Chapter 8. Carbon Fluxes Across Boundaries in the Pacific Sector of the Arctic Ocean in a Changing Environment

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CONTENT

ABSTRACT

This chapter synthesizes carbon fluxes (both organic and inorganic) across the land-ocean and air-sea boundaries in the Pacific Sector of the Arctic Ocean (PSAO) as well as ocean gateway exchanges in the region. The latter fluxes includes dissolved inorganic carbon (DIC) transported into the area from the Pacific Ocean via the Bering Strait and exported to the Atlantic Ocean via the Canadian Archipelago, as well as those exchanges between various sub-regions within the system. We emphasize the changes in the magnitudes of these fluxes in the context of climate warming and sea-ice melt, as well as other hydrological cycle changes in the Arctic.

Our synthesis concludes that while the inflow of DIC from the Pacific Ocean is relatively well quantified (605 ± 78 Tg C yr^{-1}; $T=10^{12}$), the intermittent input flux from the East Siberian Sea (ESS) is not (32 ± 16 Tg C yr^{-1}). Most of the uncertainties are associated with actual water fluxes rather than DIC concentrations, and thus are viewed as systematic errors in our DIC mass balance analysis. Furthermore, we determined an export flux of 725 Tg C yr^{-1} to the Atlantic Ocean, with the previso that this term is not well quantified due to a paucity of DIC data from the Canadian Archipelago. The Chukchi Sea is the dominant site for atmospheric carbon dioxide (CO_2) uptake (up to 35-46 Tg C yr^{-1}), while the Beaufort Sea (2.9 Tg C yr^{-1}) and the Canada Archipelago (~10 Tg C yr^{-1}) take-up much less CO_2 and the latter may be a weak source of CO_2 to the atmosphere during certain times of the year. Additionally, the ESS shelf is a net source of CO_2 for the atmosphere (< 5 Tg C yr^{-1}). Overall, the PSAO region appears to export more DIC to the Atlantic Ocean than it receives through the combined inputs from the Pacific Ocean, the ESS, the atmosphere, and the rivers by a small amount (27 Tg C yr^{-1} or 5%). Our preliminary DIC budget, with the caveat that there is significant uncertainty due to both insufficient DIC data and rapidly changing climate conditions, suggests that the PSAO is probably weakly net

heterotrophic (i.e., respiring more organic carbon, OC, than producing it). This tentative assessment of the trophic status of the PSAO, if supported by further data, suggests that in addition to labile OC produced in the highly productive marginal seas, some riverine and coastal erosion-derived OC may also be recycled internally in this part of the Arctic system. As warming progresses, we suggest that the Arctic Ocean may produce more DIC and thus it may export more DIC to the Atlantic Ocean. Whether this change will turn the Arctic Ocean into a weaker CO_2 sink or even a CO_2 source for the atmosphere is uncertain and dependent on multiple factors that control the rate of surface water CO_2 increase versus the rate of the atmospheric CO_2 increase.

8.1 **INTRODUCTION**

Accumulation of greenhouse gases such as carbon dioxide (CO_2) and methane in the atmosphere, global climate and environmental change, and the sustainability of the Earth's biosphere are of great scientific and societal concern. Improved understanding of the global carbon cycle and potential responses of the climate system requires better knowledge about key physical, chemical and biological processes that control global biogeochemical cycles, an assessment of the complex interactions and feedbacks, and a better understanding of the vulnerabilities that impact carbon pools in the Earth system. This is particularly true for the Arctic Ocean, which is widely viewed as one of the most sensitive hotspots of the Earth's physical and biological systems undergoing rapid change and Arctic amplification feedbacks (Acia 2004; Perovich et al. 2007; Serreze and Francis 2006). On land, these include reorganization of the hydrological cycle (e.g., reductions of permafrost and glacial ice), expansion of temperate ecosystems into subpolar/polar regions, and mobilization of terrestrial carbon pools (Mcguire et al. 2009). In the Arctic Ocean, changes include atmospheric and ocean warming, sea-ice loss (Serreze and Francis 2006) and "*greening*" of Arctic surface waters (Arrigo et al. 2008). As a framework for supporting carbon cycle studies, "*A U.S. Carbon Cycle Science Plan (1999)*" (Sarmiento and Wofsy 1999) proposed two long-term research goals for North America: (1) understanding the northern hemisphere land CO_2 sink, and; (2) understanding the ocean carbon sink. These goals continue to be emphasized in the new Plan for the next decade [*Michalak et al.* 2011]. As part of this framework, determining atmosphere-land-ocean interactions, fluxes and exchanges in the high latitude areas of North America (i.e., the Arctic Ocean margins) is critical for understanding high-latitude carbon cycling, assessment of vulnerable carbon pools (Mcguire et al. 2009), and decision-support activities.

This chapter focuses on the Pacific Sector of the Arctic Ocean (PSAO) or, in general, the western Arctic Ocean. Our review and analyses focus on assessing interfacial carbon exchanges within the ocean domain of the PSAO and carbon fluxes across the land-ocean and air-sea boundaries. This assessment includes organic carbon and inorganic carbon (e.g., CO_2 gas and total dissolved inorganic carbon, DIC). Carbon cycling in the PSAO domain of the Arctic Ocean is highly dynamic and seasonally driven by the extreme variability in physical conditions. A conceptual model depicting both boundary processes (this chapter) and interior processes is given Fig. 1 in the Mathis *et al* chapter (Mathis 2011). Water column physical and biogeochemical processes are reviewed in detail in the Mathis *et al* chapter as well. Only a brief description of critical processes is given in this chapter to illustrate the potential controlling mechanisms on carbon fluxes across on the key boundaries.

The inflow of nutrient-rich Pacific Ocean water from the Bering Sea into the Chukchi Sea (Codispoti et al. 2005), coupled with abundant light and the seasonal retreat and melting of sea ice, supports a brief but intensive period of marine phytoplankton photosynthesis and growth (Cota et al. 1996; Hill and Cota 2005; Springer and Mcroy). This biological production is much stronger in the Chukchi Sea than in other Arctic Ocean shelves where nutrients concentrations are persistently lower. The seasonally high biological production leads to intensive sea surface CO_2 depletion and atmospheric CO_2 uptake in the Chukchi Sea, which must influence CO_2 flux in its downstream subsystems (i.e. the Beaufort Sea and deep Canada Basin).

At the atmosphere-land interface of the high-latitudes, atmospheric CO_2 is fixed through terrestrial plant photosynthesis into organic carbon (OC). The production of OC on land will likely increases as the Arctic continues to warm and more productive species of plants establish themselves in regions that have been traditionally been dominated by tundra. Watershed drainage,

which will also likely increase with warming, will subsequently enhance transport of terrestrial organic carbon in river water through the land-ocean interface (e.g., estuaries and wetlands of the Arctic) into the coastal ocean. Once in the ocean, organic carbon may be metabolized back to CO_2 and either released back to the atmosphere or exported into the deep ocean (Mackenzie et al. 2004; Smith and Hollibaugh 1993). Within the ocean margins of the Arctic, atmosphere-ocean CO_2 exchange occurs, while net fixation of CO_2 into phytoplankton biomass also occurs, with a small portion of the ocean derived particulate organic carbon (with addition of terrestrial organic carbon) exported to the deep ocean and an even smaller fraction buried in sediments (Sarmiento and Gruber 2006). Thus CO_2 flux across the atmosphere-ocean interface is a critical variable in global carbon cycle models (Liu et al. 2010; Takahashi et al. 2009), which in the Arctic is complicated by the seasonal presence of sea-ice that can act as a barrier to the exchange of gases.

In pre-industrial times, the global ocean and in particular the coastal oceans released CO_2 as a result of the respiration and remineralization of terrestrial OC supplied through rivers (Smith and Hollibaugh 1993). In the Anthropocene, the atmosphere-ocean exchange of CO_2 is reversed with the global ocean acts as a net sink for atmosphere CO_2 due mainly to the increase in the atmospheric CO_2 concentration (Takahashi et al. 2002; Takahashi et al. 2009). However, the situation in the ocean margins is more complex. Although based on limited data, in general, the tropical and nearshore coastal seas as well as areas more influenced by rivers are more likely to be net sources of CO_2 while temperate and polar coastal seas and those regions more distant to delivery of terrestrial organic carbon are more likely to be net sinks of CO_2 (Borges et al. 2005; Cai 2011; Cai et al. 2006; Chen and Borges 2009; Ducklow and Mccallister 2004; Mackenzie et al. 2004). However, an argument can be made that increasing terrestrial inputs and discharge of anthropogenic materials associated with climate and land use changes, as well as changes in the

terrestrial hydrological cycle would tend to shift the ocean margins toward being a source of CO_2 as most terrestrial OC is respired in adjacent coastal zones. This argument is particularly relevant in the Arctic Ocean margins and probably even its interior, as riverine organic and inorganic carbon fluxes are likely to increase due to increased river runoff, permafrost thawing, and coastal erosion under current conditions and future climate change scenarios (Guo and Macdonald 2006; Mcguire et al. 2009). For example, it was shown that coastal erosion and rivers bring to the East Siberian Arctic Shelf an integrated signal of terrestrial organic matter released from the thawing onshore permafrost (Gustafsson et al. 2011; Pipko et al. 2011; Semiletov et al. 2007; Semiletov et al. 2011; Van Dongen et al. 2008; Vonk et al. 2010). This scenario may have particularly sensitive or highly non-linear consequences considering the fact that the Arctic Ocean has only 1% of global ocean volume but receives about 10% global freshwater input and the associated suspended and dissolved materials.

8.2 GEOGRAPHIC AND WATER MASS FEATURES

8.2.1. Geographic definition and description

The PSAO and its associated margins include the East Siberian, Chukchi, and Beaufort Seas, shelf waters of the Canadian Archipelago, and adjacent waters within the Canada Basin. The PSAO is bounded by the Lomonosov Ridge in the north and the shelves of the East Siberian Sea in the east, Chukchi and Beaufort Seas in the south, and the Canadian Archipelago in the west. In addition, as a gateway to the Arctic from the Pacific, the northern Bering Sea and Bering Strait are considered in this synthesis. The Arctic Ocean (excluding the Nordic Seas and Baffin Bay) covers roughly 2.6% of the surface area of the global ocean, but occupies a volume of <1% (with much of the volume held within the deep basins of the Arctic including the Canada and Eurasian basins). The shallow continental shelves of the Arctic make up about 50% of the total area of the

Arctic Ocean (Table 1), with the PSAO comprising approximately two thirds of that shelf area. In contrast, the continental shelves of the global ocean comprise only about 7.2% of the total ocean area (Cai 2011; Walsh 1988). Given the physical setting of the Arctic Ocean, interfacial processes at land-ocean, atmosphere-ocean, and ocean-ocean boundaries have great influence on the carbon cycle.

Shelves in the PSAO domain are relatively shallow along the eastern rim and increase substantially towards the western side. The Chukchi Sea shelf has a mean depth of about 80 m, is the broadest coastal sea in the entire region, and the region most impacted by inflow of Pacific Ocean water. The East Siberian Sea has the shallowest shelf with a mean depth of only 58 m and is highly influenced by river inputs from the Lena, Kolyma and Indigirka Rivers (Semiletov et al. 2005; Semiletov et al. 2011). The Beaufort Sea has a narrow shelf with a mean depth of 125 m, while the mean shelf depth further increases towards the Canadian Archipelago (Table 1), with both shelves highly influenced by Mackenzie River input (Shadwick et al. 2011; Yamamoto-Kawai et al. 2009b). The sharp bathymetric increase from the shelf to the slope separates these shelves from the adjacent deep Canada Basin, with outflows from the shelf through submarine canyons like Barrow Canyon and Herald Valley (Codispoti et al. 2005; Woodgate et al. 2005b) as well as the northern flank of the ESS (Anderson et al. 2010), facilitating the export of organic carbon to the deep Arctic, while shelf-slope topography facilitates upwelling of dissolved nutrients and dissolved inorganic carbon (DIC) and generation of mesoscale eddies that promote shelf-basin exchanges of water and materials (Mathis et al. 2007).

8.2.2 Water-mass chemistry features

There are several water masses in the slope and basin areas of the Pacific Sector of the Arctic Ocean (Anderson et al. 1990; Mclaughlin et al. 2004; Woodgate et al. 2005b) (Table 1): (1) the Surface or Polar Mixing Layer (SML, 0-40 m) with S < 31, DIC = ~1750-1900 μmoles kg^{-1}, and water residence time ~10 yrs; (2) the Upper Halocline Layer (UHL, ~40-120 m) with S ~ 33.1, DIC = ~2160-2190 μmoles kg^{-1}, $[NO_3^-]$ = ~14 μmol/L, $[PO_4]$ = ~1.8 μmol/L, and water residence time ~10 yrs; (3) Lower Halocline Layer (LHL, ~150-220 m) with S ~ 34.3, DIC = ~2170-2190 μmoles kg^{-1}, $[NO_3^-]$ = ~12 μmol/L, $[PO_4]$ = ~0.8 μmol/L, and residence time ~15 yrs; (4) Atlantic Water (AW, >250-900 m) with S ~ 34.8-34.9, DIC = ~2140-2160 μmoles kg^{-1}, $[NO_3^-]$ = ~14 μmol/L, $[PO_4]$ = ~1.0 μmol/L, and residence time ~30 yrs; and (5) Arctic Ocean Deep Water (>900 m deep). The SML and UHL waters have a Pacific origin with influx of river runoff while the LHL water is mostly of Atlantic origin but with some influence of Pacific water by shelf plumes.

8.3 PACIFIC OCEAN INFLOW FLUX

Water masses entering and forming the upper layers of the western Arctic Ocean come from the Bering Sea, which has a surface circulation consisting of relatively fresh, nutrient-rich waters derived from the North Pacific Ocean "funneling" towards the Bering Strait. Water transiting northward through Bering Strait is composed mainly of relatively colder, saltier, and more nutrient-rich and CO_2-poor water of the Anadyr Current in the west, Bering Shelf water (BSW) in the middle, and warmer, fresher, and relatively high CO_2 Alaskan Coastal Current (ACC) waters in the east. The inflow is higher in summer and lower in winter with an annual average of ~0.8 Sv ($25x10^3$ km^3 yr^{-1}) (Fig. 1) (Roach et al. 1995; Woodgate et al. 2005a).

With an average DIC value of 1997±70 μmol kg^{-1} in the northern Bering Sea from the 2010 RUSALCA (Russian-American Long-term Census of the Arctic) and the 2003-2004 SBI (Shelf-Basin Interactions) data, we estimate a DIC flux of 50.4 x 10^{12} mol yr^{1} (or 605 ± 79 Tg C yr^{1}) entering the Arctic Ocean from the Pacific Ocean (Table 2). Uncertainty attached to this Bering Strait DIC flux is primarily associated with uncertainty in water flow (± 0.1 Sv or 12.5%), which leads to an uncertainty of ±76 Tg C yr^{1} in DIC flux. Variability in DIC content (3.3%, Table 2) of the three water masses (i.e., AC, BSW and ACC) flowing through Bering Strait leads to an uncertainty of ±20 Tg C yr^{1} in DIC flux. Thus an overall uncertainty of 79 Tg C yr^{1} is derived (i.e., SQRT(76^2+20^2) = 78.6). This annual water-borne DIC flux accounts for approximately 50% of the total DIC inventory in the Chukchi Sea, meaning the flushing time of water and the physical residence time of DIC in the Chukchi Sea is probably not longer than 6 months. In addition, there is an intermittent inflow of 0-0.1 Sv (or 0-3.2x10^3 km^3 yr^{-1}) to the Chukchi Sea from the East Siberian Sea (ESS) (Woodgate et al. 2005b). Recent data indicate that the East Siberian Sea inflow into the Chukchi Sea through Long Strait has a DIC content of ~1700 μmoles kg^{-1} (RUSALCA data; N.R. Bates, unpublished), equivalent to a transport of ~32±16 Tg C $year^{-1}$ if a water flux of 0.05 Sv is assumed. Here, the large uncertainty is associated with both the water flux (±50%) and DIC values (±20%). Taken together, the total amount of DIC entering the Chukchi Sea is around 53.1 x 10^{12} mol yr^{-1}, which has a calculated error of 13% (or 637 ± 80 Tg C yr^{-1}). Uncertainty in the water-borne DIC flux is systematic for DIC mass balance analysis is concerned and will not go into the analysis as we assume a balanced water budget in the region. Thus, the DIC influx uncertainty is only 3.3% or ±20 Tg C yr^{-1}.

Early studies of the DOC content of waters passing the Bering Strait suggested a large range of DOC values (34–134 μmol L^{-1}; see Wheeler (1996) and Walsh (1997)). However, more recent

measurements at Bering Strait (RUSALCA data; N.R. Bates, unpublished data) indicate that the DOC of AC and BSW waters ranged from ~80-90 µM while the DOC content of the ACC was higher (~90-110 µM). Assuming an average DOC content of 90 µM, we estimate a DOC flux of 2.3 x 10^{12} mol yr^{1} (or 27.0 ± 3.3 Tg C yr^{1}). At Long Strait, DOC content varied from ~90 to 140 µM, with higher DOC contents in the nearshore ESS current. Assuming an average DOC content of 100 µM, we estimate a DOC flux of 0.16 x 10^{12} mol yr^{1} (or 1.9 ± 0.4 Tg C yr^{1}). Thus the DOC flux entering the Chukchi Sea is around 2.46 x 10^{12} mol yr^{-1} (or 28.9 ± 3.3 Tg C yr^{-1}).

On the broad and shallow (<100 m deep) continental shelf of the Chukchi Sea, the prevailing view is that a major part (we assume a total flux of 0.6 Sv here) of the Pacific inflow water travels northward to exit the shelf into the Canada Basin through four major outflows: Herald Valley, Long Strait, Central Channel, and Barrow Canyon (~0.1-0.3 Sv each), and smaller part (we assume a total flux of 0.25 Sv) flows eastward along the shelf break of the relatively narrow shelf of the Beaufort Sea towards the Canadian Archipelago (Codispoti et al. 2005; Overland and Roach 1987; Pickart 2004; Woodgate et al. 2005a; Woodgate et al. 2005b) (Fig. 1). A large part of the northward flow is believed to join the eastward flow of the shelf break current (Pickart et al. 2005; Weingartner et al. 1998). Despite the overall complexity of the circulation, most of the inflow of water and DIC from the Pacific and the East Siberian Sea is eventually balanced by the southward flow through the Canadian Archipelago (for the purpose of balancing the water budget, we adopted a total flux of 0.85 Sv) (Codispoti et al. 2009; Mcguire et al. 2009). Finally, a small part of the Bering Strait inflow goes to the ESS, which is evidenced from the chemical signals in the eastern part of the ESS (Anderson et al. 2011; Anderson et al. 2009; Semiletov et al. 2005). However the net flux is not known and more than likely rejoins the eastward flow towards

the North Atlantic. This is one reason why we assigned a smaller value of 0.05 Sv for the ESS current to the Chukchi Sea rather than the suggested maximum flux of 0.1 Sv.

8.4 FLUXES ACROSS THE ARCTIC LAND-SEA INTERFACE

As stated earlier, the Arctic Ocean receives a disproportionately large amount of global freshwater runoff (Aagaard and Carmack 1989) and therefore river inputs of terrigenous organic carbon and DIC are important to the biogeochemical cycling of carbon in the region. Arctic terrestrial ecosystems have been considered sinks for atmospheric carbon, resulting in the storage of large quantities of soil-based organic matter in high latitude regions (Oechel et al. 2000; Ping et al. 2011; Waelbroeck et al. 1997). Increased river runoff and terrestrial organic carbon inputs to the Arctic Ocean through permafrost thawing, accelerated coastal erosion, and increasing river runoff could dramatically change the turnover and transport rates of tundra carbon, and alter biogeochemical cycles and the marine ecosystem as a whole. Indeed, warming and environmental changes in the Arctic regions have resulted in the remobilization of soil organic carbon and terrestrial organic carbon inputs into the Arctic Ocean through increased river runoff and accelerated degradation of permafrost and peatlands (Costard et al. 2007; Frey and Smith 2005; Guo et al. 2007; Guo et al. 2004; Jorgenson and Brown 2005; Jorgenson et al. 2006; Peterson et al. 2002; Savelieva et al. 2000). Thus, quantitative measurements of riverine export fluxes are needed to determine the response of the Arctic river basins to a changing climate (Finlay et al. 2006; Guo et al. 2011; Mcguire et al. 2009; Semiletov et al. 2011). However, DOC concentrations and discharge in Arctic rivers are highly variable between seasons, making quantitative estimation of carbon fluxes difficult for Arctic rivers (Finlay et al. 2006; Guo and Macdonald 2006). As pointed out by (Guo et al. 2011), flux estimation without spring freshet

sampling would underestimate organic species but overestimate inorganic species, whereas flux estimation without winter sampling overestimates organic species but underestimates inorganic species.

In the North American side of the PSAO margins, inputs of terrestrial DOC and particulate organic carbon (POC) via river discharge are mainly derived from the Mackenzie River to the Beaufort Sea and the Yukon River to the Bering and Chukchi Seas through the Alaskan Coastal Current (ACC). Many recent studies have estimated river fluxes of DOC and DIC from the Yukon River (Guo et al. 2011; Guo and Macdonald 2006; Raymond et al. 2007; Spencer et al. 2009; Striegl et al. 2005; Striegl et al. 2007). Based on data compiled in Guo *et al*. (2011), average DOC and POC flux from the Yukon River was 1.7 and 0.85, respectively, while DIC flux was 4.6 Tg C/yr, which is higher than TOC flux (Table 3). River fluxes of TOC including DOC and POC from the Mackenzie River are ~4.1 Tg C/yr while DIC flux is ~4.8 Tg C/yr. Fluxes from other northern Alaska rivers, including the Colville, Kuparuk, and Sagavanirktok rivers, remain poorly quantified and may contribute 3-5% of fluxes from large rivers in the North America (Mcguire et al. 2009; Rember and Trefry 2004).

Riverine fluxes of DOC and POC to the East Siberian Sea have recently been estimated based on more intensive sampling (Finlay et al. 2006; Lobbes et al. 2000). The organic carbon export flux from the Kolyma River was estimated to be 0.46 Tg-C/yr for DOC and 0.31 Tg-C/yr for POC (Lobbes et al. 2000). With intensive sampling during snowmelt period, the DOC flux from the Kolyma River was significantly higher, at 0.96 Tg-C/yr (Finlay et al. 2006). Combining fluxes from both the Kolyma and Indigirka rivers to the ESS, the TOC export flux is in the order of 1.1-1.7 Tg-OC/yr, which is significantly lower than the TOC flux from either the Mackenzie River to the Beaufort Sea or the Yukon River to the Bering Sea (Table 3). DIC data

for the East Siberian rivers are scarce and some are in the form of total alkalinity (Cooper et al. 2008).

Export of terrestrial organic matter exerts a major influences in the carbon cycle on the ESS shelf. There is a significant amount of terrestrial OC stored within sediments, especially in the inner shelf most strongly influenced by coastal erosion between the Dmitry Laptev Strait and the Kolyma River mouth, where the OC is almost all of terrestrial origin (80% to 100%) (Semiletov et al. 2005). However, only 50% of the OC in the more offshore sediments underneath Pacific-origin water is of terrestrial origin (Semiletov et al. 2011; Vonk et al. 2010).

It is a challenge to precisely quantify the high seasonal variability of river fluxes of DIC, total alkalinity (TA), POC and DOC, although the recently completed PARTNERS project greatly improved the data abundance and quality (Cooper et al. 2008). However, it is still difficult to quantify the percentage of riverine POC and DOC that is labile and will subsequently be respired into CO_2 once in the ocean margins. Although a major part, if not most, of the terrestrial organic carbon is expected to be respired in estuarine and shelf areas, the ultimate fate of this material is not well known (De Haas et al. 2002; Hansell et al. 2004). Riverine DIC plays a significant role in the DIC mass balance in the Arctic Ocean (~20%, Anderson *et al*., 1990), as will the mineralized fraction of terrigenous DOC (Hansell et al., 2004; Letscher et al., 2011; Anderson et al., 2009). Taken together, the total Arctic riverine C flux is ~77 Tg C yr^{-1}, similar to the direct CO_2 flux from the atmosphere to the sea (Bates and Mathis 2009). This river carbon input may also increase rapidly as the Arctic warms and permafrost thaws. Thus, it is important to delineate this component of land-ocean carbon input.

In addition to Arctic fluvial fluxes into the Arctic Ocean, recent studies have shown the importance of lateral fluxes across the soil-water interface through Arctic coastal erosion (Jorgenson and Brown 2005; Ping et al. 2011). Total organic carbon fluxes derived from coastal erosion have been estimated to be 6-7 Tg C $year^{-1}$ (Mcguire et al. 2009; Stein and Macdonald 2004), although large uncertainties exist. Jorgenson and Brown (2005) first estimated that eroding shorelines of the Beaufort Sea contribute ~0.18 Tg C yr^{-1}. Based on estimated fluxes and scaled up to pan-Arctic regions (Mcguire et al. 2009)(Volker *et al*., 2004;), coastal erosion contributes ~15% of the total terrigenous organic carbon flux to the Arctic Ocean (41 Tg C yr^{-1}). This lateral export from pan-Arctic erosion is on the same order as riverine fluxes of particulate organic carbon, which have been estimated at 6-7 Tg C yr^{-1} (Mcguire et al. 2009). Similar to coastal erosion, the river POC fluxes are mostly derived from the erosion of river banks and permafrost, based on evidence of radiocarbon composition of riverine POC and estuarine sediments (Goñi et al. 2005; Guo and Macdonald 2006; Guo et al. 2007). In addition, while river export is restricted in the estuarine region, materials exported from coastal erosion are dispersed along the entire Arctic coastline, allowing extensive biogeochemical cycling after erosion.

Lateral export fluxes of organic carbon from coastal erosion have significant implications for the Arctic carbon cycle and ecosystem changes. Although only ~1-2% of the total soil organic carbon could be released in dissolved form during soil leaching experiments (Dou et al. 2010), inputs of soil organic matter through both coastal erosion and river export and the subsequent degradation of both dissolved and particulate organic matter could significantly alter the water and environmental quality and shift the Arctic coastal ecosystem to net heterotrophy (i.e., respiring more OC than it produces). Unfortunately, the fate of organic matter exported from

coastal erosion and rivers is largely unknown (Holmes et al. 2002). Further studies are needed to examine the lability and biogeochemical cycling of soil organic carbon in the Arctic Ocean

8.5 CO_2 FLUX ACROSS THE AIR-SEA BOUNDARY

8.5.1 Sea Surface pCO_2 distribution

In early studies of the Chukchi Sea, it was observed that seawater pCO_2 values were lower than pCO_2 in the atmosphere during the sea-ice free period (i.e., the Arctic Ocean Section (AOS) expedition in 1994, (Jutterström and Anderson 2010)). Since then, other studies have observed low seawater pCO_2 conditions on the Chukchi Sea shelf during summertime (Andreev et al. 2010; Bates 2006; Bates et al. 2005; Chen and Gao 2007; Fransson et al. 2009; Murata and Takizawa 2003; Pipko et al. 2002). More recently, similarly low values for seawater pCO_2 have been observed during the 2008 CHINARE project (**Figure 2**). Seasonal changes in surface pCO_2 on the Chukchi Sea shelf have been largely attributed to cooling of surface waters during the northward transit of waters across the Chukchi Sea shelf (Bates 2006; Murata and Takizawa 2003) and high rates of summertime phytoplankton primary production that acts to decrease seawater DIC and pCO_2 (Bates 2006). These processes act to produce a dynamic shelf to basin carbon pump (Anderson et al. 2010; Bates 2006). The seasonal rebound of seawater pCO_2 and DIC during wintertime likely results from a continued uptake of CO_2 through gas exchange during sea-ice formation and brine rejection (Anderson et al. 2004; Omar et al. 2005), continued transport of Pacific Ocean waters into the Chukchi Sea through Bering Strait and vertical entrainment by mixing with CO_2 rich subsurface waters. These processes are discussed in details in the Mathis chapter.

On the ESS shelf, surface water pCO_2 values significantly above atmospheric values have

been reported (Anderson et al. 2011; Anderson et al. 2009; Pipko et al. 2011; Semiletov 1999; Semiletov et al. 2007), with much higher values near the outflow of the Kolyma River that drains into the ESS shelf (Semiletov 1999; Semiletov et al. 2007). The high seawater pCO_2 values can be attributed primarily to the remineralization of organic matter introduced from the coastal erosion and Siberian Rivers (Anderson et al. 1990; Cauwet and Sidorov 1996; Semiletov 1999; Semiletov et al. 2007; Semiletov et al. 2011).

In the Beaufort Sea, seawater pCO_2 appears to be highly variable (~150-350 µatm) in the western parts of the shelf (Bates 2006; Murata and Takizawa 2003), with low values observed in areas with high proportions of freshwater and sea-ice melt (Bates 2006; Cooper et al. 2005; Murata and Takizawa 2003). In the eastern Beaufort Sea shelf, summertime surface seawater pCO_2 values were generally low close to equilibrium with the atmosphere (Fransson et al. 2009).

The central basin has not been extensively sampled for the marine carbon cycle due to heavy ice-coverage. In early studies, the AOS expedition in 1994 suggested that surface waters under sea-ice had seawater pCO_2 values lower than the atmosphere. Several repeated sections across the central basin also have shown similar results (Jutterström and Anderson 2010). In the early 2000's, very low seawater pCO_2 values have been observed in the Canada Basin off the Chukchi Sea shelf (Bates 2006) and in the Makarov Basin of the Canada Basin (Fransson et al. 2009). However, more recently, Yamamoto-Kawai (2009a) showed that some surface areas of the Canada Basin had seawater pCO_2 values close to equilibrium with the atmosphere in areas with significant sea-ice loss (particularly during the unprecedented sea-ice loss in 2007). After the major summertime sea-ice retreat observed in 2007, based on high resolution underway pCO_2 measurements, Cai (2010) showed that ice-free surface areas of the Canada Basin (mostly the southern part of the basin) had seawater pCO_2 conditions close to equilibrium with the

atmosphere, reflecting uptake of CO_2 from the atmosphere and warming during the exposure of surface waters, whereas areas with heavy ice-cover (mostly the northern and western part) had lower surface water pCO_2 (Figure 2).

8.5.2. Air-sea CO_2 flux

Estimating air-sea CO_2 flux rates in various areas of the Arctic Ocean has been an important goal over the last two decades. Early work based on DIC mass balance suggested that the entire Arctic Ocean absorbed atmospheric CO_2 at a rate of 24 Tg C yr^{-1} (Anderson et al. 1998). Based on the reports prior to 2005, Cai et al. (2006), in a global ocean margin synthesis, assigned an overall atmospheric CO_2 uptake in the entire Arctic Ocean as 41 Tg C yr^{-1}. More recent pCO_2 data, calculated from high precision DIC and TA data at discrete stations, however, allowed (Bates et al. 2005) and (Bates 2006) to estimate annual net air-to-sea CO_2 fluxes as 38 and 66 Tg C yr^{-1}, respectively for the Chukchi Sea and the entire Arctic Ocean margins. We thus adopt a conservative CO_2 uptake flux of 35±6 Tg C yr^{-1} in the Chukchi Sea and 10 Tg C yr^{-1} in the Canada Archipelagos for budget analysis in Fig. 3. Most recently, Bates and Mathis (2009) summarized all available studies conducted prior to the 2007 major sea-ice loss event and concluded that the Arctic Ocean surface waters have the ability to absorb relatively large amounts of carbon dioxide (with a range of reported CO_2 sink rates ranging from 66 to 175 Tg C yr^{-1} or 5-14% of global ocean CO_2 uptake). However, the 2007 major sea-ice retreat event in the basin areas, may have tipped the Arctic Ocean to a smaller sink of CO_2 given more recent observations (Cai et al. 2010). It is probably reasonable to assume that the recent decrease in air-to-sea CO_2 flux reflects dynamic changes in the Arctic result of climate change and that the status of CO_2 sinks and sources in the Arctic is rapidly changing (Bates et al. 2011).

The summarized CO_2 fluxes given in Table 3 is largely based on the recent synthesis of (Bates and Mathis 2009) and (Jutterström and Anderson 2010), and a post 2007 reduced CO_2 flux in the Canada Basin based on recent work of (Cai et al. 2010). The accompany chapter on C processes [Mathis *et al.*, this volume] will discuss the biogeochemical processes controlling the CO_2 fluxes and the climate sensitivity of them.

8.6 IMPACT OF SEASONAL SEA-ICE CYCLE

The western Arctic Ocean margins experience extreme seasonal variations in insolation, sea-ice coverage, and freshwater inputs from Arctic rivers. Seasonal variations in sea-ice cover play an extremely important role in shaping the water-masses and ecosystem. During the wintertime, sea-ice covers most of the shelf areas and the water column is mostly homogeneous. During the summer, a high Bering Strait inflow brings nutrient-rich Pacific Ocean water to the Chukchi Sea and beyond. On the Chukchi Sea shelf, local sea-ice melt further modify water of Pacific Ocean origin to relatively warm, fresher Polar Mixed Layer (PML) water (upper 0-40 m, salinity typically < 31; temperature > -1.5°C). In the later part of the sea-ice free season, the temperature and salinity properties of the PML on the Chukchi Sea shelf widen from their wintertime characteristics (Woodgate et al. 2005b). The surface water in the Beaufort Sea is also modified by the Mackenzie River input.

In the southern part of the Canada Basin the river derived freshwater often contributes as much as 10% of the source water while sea-ice meltwater about 5% with the rest, 85%, as source seawater to the upper 50-m water column (Yamamoto-Kawai et al. 2009b). However, in recent summers, in the ice-free area at around 74˚N, sea-ice melt contributes to the freshwater flux equally as the river flux (Yamamoto-Kawai et al. 2009b) (also, W.-J. Cai unpublished summer 2008 results). If we apply an average of 6.0±2% of meltwater contribution to the top 50-m water

in half the area of the PSAO (total area = 3036×10^3 km^2 , Table 1) over a 4 month sea-ice melt during May to September, then net freshwater flux to this area is 9.1×10^3 km^3 or 0.29 Sv. This is a quite significant number on seasonal basis although annual net flux is probably not significant. Based on a salinity-oxygen isotopic study, (Yamamoto-Kawai et al. 2009b) concluded that the sea-ice meltwater component of surface water in the southern part of the Canada Basin has progressively increased at a mean rate of 0.27 m/yr in the top 50-m water column since 1987.

When sea ice is formed, pure crystals of water molecules are produced and the salts are expelled to a concentrated brine solution between the ice crystals. About two thirds of the salts escape the sea ice when formed. Theoretically, the cold concentrated brine solution leads to chemical oversaturation and precipitation of $CaCO_3$ (Richardson 1976). The precipitation will remove TA and DIC in a ratio of 2:1. Thus pCO_2 in the brine will increase. The high pCO_2 in the brine can lead to a flux of CO_2 from the sea ice to the atmosphere although the gas exchange velocity is likely very low and the inventory of the brine solution is limited. With time the brine drains out of the sea ice to give a bulk salinity of ~5 after one winter season to further decrease somewhat over coming seasons.

The chemical compositions of sea ice and brine have been studied in the field and laboratory. However, no unambiguous understanding has emerged, illustrating the variable conditions that sea ice is exposed to in the natural environment (Anderson and Jones 1985). High TA - DIC ratio has been shown in sea-ice meltwater collected north of Greenland (Rysgaard et al. 2007) and was suggested to be a result of the dissolution of $CaCO_3$ crystals which had formed in the sea ice. It was further argued that, when the sea ice melts, the $CaCO_3$ dissolution would cause a pCO_2 under-saturation in the surface water and thus an uptake of CO_2 from the atmosphere (Rysgaard et al. 2007). Others have been suggested that the production of brine

during sea ice formation promotes an uptake of CO_2 from the atmosphere as long as the surface water is under-saturated relative to the atmosphere (Anderson et al. 2004; Else et al. 2011).

Average values of S, TA and DIC derived from the work of (Rysgaard et al. 2007) are 5, 450 μmol/kg, and 400 μmol/kg respectively, which are equivalent to TA = 104.0 μmol/kg and DIC = 59.8 μmol/kg at 0 salinity (Cai et al. 2010). Taking the above sea-ice meltwater flux at face value, we derived a DIC flux at the level of 3.6 Tmol/yr or 44 TgC/yr (with probably one third of uncertainty). While this is not a trivial flux term, it is largely an internal or a seasonal source (during spring and summer) and sink (fall and winter). Therefore, for the annual net flux we do not count this part in the overall budget exercise given below. The current trend of increased summertime sea-ice melt will however require a reassessment of this issue.

8.7 OVERALL DIC BUDGET

DIC flux from the Pacific (605 TgC/yr) and from the ESS (32 Tg C yr^{-1}) to the western Arctic Ocean is estimated as 637±20 Tg C yr^{-1} based on the 2010 RUSALCA and the 2003-2004 SBI data (Table 2) if we ignore the inflow water flux uncertainty. We estimate DIC export flux to the Atlantic Ocean via the Canadian Archipelago by adopting a DIC value from an recent measurement that reported that the average DIC value exported from the Archipelago into the Baffin Bay is as high as 2140 μmol kg^{-1} (Shadwick et al. 2011). We also assume a balance in the input and output of water, and thus, assign the total input water flux from the Pacific and the ESS to the export through the Archipelago (i.e., 0.85 Sv, see Fig. 1). Thus a total DIC export flux to the Atlantic Ocean is estimated as 725±20 Tg C yr^{-1}.

Most of the DIC flux into the region of the Chukchi and Beaufort Seas is from the Pacific Ocean (605 Tg C yr^{-1}) whereas that from the ESS (32 Tg C yr^{-1}) and from the atmosphere (35 Tg C yr^{-1}) is also important. However, the total amount of DIC flux from ocean currents and rivers and from atmospheric CO_2 uptake into the Chukchi and Beaufort Seas and the Canadian Archipelago (698 Tg C yr^{-1}) is slight less than the export through the Archipelago (725 Tg C yr^{-1}). This difference is probably is within the uncertainty of our estimates as we used the lower boundary of atmospheric CO_2 uptake rates and as DIC data from the exiting water (i.e., the Archipelagos) is very limited. However, if we assume the values going into the budget analysis are accurate, then, the total DIC input is less than the export by 27 Tg C yr^{-1} or 5% of the total input or export. If supported by further data, this result suggests that the PSAO is slightly net heterotrophic, which indicates that not only the organic carbon generated in the highly productive Chukchi Sea is recycled within the system, part of the OC from river and coastal erosion is also respired into CO_2. However, we also recognize the fact that part of the OC production in the marginal seas must be exported to the deep Arctic Ocean (Moran et al. 2005).

While high uncertainty is involved in deriving the above conclusion, it is consistent with our understanding of the physical and biogeochemical conditions in the Arctic Ocean. The Arctic Ocean is a land locked ocean with large inputs of organic and inorganic carbon from the rivers and coastal erosion (total riverine OC and DIC flux 7.5 and 9.4 Tg C yr^{-1} respectively in the Pacific Sector, see Table 3). It is also known that newly produced marine OC is generally short-lived and recycled in within the upper ocean, thus may only contribute a small quantity to system-wide net production. Therefore, the Arctic Ocean margin being net heterotrophic probably is consistent with our current understanding of global carbon cycle and biogeochemistry (Cai 2011; Ducklow and Mccallister 2004; Pipko et al. 2011; Smith and

Hollibaugh 1993). Admittedly, this conclusion is very preliminary and requires both additional field observations and synthesis/modeling efforts. As warming progresses, we suggest that the Arctic Ocean likely will produce more DIC and thus export more DIC to the Atlantic Ocean. Whether this will turn the Arctic Ocean into a weaker CO_2 sink or even a CO_2 source is currently unknown and will depend on multiple factors controlling the rate of surface water pCO_2 increases versus that of the atmospheric CO_2 increase.

8.7 SUMMARY

This chapter synthesizes CO_2/DIC and organic carbon fluxes across various boundaries in the Pacific Sector of the Arctic Ocean (PSAO). At ~45 Tg C yr^{-1}, the PSAO is a significant part of the global oceanic sink of atmospheric CO_2. Uptake of atmospheric CO_2, plus inputs from rivers and coastal erosion (including respired CO_2), enables the PSAO to export more DIC to the Atlantic Ocean than it receives from the Pacific Ocean and other sources. Therefore while there are large uncertainties in our flux estimates and budget analysis, we suggest that with further increasing of warming, ice retreat, and transport of terrestrial OC to the Arctic (i.e., permafrost thawing and coastal erosion), the Arctic Ocean likely is likely to export more DIC to the Atlantic Ocean, contributing more DIC to the starting point of the global ocean deep water conveyor belt. It is unclear whether this trend will also lead to less CO_2 uptake from the atmosphere or even CO_2 release from the Arctic Ocean to the atmosphere in the future.

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References are given below the figures and tables

Figures

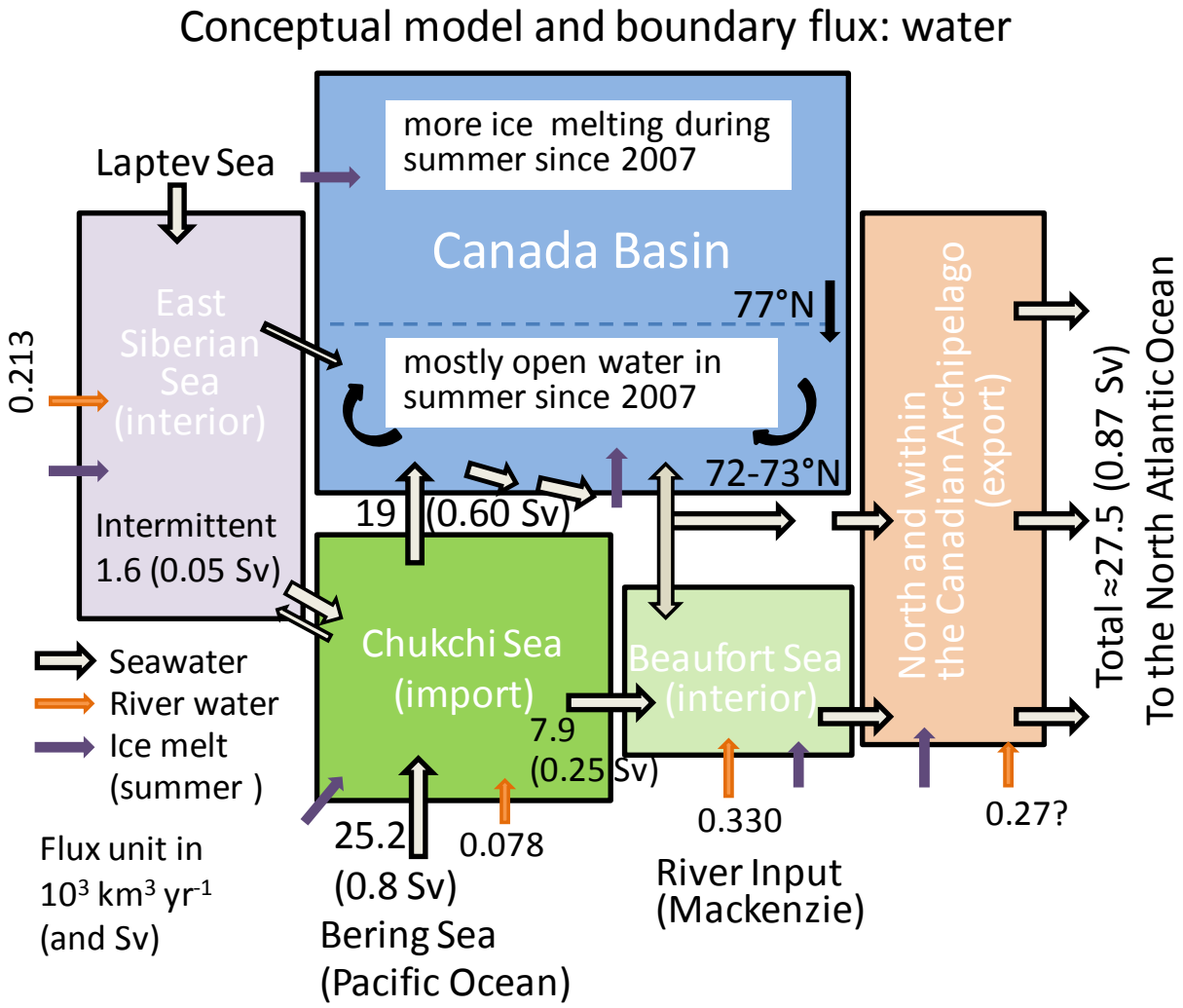

Fig. 1 Water flux within the Pacific Sector of the Arctic Ocean and margins. The larger hollow arrows represent seawater flux. The orange color arrows represent river water flux. The purple arrows represent water input from summer ice melt. The ice-melt water fluxes do not indicate flux from one box into the other. The Chukchi Sea is classified as an import shelf as it receives water and nutrients from the Pacific Ocean, the East Siberian Sea and the Beaufort Sea are classified as the interior sea, and the Canadian Archipelago is classified as the export sea.

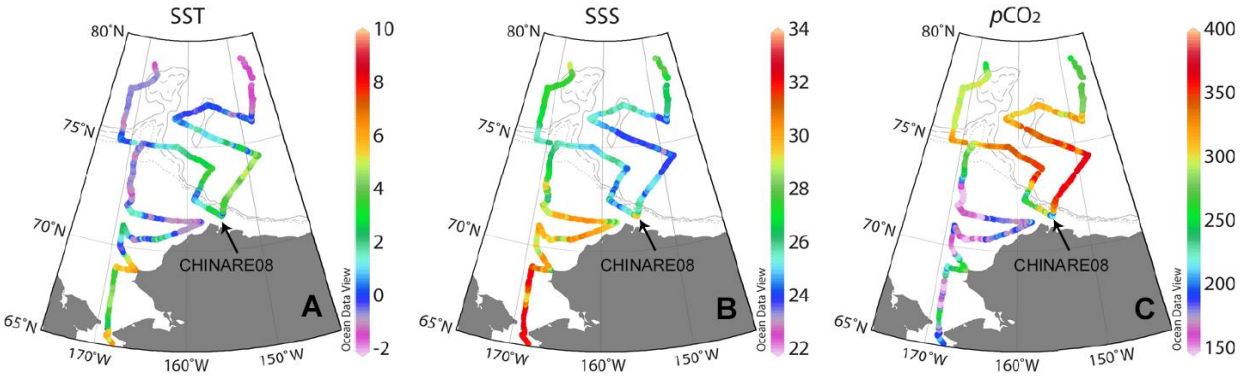

Fig. 2. Sea surface temperature (SST) (C), sea surface salinity (SSS), and pCO_2 (μatm) distributions measured during the 2008 CHINARE survey. Note that in the Southern Canada Basin temperature was high, salinity was low and pCO_2 was high.

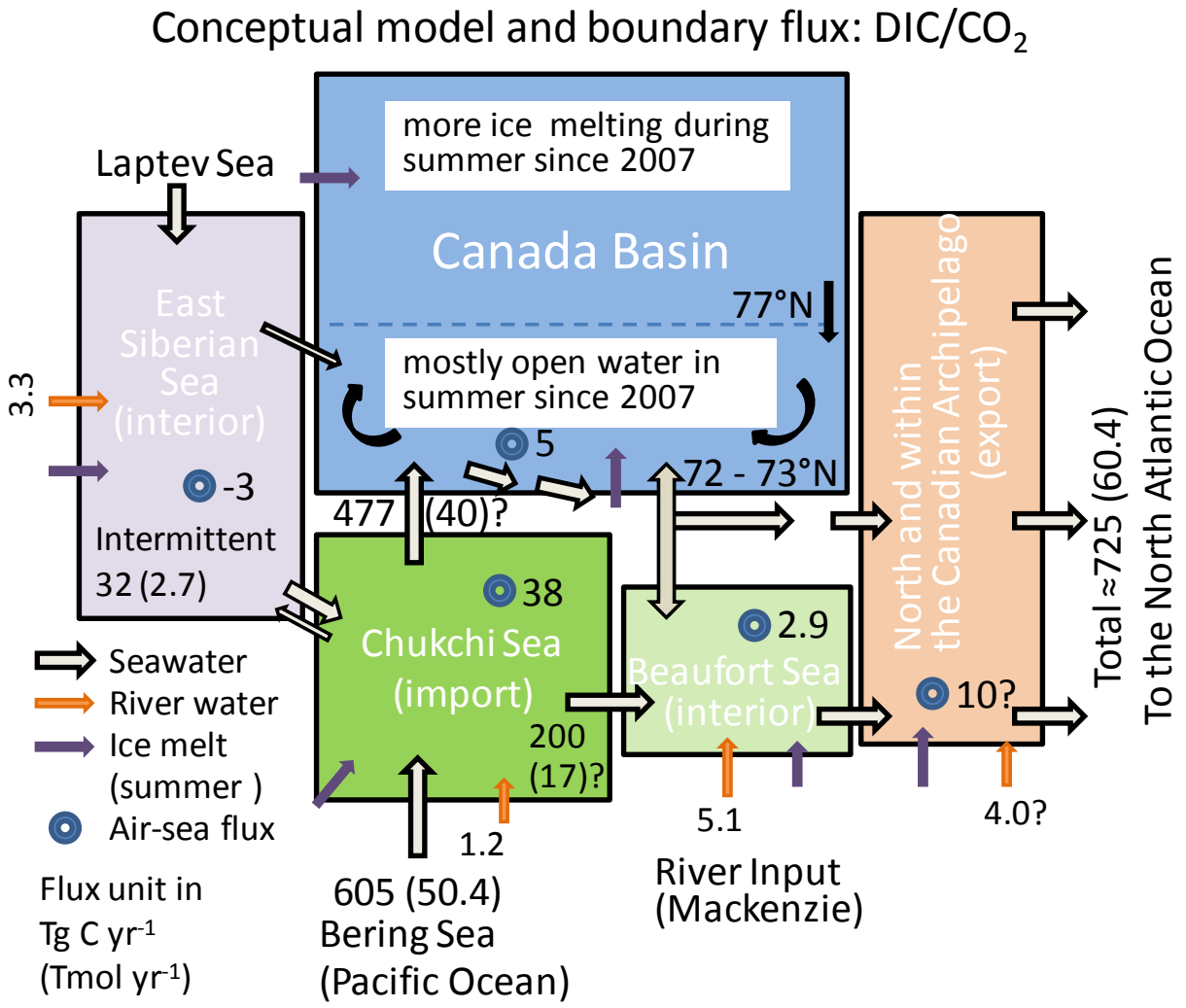

Fig. 3. Dissolved inorganic carbon (DIC) and air-sea CO_2 fluxes within the Pacific Sector of the Arctic Ocean and margins. The larger hollow arrows represent seawater DIC flux. The orange color arrows represent river water DIC flux. The blue circles indicate uptake of atmospheric CO_2 (values from Table 4 but in opposite sign as ocean gain is positive and loss is negative).

Table 1. Basic Information and Carbon Inventory in the Pacific Sector of the Arctic Ocean and margins. Modified from McGuire (2009) and Macdonald (2010) and references therein. Most DIC concentrations were from L. Anderson. During summer 2008 average DIC values in the upper 75-m water however are: 2040 (Bering Strait), 2062 (Chukchi Sea), 1997 (Beaufort Sea), and 2012 (Canada Basin) (W-J. Cai unpublished). DOC data are from Hansell and coworkers (Fig. 4 in (Mathis 2011) chapter).

					concentration (μmol/kg)		inventary (Tmol)		inventary (Pg C)	
Basin and Sea	Area (10^3 km^2)	Depth (m)	Volume (10^3 km^3)	Residence	DIC	DOC	DIC	DOC	DIC	DOC
Canada Basin	2797	2700	6900	2-30*						
SML		0-80	228	<10	2050	<70	467.4	16.0	5.61	0.19
UH		80-220	398	<10	2210	66	879.6	26.3	10.55	0.32
LH		220-300	228	>10	2155	60	491.3	13.7	5.90	0.16
AL		300-1000	1992		2159	54	4301	108	51.61	1.29
DBW		below 1000	4054		2050	47	8311	191	99.73	2.29
Chukchi	620	80	50	0.2-1.2	2050	70-90	102.5	4.0	1.23	0.05
East Siberian	987	58	57	1.5-5.5	2050	70-100	116.9	4.8	1.40	0.06
Beaufort	178	125	22	0.5-1	2050	70-80	45.1	1.7	0.54	0.02
Archipelago										
north of	240	290	69.6	~0.5	2145	70-100	149.3	5.9	1.79	0.07
within	1250	250	312.5	~12	2145	70-100	670.3	26.6	8.04	0.32
Total shelf	3275		511.1				1084.1	43.0	13.0	0.5
Total	6072		7411.1				15533.8	397.0	186.4	4.8
shelf in the total	54									
% of the total Arctic	56.7		59.7							
Eurasian Basin	1704		4556		2120	70-100	9658.7	387.3	115.90	4.65
Laptev	498		24		2120	100-130	50.9	2.8	0.61	0.03
Kara	926		121		2120	200-250	256.5	27.2	3.08	0.33
Barents	1512		302		2120	70-100	640.2	25.7	7.68	0.31
total arctic	10712		12414.1				26140.2	839.9	313.7	10.1

SML: the Surface Mixing Layer; UHL: Upper Halocline Layer; LHL: Lower Halocline Layer;

Table 2. Bering Strait and East Siberian water and DIC inflow

Bering Strait inorganic carbon inflow						
	% of flow	DIC range	mean DIC	water	Mol C	Tg C/yr
Anadyr Water	50	1980-2040	2010	1.26E+13	2.535E+13	304
Bering Sea water	30	1900-1980	1940	7.57E+12	1.468E+13	176
Alaskan Coastal	20	2020-2080	2050	5.05E+12	1.034E+13	124
mean			1997			**605**
total flow	0.8	Sv				
uncertainty	0.1	Sv	or 12.5%			76
DIC error estimate			error			
Anadyr Water			60	1.26E+13	7.569E+11	9.1
Bering Sea water			80	7.57E+12	6.055E+11	7.3
Alaskan Coastal			60	5.05E+12	3.027E+11	3.6
						20
						or 3.3%
East Siberian Sea inflow						
	% of flow	DIC range	mean DIC	water	Mol C	Tg C/yr
Anadyr Water	100	1600-1750	1700	1.58E+12	2.681E+12	32
						32
total flow	0.1	Sv				
net flow	0.05	Sv				

Table 3. Carbon flux from rivers to the the Pacific Sector of the Arctic Ocean. Data of Yukon River are from Guo et al (2011) and fluxes are average values of recent studies listed in Table 5 of Guo et al (2011, and references therein). Data of DOC and POC from Colville, Sagavaniktov and Kuparuk are from Rember and Trefry (2004) using average of high flow and low flow samples. Other data are taken from **McGuire et al. (2009).** Tg = 10^{12} g.

River	Basin area 10^3 km^2	Discharge km^3 yr^{-1}	Concentration (mg-C/L)			Flux (Tg-C yr^{-1})		
			DOC	POC	DIC	DOC	POC	DIC
Mackenzie	1787	330	5.2	7.2	14.7	1.72	2.3	4.84
Yukon	839	205	5.14	3.8	19.5	1.7	1.16	4.41
Colville	57	16	7.7	6.2	-	0.12	0.099	-
Sagavanirktok	15	6.5	4.1	2.4	22.1	0.027	0.016	0.14
Kuparuk	8	1.2	11.4	1.6	-	0.014	0.0019	-
Others	726	37	-	-	-	0.055	0.24	-
Total	16369	3531	-	-	-	3.63	3.87	9.39

Table 4. Air-sea CO_2 exchange rates expressed in mmol C $m^{-2}d^{-1}$ and annual air-sea CO_2 exchange rate expressed in Tg C (or 10^{12} g C). A negative air-sea CO_2 exchange rate indicates ocean uptake of CO_2 (i.e., CO_2 sink) (i.e., a loss term for the atmosphere). In Fig. 3, a negative value is converted to a positive one to show a gain for the ocean. Modified from (Bates and Mathis 2009).

	Air-Sea flux (mmol m^{-2} d^{-1})	Annual flux (Tg C yr^{-1})	Reference
East Siberian Sea	-1 to -10.9	-1.2/-13	Semiletov et al. 2007
	+0.3	+0.3	Nitishinsky et al. 2007
	n/a	-5.9	Anderson et al., 1998a,b
Chukchi Sea	-12	-11	Murata and Takizawa 2003
	-40 $\pm$22	-36 $\pm$6	Bates et al. 2006
	n/a	-46 $\pm$6	Bates et al. 2006
	n/a	-53 $\pm$14	Kaltin and Anderson 2001
Beaufort Sea	n/a	-2.9	Anderson et al., 1998a,b
	-12	-2	Murata and Takizawa 2003
Canadian Archipelago		-20	Bates and Mathis 2010 (by scaling to the Beaufort Sea)
Central basin	<-1 to -3	-6 to -19	Bates et al. 2006
		-5	Cai et al. 2010
Arctic Ocean		-129 +65	Anderson et al., 1990
		-70 $\pm$65	Anderson et al., 1994
		-110	Lundberg and Haugen, 1996
		-24 $\pm$17	Anderson et al., 1998b
		-41 $\pm$18	Anderson et al., 1998b
		-31	Kaltin and Anderson. 2005
		-66	Bates, 2006
		-66 to -199	Bates and Mathis, 2009

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