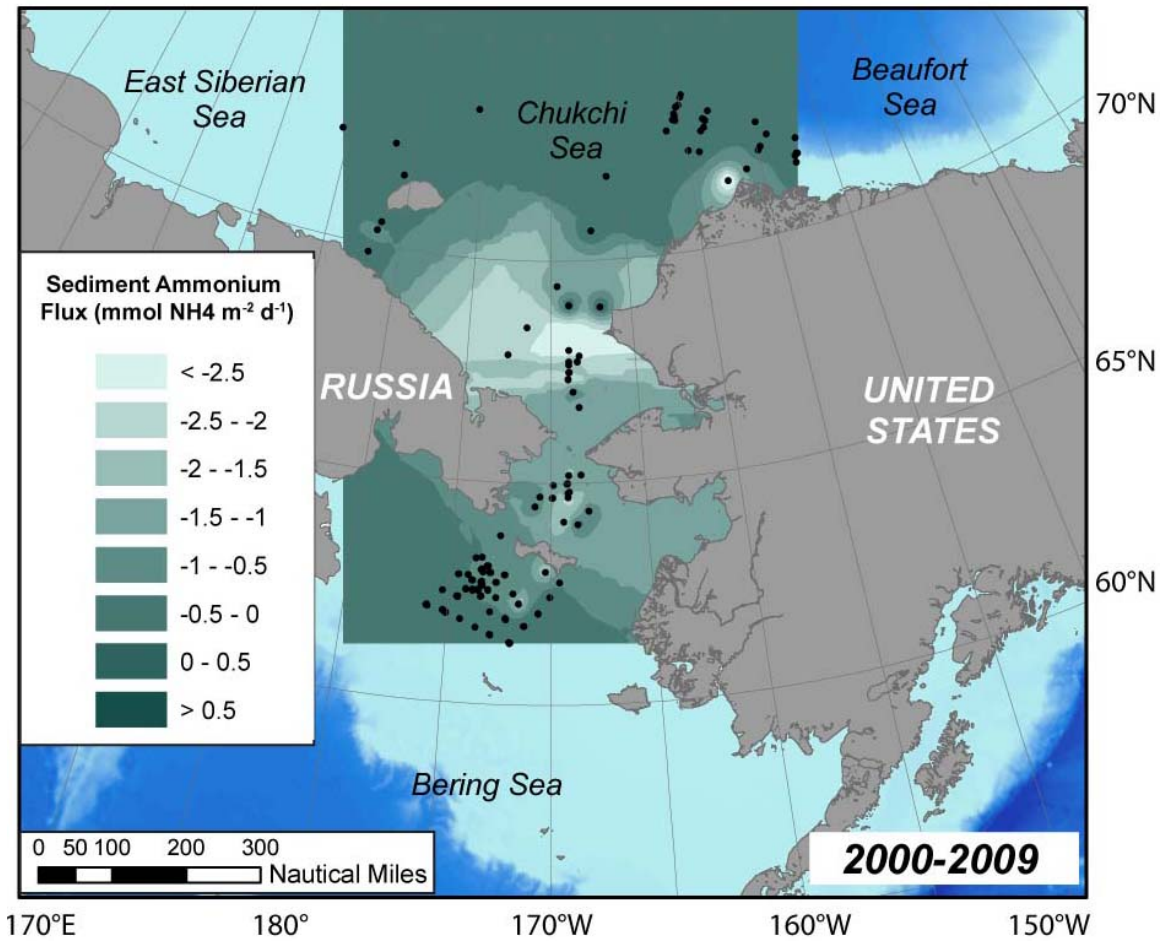

Figure 10 - Efflux of ammonium from sediments (negative values) in the northern Bering and Chukchi seas from 2000-2009.

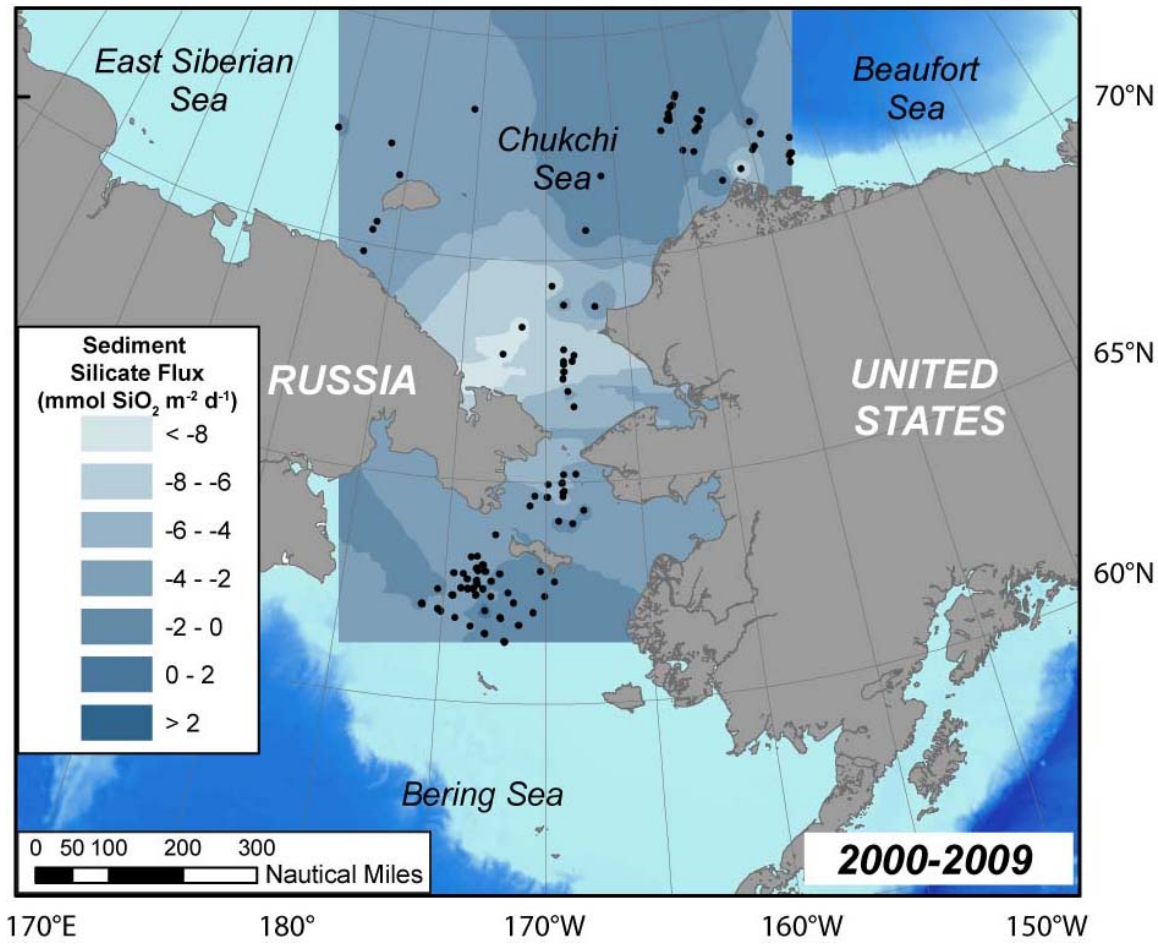

Figure 11 - Efflux of silicate from sediments (negative values) in the northern Bering and Chukchi seas from 2000-2009.

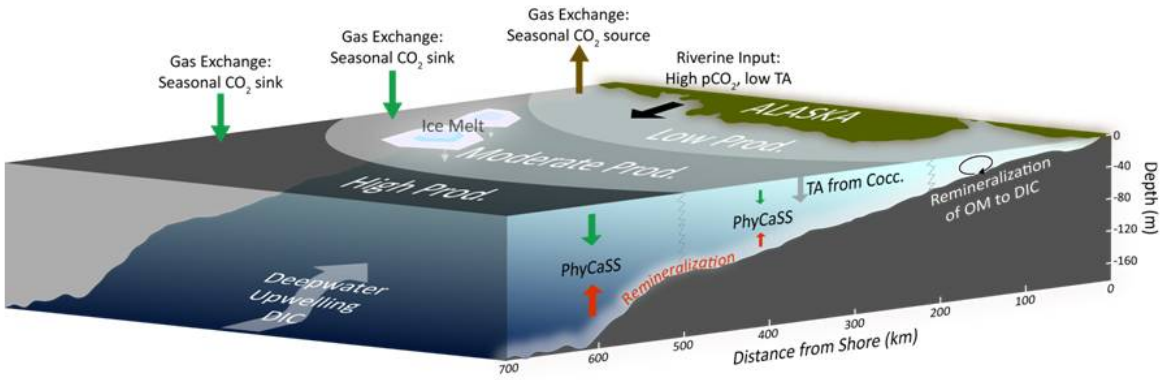

Figure 12 - Generalized description of the processes affecting the carbonate chemistry of the eastern Bering Sea shelf. The influx of runoff from the coast delivers water with high pCO_2, low TA, and moderate concentrations of dissolved organic matter (OM). The high pCO_2 of the water creates a seasonal source of CO_2 to the atmosphere while reducing carbonate mineral saturation states. Offshore, the upper water column is dominated by sea ice melt in late spring and summer that creates a highly satisfied surface layer where primary production is controlled by the confluence of coastal waters rich in micronutrients and basin water replete in macronutrients. Seasonally high rates of NCP lead to a rapid drawdown of CO_2 at the surface creating a strong seasonal sink for atmospheric CO_2. In 2009, coccolithophore (Cocc.) blooms were observed in the intermediate shelf waters and lowered TA concentrations at the surface. The varying degree of export production at the surface determined the amount of remineralization that occurred at depth which ultimately controlled saturation states. This PhyCaSS interaction can be observed to varying degrees across the shelf (adapted from Mathis et al., in review).