# Annual cycles of $pCO_{2sw}$ in the southeastern Beaufort Sea: New understandings of air-sea $CO_2$ exchange in arctic polynya regions

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[1] From 23 October 2007 to 1 August 2008, we made continuous measurements of sea surface partial pressure of $CO_2$ ($pCO_{2sw}$) in three regions of the southeastern Beaufort Sea (Canada): the Amundsen Gulf, the Banks Island Shelf, and the Mackenzie Shelf. All three regions are seasonally ice covered, with mobile winter ice and an early spring opening that defines them as polynya regions. Amundsen Gulf was characterized by undersaturated $pCO_{2sw}$ (with respect to the atmosphere) in the late fall, followed by an under-ice increase to near saturation in winter, a return to undersaturation during the spring, and an increase to near saturation in summer. The Banks Island Shelf acted similarly, while the Mackenzie Shelf experienced high supersaturation in the fall, followed by a spring undersaturation and a complex, spatially heterogeneous summer season. None of these patterns are similar to the annual cycle described or proposed for other Arctic polynya regions. We hypothesize that the discrepancy reflects the influence of several previously unconsidered processes including fall phytoplankton blooms, upwelling, winter air-sea gas exchange, the continental shelf pump, spring nutrient limitation, summer surface warming, horizontal advection, and riverine input. In order to properly predict current and future rates of air-sea $CO_2$ exchange in such regions, these processes must be considered on a location-by-location basis.

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## 1. Introduction

[2] Polynyas are recurring areas of open water or thin ice in polar seas that persist under conditions where a complete ice cover would otherwise be expected [*Barber and Massom*, 2007]. The persistence of open water can be caused by removal of ice by wind and currents, by warm water upwelling, or by some combination of the two [*Smith et al.*, 1990]. Although accounting for a small fraction of the Arctic Ocean icescape, polynyas play a disproportionately large role in heat budgets [*Maykut*, 1978], are often centers of intense biological activity [*Massom*, 1988], and generate a significant amount of ice relative to established ice covers [*Smith et al.*, 1990]. Because they are ice free, they provide a direct link between ocean and atmosphere and thus serve as conduits for air-sea gas exchange. Also of interest is the role that sea ice may play in modulating air-sea gas exchange in polynya regions (a term that we use to describe a geographic area that hosts a polynya at some point during the year) during the ice-covered or partially ice-covered portions of the annual cycle.

[3] *Yager et al.* [1995] proposed that these regions act as a strong annual sink of atmospheric $CO_2$ because the seasonal cycle of sea surface partial pressure of $CO_2$ ($pCO_{2sw}$) is in phase with seasonal ice cycles; $pCO_{2sw}$ is lower than the overlying atmosphere (undersaturated) due to phytoplankton blooms in spring and summer when ice concentrations are lowest, and higher than the atmosphere (supersaturated) due to excess respiration in the winter when ice concentrations are highest. They assumed that the winter ice cover would prevent any outgassing, leaving only the uptake of $CO_2$ during the open water season to contribute to the net annual exchange, a cycle they termed "seasonal rectification". This hypothesis is far-reaching, because it can also be applied to other regions of the Arctic that are seasonally ice free.

[4] Although this hypothesis is elegant, relatively little data exist to support it. In the Northeast Water (NEW) polynya, *Yager et al.* [1995] only observed the summer undersaturation and hypothesized that a stormy fall season

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would drive enough gas exchange to replace the $CO_2$ absorbed by the spring bloom. Observations from the North Water (NOW) polynya [*Miller et al.*, 2002] provided more evidence for the seasonal rectification hypothesis by documenting a brief period of supersaturation at ice breakup and a subsequent reduction of $pCO_{2sw}$ by a strong spring bloom. In this case, the undersaturation persisted until the fall freezeup, and no data were collected during the subsequent winter.

[5] Another important characteristic of Arctic polynyas is their frequent occurrence on continental shelves [*Barber and Massom*, 2007] whose role in air-sea $CO_2$ exchange has been the source of much discussion over recent years [*Tsunogai et al.*, 1999; *Thomas et al.*, 2004; *Borges et al.*, 2005; *Cai et al.*, 2006; *Chen and Borges*, 2009]. Shelves are at the distal end of the complex coupling between marine and terrestrial carbon cycles that begins where rivers enter the ocean. Near their discharge point, rivers are typically supersaturated in $pCO_{2sw}$ due to net heterotrophy sustained by their high terrestrial carbon load and relatively low alkalinity, but most of the excess $CO_2$ is outgassed in the inner estuaries and the nearshore coastal environments [*Chen and Borges*, 2009]. Seaward of these outgassing regions, most mid- and high-latitude shelves act as sinks for atmospheric $CO_2$ [*Borges et al.*, 2005; *Cai et al.*, 2006; *Chen and Borges*, 2009]. This net sink occurs offshore because of high biological productivity during spring and summer promoted by the delivery of upwelled and riverine nutrients, and the export of decay products to the deep basins during winter. This export is driven by the formation of dense water that sinks and exits the shelf below the pycnocline [*Tsunogai et al.*, 1999], or by the sinking of particulate organic carbon to either the sediments (where some portion becomes sequestered), or to deeper layers where it is respired and eventually exported [*Thomas et al.*, 2004]. This so-called "continental shelf pump" is thought to be particularly important on Arctic shelves where brine production and rapid winter cooling enhance the formation and export of dense water [*Anderson et al.*, 2010], and a large fraction of primary production occurs in episodic blooms that tend to have higher vertical carbon export ratios [*Sarmiento and Gruber*, 2006].

[6] *Yager et al.* [1995] wrote that "as more data become available for the NEW polynya and other Arctic regions, the [seasonal rectification] hypothesis will be tested rigorously". In this paper, we make a significant contribution toward this effort by describing the annual $pCO_{2sw}$ cycle in three polynya regions of the southeastern Beaufort Sea: the Mackenzie Shelf, the Banks Island Shelf and Amundsen Gulf. Our study expands on the work of *Shadwick et al.* [2011],who provided an overview of the annual $pCO_{2sw}$ cycle in Amundsen Gulf as part of their work on inorganic carbon cycling. The expanded data set presented here allows us to improve upon their discussion of processes controlling $pCO_{2sw}$ in Amundsen Gulf, and to place it in the context of $pCO_{2sw}$ cycling on the continental shelf seas of the southeastern Beaufort Sea. The spatiotemporal resolution and coverage of our data set allows for a rigorous test of the *Yager et al.* [1995] hypothesis in a complex Arctic polynya region.

## 2. Study Area

[7] This study was conducted from 23 October 2007 to 1 August 2008 in the southeastern Beaufort Sea (Figure 1) as part of the fourth International Polar Year Circumpolar Flaw Lead System Study (CFL) and ArcticNet projects onboard the research icebreaker CCGS *Amundsen.* The goal of these projects was to conduct a multidisciplinary sampling program overwintering in the southeastern Beaufort Sea. The ship conducted transects in Amundsen Gulf and on the Mackenzie and Banks Island shelves during the fall and early winter of 2007. The overwintering was done in the mobile ice of Amundsen Gulf with the ship drifting in ice floes and repositioning by traveling through leads and thin ice. In the spring and summer of 2008, the fall sampling locations were revisited to construct a near complete annual cycle.

[8] As shown in Figure 1, the portion of the southeastern Beaufort Sea discussed in this paper can be subdivided into several distinct regions. The Mackenzie Shelf is a broad continental shelf with a mean depth of 35 m and a shelf break about 120 km offshore. The entire shelf is seasonally affected by the outflow from the Mackenzie River, which modulates salinity, turbidity, temperature, nutrient concentrations and circulation [*Macdonald et al.*, 1987; *Carmack et al.*, 1989; *Carmack and Macdonald*, 2002]. Phytoplankton productivity is low in the winter, intensifies following an ice algae bloom in April and May and becomes highest during a modest open water bloom that is nutrient limited due to surface stratification [*Carmack et al.*, 2004]. As a result of these blooms, *Mucci et al.* [2010] observed strong undersaturations of $pCO_{2sw}$ in the summer and fall.

[9] Amundsen Gulf is deeper than the Mackenzie Shelf (max depth of ~500 m) and is not strongly affected by the Mackenzie River outflow at most times of the year [*Tremblay et al.*, 2008; *Magen et al.*, 2010; *Chierici et al.*, 2011; *Thomas et al.*, 2011]. The region is nutrient limited due to surface stratification (mostly from sea ice melt), and therefore the spring bloom has been shown to be less intense than in other polynya systems [*Tremblay et al.*, 2008]. There is also evidence that this area experiences a bloom in the fall season as storms entrain deeper nutrient-rich water to the surface [*Arrigo and van Dijken*, 2004; *Brugel et al.*, 2009]. *Mucci et al.* [2010] observed $pCO_{2sw}$ values close to equilibrium with the atmosphere in the summer and undersaturated $pCO_{2sw}$ values in the previous fall.

[10] The Banks Island Shelf is not as broad as the Mackenzie Shelf and, unlike the latter, is not host to significant river discharge. The areas sampled during this project were shallower than the Amundsen Gulf, with most depths less than 200 m. To our knowledge, this region has not been the subject of any major oceanographic studies. The large-scale remote sensing study of primary productivity by *Pabi et al.* [2008] indicates that the region has similar productivity to Amundsen Gulf, but no data on $pCO_{2sw}$ are available.

[11] Combined, these areas make up a complex polynya/flaw lead region whose annual ice cycle has been described by *Galley et al.* [2008]. Ice formation begins in October with landfast ice developing around the coastal margins and mobile ice accumulating in the Beaufort Sea and Amundsen Gulf. The ice in Amundsen Gulf does become landfast in some years, but it typically remains dynamic throughout the winter with small, transient flaw leads developing in response to wind-driven ice motion. Meanwhile, the ice in the Beaufort Sea is mobile all year, creating a shear zone along the coastal margins (along the Banks and Mackenzie shelves) where persistent winter flaw leads exist. The motion

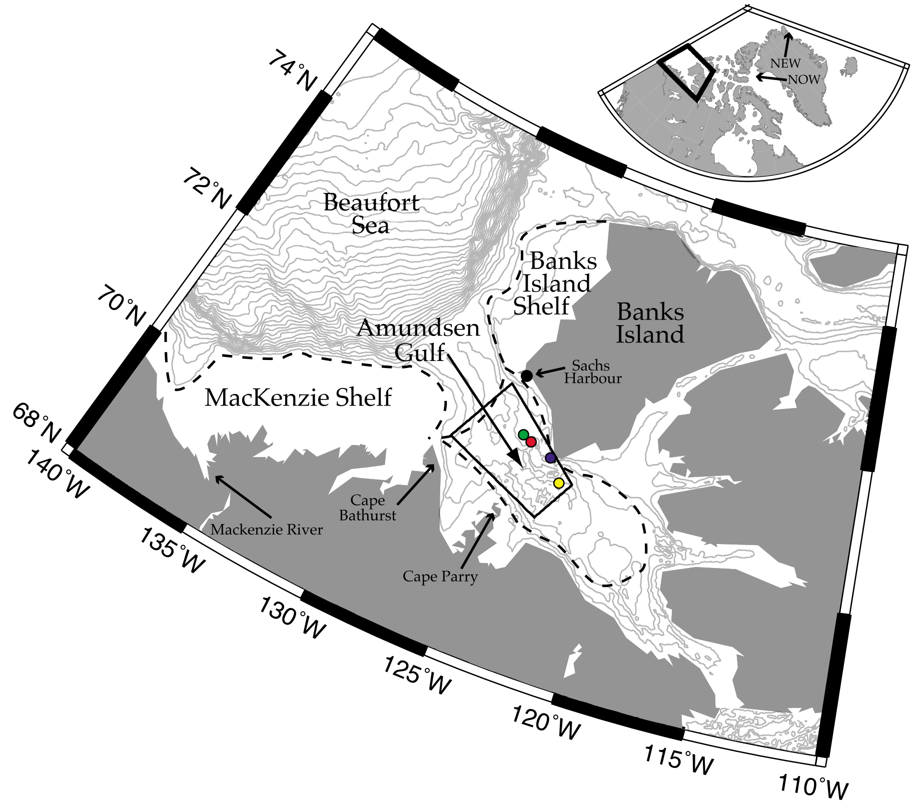


**Figure 1.** Map of study area with bathymetry (contour interval is 100 m). The regions discussed in the text are outlined with a dashed line, and the black bounding box delineates the region used to create Figures 3 and 4. The colored dots indicate the location of CTD casts described in Table 1: red, 5 November; yellow, 2 March; green, 31 May; blue, 11 July. The inset map shows the locations of the Northeast Water (NEW) and North Water (NOW) polynyas in relation to the study area (black box).

of ice in the Beaufort Sea allows for dynamic ice export from Amundsen Gulf through the fall and winter [*Kwok*, 2006], eventually creating the spring open water feature known as the Cape Bathurst polynya. The Beaufort Sea mobile ice typically moves offshore at around the same time, creating early open water on the Mackenzie and Banks Island shelves.

## 3. Methods

### 3.1. Surface Water $pCO_2$ Sampling

[12] Continuous $pCO_{2sw}$ sampling was conducted using a shower-type equilibrator system composed of a sealed cylindrical tank (volume ~15 L) with a shower head at the top and a drain at the bottom through which water was cycled at a rate of 1.5–2 L $min^{-1}$. The system was set up to maintain a water volume of about 2 L, while the headspace air (volume ~13 L) was cycled through a LI-COR LI-7000 $CO_2/H_2O$ gas analyzer at a rate of 3.5 L $min^{-1}$. Calibration of the LI-7000 was performed daily using ultra high purity $N_2$ as a zero gas and a $CO_2$/air mixture (in the range of 380 ppm) traceable to WMO standards as a span gas. Atmospheric $pCO_2$ measurements were made using a separate LI-7000 (also calibrated daily with high-purity $N_2$ and a similar traceable span gas) which drew sample air from a meteorological tower on the foredeck of the ship at a height of ~14 m above sea level.

[13] The equilibrator system was located in the engine room of the ship, a short distance (<5 m) downstream from a high volume scientific water intake at a nominal subsurface depth of 5 m. Despite the proximity to the intake, a thermocouple immersed in the equilibrator water registered a slight increase in water temperature relative to *in situ* conditions. To correct for this increase, a regression analysis was performed by comparing equilibrator water temperature to coincident surface water temperature measurements obtained by the ship's conductivity-temperature-depth (CTD)/Rosette system (see section 3.2). A total of 105 CTD casts were used in the analysis, which revealed a strong ($R^2$ = 0.97) and consistent linear relationship ($T_{sw} = 0.98T_{eq} - 1.7°C$) between *in situ* surface water temperature ($T_{sw}$) and equilibrator water temperature ($T_{eq}$). That relationship was then used to correct $pCO_{2sw}$ for thermodynamic effects following the procedure described by *Takahashi et al.* [1993].

[14] Periodic interruptions of the $pCO_{2sw}$ system occurred during ice-breaking operations. During these operations, ice clogged the water intake at the ship's hull, stopping or severely restricting flow to the equilibrator. Data acquired during these instances were removed in post processing and represent the most significant cause of data loss.

### 3.2. Ancillary Data

[15] To examine processes controlling $pCO_{2sw}$ (section 3.3), we required ancillary data from collaborators who participated in the cruises (see *Barber et al.* [2010] for details on instruments and sampling strategies). Stations

were sampled throughout the study area, as a network of transects during open water conditions, and opportunistically when the ship was drifting in floes during the winter. Whenever possible, stations were revisited seasonally. From CTD/Rosette casts (conducted at every station), we obtained salinity (S) and sea surface temperature (SST) from the shallowest possible depth; typically 1–5 m when deployed over the side of the ship (15 October to 5 November 2007 and 17 July to 5 August 2008) and 10–15 m when deployed through the moon pool (5 November 2007 to 17 July 2008). Uncertainty caused by sampling at these different depths depends on the season. In winter, when the surface mixed layer was deep, we expect very little variation in SST or S; for example, during the fall side of ship deployments (when the mixed layer was >30 m deep) SST at 5 m was on average 0.1°C cooler and S was 0.1 lower than at 10 m. In spring and summer as the mixed layer shoaled this uncertainty likely became greater; during the summer side of ship deployments (when the mixed layer was sometimes as shallow as 10 m) SST at 5 m was on average 0.5°C warmer and S remained 0.1 lower than at 10 m. S measurements were also obtained from a thermosalinograph sensor installed on the same continuous water sample line as the $pCO_{2sw}$ equilibrator. At several of the stations, we also obtained surface dissolved inorganic carbon (DIC), total alkalinity (TA), and chlorophyll *a* (Chl *a*) measurements from discrete seawater samples collected by the rosette Niskin bottles. The analytical techniques for the DIC and TA samples are described by *Shadwick et al.* [2011], while the Chl *a* sampling protocol was similar to that described by *Brugel et al.* [2009].

[16] Information on the extent of sea ice coverage (i.e., sea ice concentration) was obtained from Canadian Ice Service (CIS) charts (available online) which were created daily for the areas where the CCGS *Amundsen* was operating, and weekly for the broader western Arctic region. Hourly wind velocity data from Environment Canada weather stations at Sachs Harbour and Cape Parry (obtained online, see Figure 1 for locations) were used for bulk $CO_2$ flux calculations (section 3.3). MODIS SST imagery (500 m pixels, daytime 11 and 12 $\mu$m bands, obtained from the MODIS Rapid Response System) was used to locate the Mackenzie River plume and upwelling areas during the ice free seasons. The Mackenzie river plume can be identified visually on SST images as it is significantly warmer than shelf water [e.g., *Vallières et al.*, 2008], while upwelled water is significantly colder [e.g., *Williams and Carmack*, 2008].

### 3.3. Determination of Processes Controlling $pCO_{2sw}$

[17] Where possible, we calculated how various physical, chemical, and biological processes contributed to observed changes in $pCO_{2sw}$. The processes that we identified as potentially important and the techniques used to quantify their relative influence on $pCO_{2sw}$ are as follows:

[18] 1. Gas exchange reduces (increases) $pCO_{2sw}$ when $pCO_{2sw}$ is higher (lower) than atmospheric $CO_2$ ($pCO_{2atm}$). We used a bulk flux approach to estimate $CO_2$ flux ($F_{CO_2}$)

$$F_{CO_2} = k\alpha(pCO_{2sw} - pCO_{2atm})(1 - C_i), \quad (1)$$

where $k$ is the transfer velocity (computed as a function of wind velocity using *Sweeney et al.* [2007]), $\alpha$ is the solubility of $CO_2$ [*Weiss*, 1974] and $C_i$ is the fractional ice coverage. We used hourly wind velocity measurements from the Cape Parry weather station for Amundsen Gulf, and from the Sachs Harbour station for the Banks Island and Mackenzie shelves. To compute change in DIC driven by gas exchange, $F_{CO_2}$ was divided by the mixed layer depth (defined as the position of the vertical density gradient maximum as observed from CTD profiles) and multiplied by the length of time of interest. We then used the CO2calc program [*Robbins et al.*, 2010] with the dissociation constants of *Mehrbach et al.* [1973] as refit by *Dickson and Millero* [1987] to calculate the resulting change in $pCO_{2sw}$. To estimate a complete annual cycle of $pCO_{2sw}$ in Amundsen Gulf for 2007–2008, we performed a simple linear interpolation between measurements obtained at the start of August 2008 and the end of October 2007.

[19] 2. Sea surface temperature exerts a thermodynamic control on the seawater carbonate system and thus increases $pCO_{2sw}$ by about 4% per °C [*Takahashi et al.*, 1993]. For time periods of interest, we used the CO2calc program to calculate $pCO_{2sw}$ from DIC, TA, S and SST measurements when a station was first visited, and then recalculated $pCO_{2sw}$ at the SST measured when the station (or a station nearby) was revisited. The difference between these two calculated values reflects the change in $pCO_{2sw}$ caused by the change in SST.

[20] 3. Salinity also affects the carbonate chemistry and hence $pCO_{2sw}$. If TA and DIC are held constant, an increase (decrease) in S would cause an increase (decrease) in $pCO_{2sw}$ by reducing (increasing) the solubility of the gas. However, the processes that change S also typically modify TA and DIC concentrations, thus modifying the equilibrium state of the carbonate system and exerting a further control on $pCO_{2sw}$. Sea ice melt dilutes TA and DIC along with S, lowering $pCO_{2sw}$. Conversely, sea ice formation increases S along with TA and DIC of the residual water, raising $pCO_{2sw}$. For the Amundsen Gulf region, *Shadwick et al.* [2011] derived a series of equations to predict changes in surface water TA (dTA) and DIC (dDIC) concentrations as a function of change in S (dS)

$$\mathrm{dTA} = 49.38\mathrm{dS} + 0.42 \quad (2)$$

$$\mathrm{dDIC} = \mathrm{dTA}(\mathrm{DIC}/\mathrm{TA}). \quad (3)$$

This equation implicitly includes ice melt and river inputs, and is specific to Amundsen Gulf. Without as comprehensive a data set for the Mackenzie and Banks Island shelves, we were unable to carry out similar analyses. For Amundsen Gulf, we calculated dTA and dDIC over a given time period using the change in S between two visits to the same or neighboring stations. The effect on $pCO_{2sw}$ was then determined as the difference between $pCO_{2sw}$ computed from the surface water properties (TA, DIC) measured on the initial visit to the station and at the S measured on the subsequent visit combined with the calculated dTA/dDIC.

[21] 4. Upwelling and vertical mixing can have a significant impact on $pCO_{2sw}$ by modifying the surface water properties and carbonate chemistry [*Chierici et al.*, 2011]. *Shadwick et al.* [2011] and *Lansard et al.* [2012] showed that DIC, TA and $pCO_2$ in Amundsen Gulf are typically

much higher below the mixed layer, and data from the Mackenzie and Banks Island shelves show similar profiles. Transport of this water into the surface layer thus typically increases $p\mathrm{CO}_{2sw}$. For simple vertical mixing caused by mixed layer deepening, we calculated change in surface water DIC and TA ($\mathrm{DIC}_{sw}$/$\mathrm{TA}_{sw}$) following *Gruber et al.* [1998]

$$\mathrm{dTA_{sw}} = \mathrm{dh}(\mathrm{TA_{pyc}} - \mathrm{TA_{sw}})\mathrm{h}^{-1} \tag{4}$$

$$\mathrm{dDIC_{sw}} = \mathrm{dh}(\mathrm{DIC_{pyc}} - \mathrm{DIC_{sw}})\mathrm{h}^{-1}, \tag{5}$$

where h is the depth of the mixed layer on the first visit to a station, dh is the change in mixed layer depth between the initial station and subsequent visits to the same (or neighboring) station, and the subscript "pyc" denotes the mean DIC and TA concentrations measured on the first visit to the station at a depth between the original and subsequent mixed layer depths. The effect of these changes in $\mathrm{DIC}_{sw}$ and $\mathrm{TA}_{sw}$ concentration on $p\mathrm{CO}_{2sw}$ were then calculated in CO2calc. As per *Gruber et al.* [1998], we did not calculate any change in DIC or TA for time periods where the mixed layer shoaled.

[22] 5. Biology (excluding the biogenic $\mathrm{CaCO_3}$ cycle) influences $p\mathrm{CO}_{2sw}$ by removing DIC and adding smaller amounts of TA during periods of net photosynthesis and adding DIC and removing TA during periods of net respiration. The biological controls on DIC and TA are often calculated from nutrient uptake, but such analyses are difficult in the Arctic due to the varied source waters of nutrients [e.g., *Anderson et al.*, 2010]. In Amundsen Gulf, *Shadwick et al.* [2011] assumed that any residual change in DIC and TA not accounted for by changes in S, gas exchange or upwelling was due to biological activity. We adopted a similar approach, and assigned any residual changes in $p\mathrm{CO}_{2sw}$ not accounted for by other processes to biological processes. To add some understanding of the timing and magnitude of biological $p\mathrm{CO}_{2sw}$ reduction, we used surface water Chl *a* measurements as a proxy to identify periods of high photosynthetic activity.

[23] 6. Horizontal advection can modify $p\mathrm{CO}_{2sw}$ in regions where strong horizontal $p\mathrm{CO}_{2sw}$ gradients exist in conjunction with significant surface currents. *Shadwick et al.* [2011] showed that horizontal advection is negligible in Amundsen Gulf due to slow surface currents and minimal horizontal $p\mathrm{CO}_{2sw}$ gradients. We therefore ignored horizontal advection as a potentially important influence in that region. For the Mackenzie and Banks Island shelves, we used the daily sea ice motion vector product (averaged bimonthly) provided by the National Snow and Ice Data Center [*Fowler*, 2003] to characterize surface currents. Where possible, we combined these surface current data

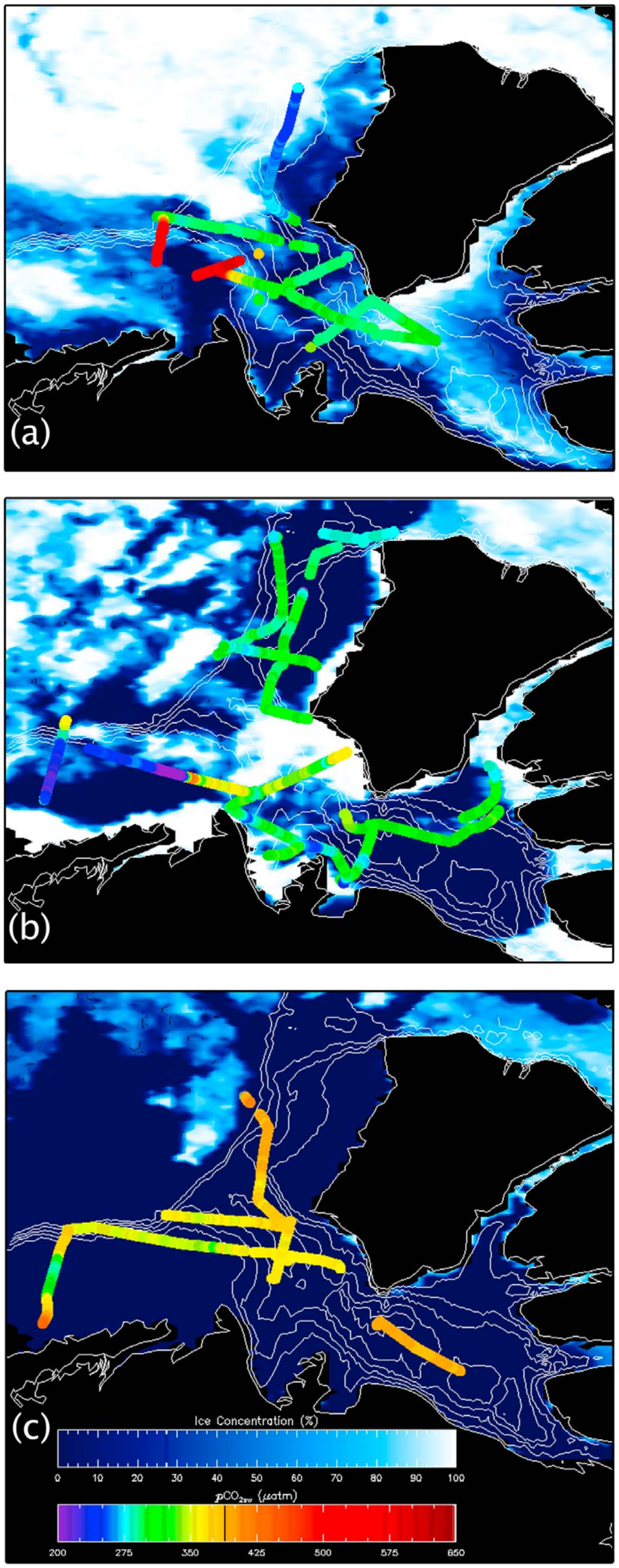


**Figure 2.** Measured $p\mathrm{CO}_{2sw}$ ($\mu$atm) during transects conducted in the study area. Colored dots are $p\mathrm{CO}_{2sw}$, the background image is ice concentration from the Advanced Microwave Scanning Radiometer-EOS (AMSR-E) satellite [*Spreen et al.*, 2008], and the white lines are bathymetric contours with a depth interval of 100 m. The black line in the $p\mathrm{CO}_{2sw}$ scale indicates the approximate atmospheric $p\mathrm{CO}_2$. (a) Transects conducted 23 October to 2 November 2007 overlain on an AMSR-E image from 31 October, (b) transects conducted 21 May to 27 June 2008 overlain on an AMSR-E image from 25 May, and (c) transects conducted 10–27 July 2008 overlain on an AMSR-E image from 15 July are shown.

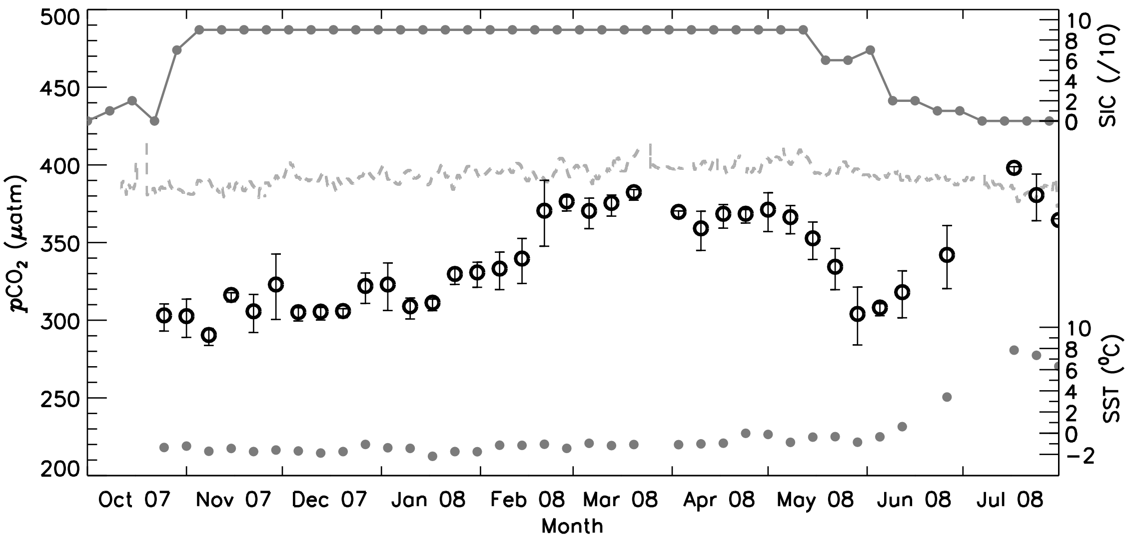


**Figure 3.** Weekly average $pCO_{2sw}$ measurements in Amundsen Gulf (open circles); error bars are 1 standard deviation. Also shown is SST from the equilibration system (solid circles), atmospheric $pCO_2$ from the meteorological tower (gray dashed line), and sea ice concentration from weekly Canadian Ice Service charts (solid line).

with $pCO_{2sw}$ to derive qualitative estimates of the role of horizontal advection in modifying $pCO_{2sw}$.

## 4. Results and Discussion

### 4.1. Amundsen Gulf

[24] Amundsen Gulf was the most frequently sampled area of the southeastern Beaufort Sea during this project, partly because the ship was confined to the area during the winter, and partly because transects were repeated there regularly during the open water seasons (Figure 2). This allowed us to create a detailed time series of $pCO_{2sw}$ (Figure 3) within a box covering western Amundsen Gulf (see Figure 1), by averaging observations made within the box in weekly intervals. We also compiled a similar time series of Chl *a* (Figure 4). The long occupation of Amundsen Gulf also allowed us to evaluate the processes controlling $pCO_{2sw}$ during each season. We did this by applying the methods outlined in section 3.3 between four dates that roughly represent the endpoints of fall, winter, spring and summer. The surface water data collected on these four dates are shown in Table 1, and the calculated change that each process imparted upon $pCO_{2sw}$ between the dates are reported in Table 2.

#### 4.1.1. Fall (November 2007)

[25] The transects made shortly prior to freezeup (Figure 2a), reveal that the surface mixed layer in Amundsen Gulf was consistently undersaturated, with a mean $pCO_{2sw}$

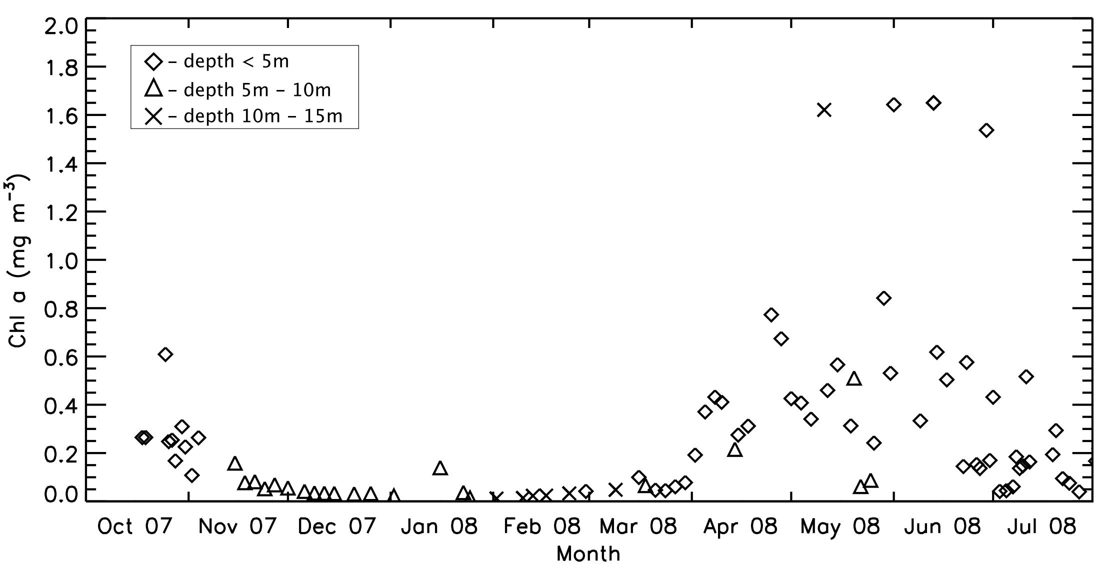


**Figure 4.** Time series of measured surface water Chl *a* in Amundsen Gulf. Sample depth is indicated by the different symbols.

**Table 1.** Surface Water Conditions at Four Stations Used to Calculate the Contribution of Processes Affecting $pCO_{2sw}$ Change in Amundsen Gulf[a]

| Date | SST (°C) | Salinity | $TA_s$ ($\mu$mol kg$^{-1}$) | $DIC_s$ ($\mu$mol kg$^{-1}$) | $TA_{pyc}$ ($\mu$mol kg$^{-1}$) | $DIC_{pyc}$ ($\mu$mol kg$^{-1}$) | Mixed Layer Depth (m) |
|---|---|---|---|---|---|---|---|
| 5 Nov 2007 | −1.57 | 29.11 | 2077.8 | 1965.4 | 2204.3 | 2089.3 | 35 |
| 2 Mar 2008 | −1.72 | 31.64 | 2235.8 | 2127.3 | – | – | 37 |
| 31 May 2008 | −1.57 | 31.66 | 2224.5 | 2091.8 | – | – | 23 |
| 11 Jul 2008 | 8.33 | 29.29 | 2077.0 | 1951.0 | 2195.4 | 2052.7 | 12.5 |

[a]Station locations are shown in Figure 1. The subscript "*sw*" indicates a measurement made in the surface seawater (depth ~5 m), while the subscript "pyc" denotes a measurement made at a depth between the original and subsequent mixed layer depths (see section 3.3).

of 302 $\mu$atm and a standard deviation of 10 $\mu$atm. To explain this undersaturation, we have to assume that the conditions observed the following summer (July 2008) are representative of those in July 2007, prior to our arrival in the region [see, e.g., *Shadwick et al.*, 2011]. If this is the case, a significant (94 $\mu$atm) decrease in $pCO_{2sw}$ occurred between mid-July and early November (Table 2 and Figure 3).

[26] The cooling from peak summer SST (8.3°C) to near the freezing point accounts for a $pCO_{2sw}$ reduction of 142 $\mu$atm, but our calculations of air-sea exchange show that this decrease would have been largely countered by $CO_2$ invasion from the atmosphere (Table 2). An observed deepening of the mixed layer (Table 1) [*Shadwick et al.*, 2011] may have also contributed slightly to the overall $pCO_{2sw}$ decrease (Table 2) because the June profile of $pCO_2$ (derived from the DIC and TA profiles) contained a minimum within the pycnocline [*Chierici et al.*, 2011], corresponding to a subsurface chlorophyll maximum, a ubiquitous summer feature of seasonally ice-free Canadian Arctic waters [*Martin et al.*, 2010]. To balance the budget, a biology-driven reduction of 63 $\mu$atm must have occurred (Table 2). This is consistent with past observations of significant fall phytoplankton blooms in Amundsen Gulf [*Arrigo and van Dijken*, 2004; *Brugel et al.*, 2009] and with the high Chl *a* levels observed in October 2007 (Figure 4).

#### 4.1.2. Winter (November 2007 to March 2008)

[27] From late fall 2007 to early March 2008, we observed a gradual increase in $pCO_{2sw}$ to a maximum near 380 $\mu$atm (Figure 3). During this period, surface S increased from 29.3 to 31.8, which *Shadwick et al.* [2011] attributed primarily to brine rejection by sea ice formation. Table 2 shows that this S increase (and the concomitant increase in DIC and TA) played an important role in the overall $pCO_{2sw}$ increase (29 $\mu$atm of the observed 74 $\mu$atm increase). Vertical mixing and SST change imparted only minor impacts on $pCO_{2sw}$, suggesting that biology played a more important role by increasing $pCO_{2sw}$ by 44 $\mu$atm (Table 2).

[28] The change in $pCO_{2sw}$ due to air-sea gas exchange (estimated using equation (1)) is small over this period (1.5 $\mu$atm). However, eddy covariance measurements that we made during the study [*Else et al.*, 2011] suggest that very rapid gas exchange may occur through open leads due to processes associated with new ice formation. Our measurements of $CO_2$ flux were typically 1 order of magnitude larger than fluxes estimated by the bulk flux approach, and we show the effect this enhanced flux would have on changes in $pCO_{2sw}$ in parentheses in Table 2. If air-sea gas exchange was indeed as strong as our measurements suggest, the biological contribution to the $pCO_{2sw}$ change must have been less. This in part shows that our budget-balancing approach yields a rather uncertain estimate of the impact of biological processes on $pCO_{2sw}$ when certain processes cannot be accurately accounted.

#### 4.1.3. Spring (March 2008 to May 2008)

[29] In March, $pCO_{2sw}$ began to decrease from the maximum of 380 $\mu$atm to 363 $\mu$atm in April, followed by a sharp decrease in May that bottomed out at ~305 $\mu$atm (Figures 2b and 3). As shown in Table 2, this decrease was driven almost entirely by biological production, and the decrease correlates well with an observed increase in Chl *a* (Figure 4). The March/April increase in Chl *a* was caused by an under-ice algae bloom [*Shadwick et al.*, 2011] and was followed by a more intense open water bloom as ice cover decreased in mid-May (Figure 3). S and SST remained fairly constant over this time period, producing very little change in $pCO_{2sw}$ (Table 2), and the mixed layer shoaled slightly (Table 1) preventing vertical mixing.

#### 4.1.4. Summer (June–July 2008)

[30] Figure 3 shows that $pCO_{2sw}$ began to increase toward the end of June, reaching a maximum of about 400 $\mu$atm and creating a short-lived supersaturation in the second week of July. Transects in Amundsen Gulf (Figure 2c) confirmed that the near-saturation values extended throughout the region. Changes to the physical characteristics of the surface mixed layer were responsible for most of this increase (Table 2). A warming from −1.6 to 8.3°C accounted for an increase of 162 $\mu$atm, while a decrease in S from 31.6 to 29.5 (and the accompanying dilution of DIC and TA) reduced $pCO_{2sw}$ by 10 $\mu$atm. Results from *Shadwick et al.* [2011] show that the mixed layer became strongly stratified during this period due to warming and freshening, which must have suppressed vertical mixing. Biological $pCO_{2sw}$ uptake was

**Table 2.** Observed Seasonal Changes in $pCO_{2sw}$ in Amundsen Gulf and Calculated Contributions of Various Processes to Those Changes[a]

| Process | Change in $pCO_2$ ($\mu$atm) 2 | 31 | 11 | 5 |
|---|---|---|---|---|
| SST | −2 | 2 | 162 | −142 |
| Air-sea | 1.5 (15) | 0.8 (8) | 22 | 114 |
| Salinity | 29 | 0 | −10 | −2 |
| Vertical mixing | 2 | 0 | 0 | −2 |
| Biology | 44 | −77 | −81 | −63 |
| Total | 74 | −73 | 93 | −94 |

[a]Changes due to SST during each time period were determined by calculating $pCO_{2sw}$ with CO2calc using DIC/TA/SST and salinity measured on the first visit to a station (Table 1) and then adjusting SST to measurements on subsequent visits to the same or a neighboring station. Changes due to air-sea gas exchange were determined by calculating $CO_2$ flux using the bulk approach and then dividing the flux by the mixed layer depth. The values in parentheses represents an estimate of the potential flux enhancement caused by ice formation. Changes due to salinity were calculated using the TA/DIC/salinity relationships of *Shadwick et al.* [2011]. Changes due to vertical mixing were calculated based on changes in mixed layer depth and TA/DIC in the pycnocline on the first visit to a station. Changes due to biology were calculated as the difference between the sum of the other processes and the observed change. See section 3.3 for a complete description of these methods.

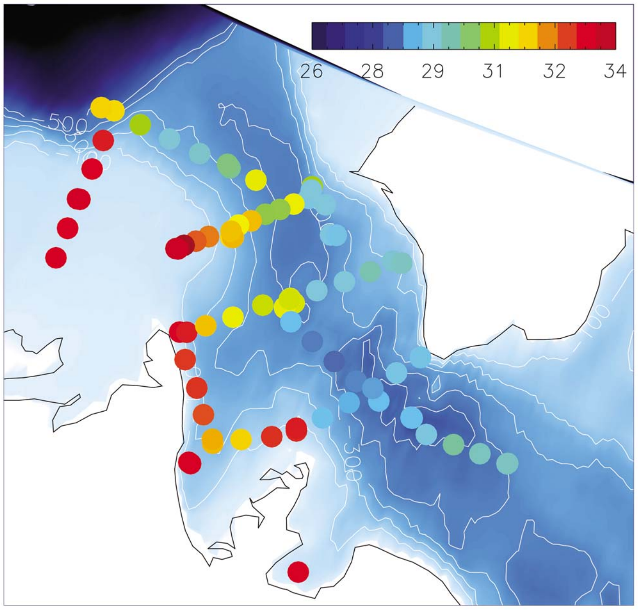


**Figure 5.** Surface salinity measurements made in the study region between 21 October to 17 November 2007.

still significant during this period, but about a quarter of it was offset by air-sea gas exchange (Table 2).

### 4.2. Mackenzie Shelf

#### 4.2.1. Fall (November 2007)

[31] The Mackenzie Shelf showed very high (supersaturated) $pCO_{2sw}$ (mean values of 553 $\mu$atm and a maximum value of 590 $\mu$atm) in fall 2007. This supersaturation was constrained shoreward of the shelf break, with sharp gradients observed along the shelf slope (Figure 2a). The surface S measurements collected in the region between 21 October and 17 November (Figure 5) show that S was much higher on the shelf (typically > 32) than beyond the shelf break (typically < 30). S was also high along the southern margins of Amundsen Gulf. These high salinities were also associated with high $pCO_{2sw}$ (not shown in Figure 2a), which we discuss in a forthcoming paper on $pCO_{2sw}$ near landfast ice edges (B. G. T. Else et al., Sea surface $pCO_{2sw}$ cycles and $CO_2$ fluxes at landfast sea ice edges in Amundsen Gulf, Canada, submitted to *Journal of Geophysical Research*, 2012).

[32] On the Mackenzie Shelf the polar mixed layer has a characteristic S of 31.6, while the upper halocline waters (of Pacific origin) have a characteristic S of 33.1 [*Macdonald et al.*, 1989]. This upper halocline water is rich in nutrients and $CO_2$ and sits at depths corresponding to the shelf break [*Carmack and Chapman*, 2003]. When the edge of the Beaufort Sea mobile ice is beyond the shelf break, easterly winds can drive an upwelling of upper halocline water onto the shelf [*Macdonald et al.*, 1987; *Carmack and Chapman*, 2003]. In fall 2007, the mobile ice was well beyond the shelf break, and strong easterly winds were frequent. Figure 6 shows that the high $pCO_{2sw}$ measurements were strongly correlated with S, suggesting that shelf break upwelling of upper halocline water is responsible for the elevated $pCO_{2sw}$ (see also *Tremblay et al.* [2011] for a complete description of the 2007 upwelling events in this region). The formation of sea ice and subsequent rejection of $CO_2$-rich brine [e.g., *Miller et al.*, 2011; *Rysgaard et al.*, 2007] is another possible source of high $pCO_{2sw}$, but the amount of sea ice that had formed at this early point in the season could not have caused such a significant increase in S (see, for example, the winter evolution of S in Amundsen Gulf as described by *Shadwick et al.* [2011]).

[33] Figure 7 shows that ice (and hence surface water) circulation in this region is dominated by westward flow. During the fall, this would have moved the relatively low $pCO_{2sw}$ water of Amundsen Gulf toward the Mackenzie Shelf. We expect that over the short period of time that the research vessel was in the region, this relatively slow (2–6 cm $s^{-1}$) transport would not have played an important role in determining the spatial distribution of $pCO_{2sw}$ relative to the upwelling, which clearly dominated the $pCO_{2sw}$ signal. However, since ice motion continued through the winter (Figure 7a), horizontal advection may have played an important role in eventually replacing this upwelled water with low $pCO_{2sw}$ water. With a current of ~4 cm $s^{-1}$, surface water flowing from Cape Bathurst toward the Mackenzie River could have replaced the fall surface water in approximately 4 months.

#### 4.2.2. Spring (June 2008)

[34] With no winter data for the Mackenzie Shelf, our next observation in the area was of strong undersaturation ($pCO_{2sw}$ values from ~150 to 300 $\mu$atm, Figure 2b) in June 2008. Estimates of annual phytoplankton productivity indicate that the Mackenzie Shelf is more productive than Amundsen Gulf [*Pabi et al.*, 2008], and that peak productivity occurs in June and July [*Carmack et al.*, 2004]. We would therefore expect a more significant biological $pCO_{2sw}$ reduction, which may be the cause of the lower $pCO_{2sw}$ relative to Amundsen Gulf.

[35] Processes on the Mackenzie Shelf are further complicated by the presence of the Mackenzie River plume [*Carmack and Macdonald*, 2002] and upwelling forced by

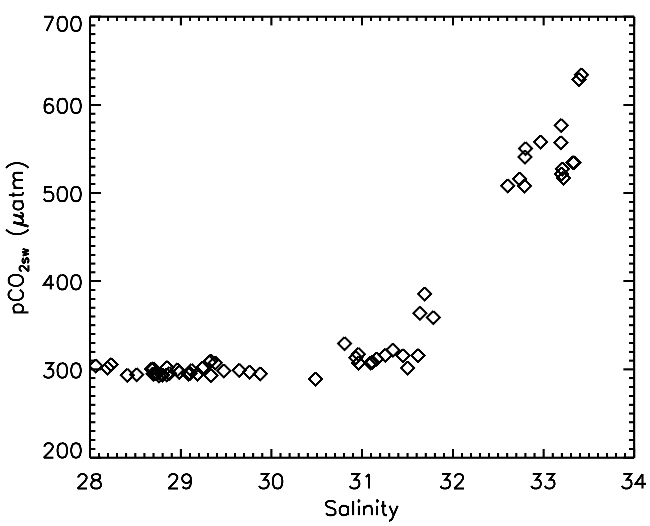


**Figure 6.** Correlation plot of surface salinity versus $pCO_{2sw}$ measurements made between 21 October and 17 November 2007. The figure includes $pCO_{2sw}$ data from landfast ice margins of southern Amundsen Gulf not shown in Figure 2a.

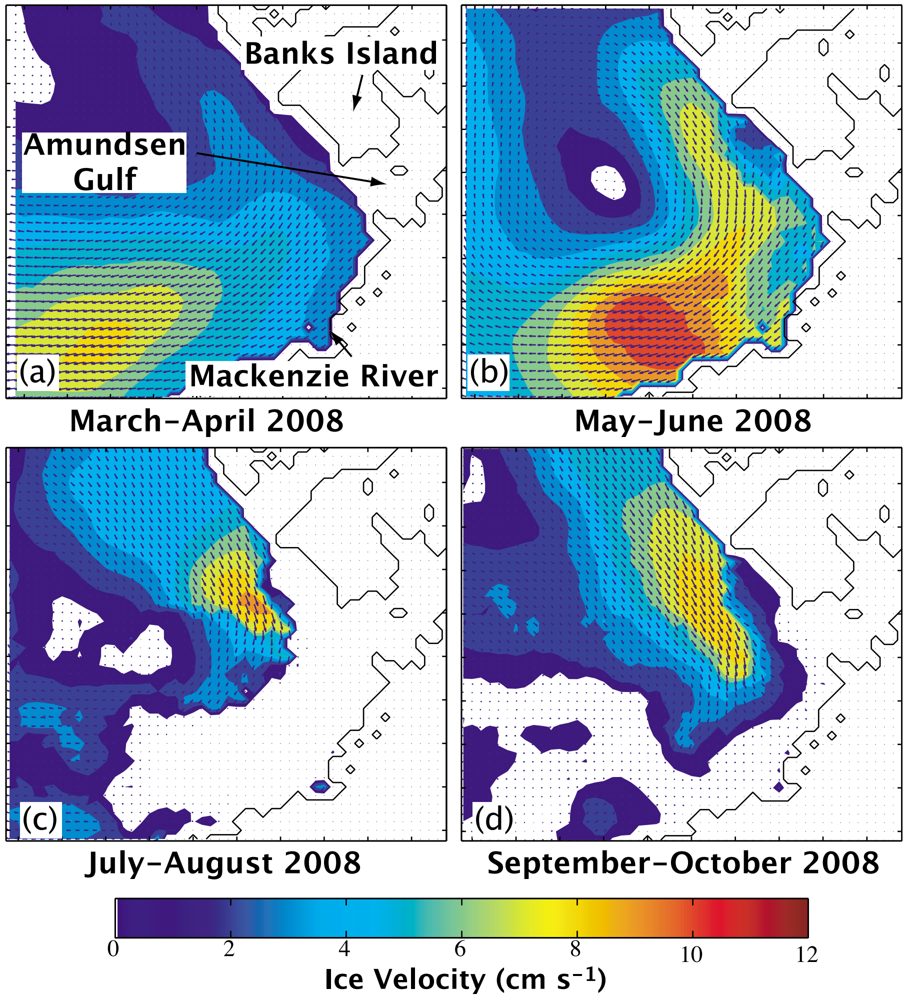


**Figure 7.** Bimonthly mean sea ice velocity and direction, from the National Snow and Ice Data Center buoy/passive microwave sea ice motion vector product.

the bathymetry of Cape Bathurst and other underwater features on the shelf [*Williams et al.*, 2008; *Williams and Carmack*, 2008]. The impact of these features was evident in two transects conducted 29–30 June (Figure 8). The first transect started in western Amundsen Gulf where mean $pCO_{2sw}$ was 356 $\mu$atm (Figures 8a and 8b). Slightly to the west of Cape Bathurst (at approximately 17:30 in Figure 8b), the ship encountered a small ($\sim$10 km wide) patch of water with high $pCO_{2sw}$ (mean of 412 $\mu$atm). This patch of water was cold (0.6°C) and saline (32.1), and it was part of a larger cold water structure around Cape Bathurst (Figure 8a) that corresponds to the upwelling feature described by *Williams and Carmack* [2008]. After traveling through this upwelling patch, we encountered a larger patch ($\sim$30 km wide, 19:00–20:00 on Figure 8b) of very low $pCO_{2sw}$ (minimum 152 $\mu$atm). This patch was also quite saline (S $\sim$ 31–32), but was significantly warmer ($\sim$ 4˚C) than the patch to the east. *Williams and Carmack* [2008] showed that the Cape Bathurst upwelling system can easily stretch as far west as this anomaly, and *Tremblay et al.* [2011] documented that upwelling events in this area bring nutrient-rich waters to the surface that stimulate strong phytoplankton blooms. Therefore, nutrient enrichment by a previous upwelling event and a subsequent phytoplankton bloom (accompanied by surface warming) is a likely explanation for this feature. In June 2004, *Mucci et al.* [2010] observed nearly identical patches of high and low $pCO_{2sw}$ in this region, and reached a similar conclusion regarding their genesis. Finally, the ship entered the Mackenzie River plume (shown by warm water in Figure 8a and the decrease in S in Figure 8b), where an across-shelf transect was conducted on 30 June (Figure 8c). This transect showed $pCO_{2sw}$ in the plume was consistently low, with a mean and standard deviation of 237 $\pm$ 12 $\mu$atm (Figure 8c).

[36] Figure 7b shows that ice motion in this region remained westerly during this period, increasing slightly from winter. The main impact of this surface current on the Mackenzie Shelf is to keep the Mackenzie River plume to the west. It may also import higher $pCO_{2sw}$ water onto the shelf from Amundsen Gulf, but the long timescale of this process probably keeps it from being important relative to the dominant processes of upwelling and river discharge.

#### 4.2.3. Summer (July 2008)

[37] A final visit to the Mackenzie Shelf was made in late July 2008 and consisted of two transects. The along-shelf

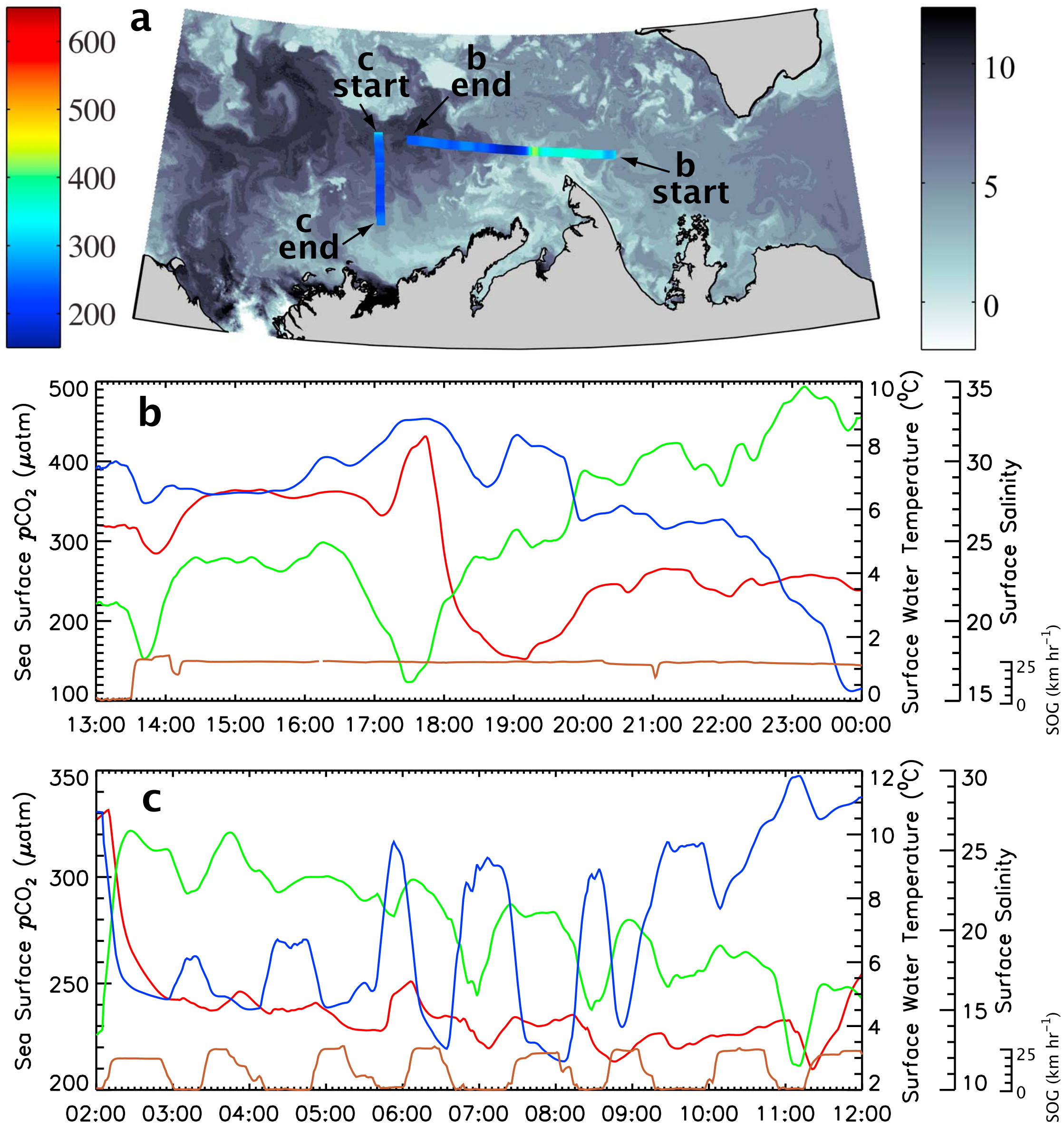


**Figure 8.** (a) The $pCO_{2sw}$ (colored bar, in $\mu$atm) on the Mackenzie Shelf during transects conducted 29–30 June 2008, overlying a MODIS SST image obtained on 30 June (grayscale bar, in °C). Areas of high SST (7–15°C) are associated with the Mackenzie river plume, while low SST areas (−1–1°C) are associated with upwelling. (b and c) The $pCO_{2sw}$ (red line), S (blue line), SST (green line), and ship speed over ground (SOG, brown line) during the two transects. SOG is shown to highlight a problem with the second transect (Figure 8c): during the transect the ship made several 30 min stops (SOG = 0) for station sampling. At the stations, salinity increased rapidly while SST decreased, which was likely caused by ship maneuvers mixing the highly stratified surface water.

transect was conducted further north than in June (Figure 2c), and SST imagery (not shown) showed no clear evidence of the influence of the Cape Bathurst upwelling or the Mackenzie River plume. On the shelf, $pCO_{2sw}$ was lower (mean 350 $\mu$atm) than beyond the shelf break (~375 $\mu$atm), a pattern that was repeated in the across-shelf transect. The across-shelf transect was characterized by lower (mean 308 $\mu$atm) $pCO_{2sw}$ than the along-shelf transect, and a rapid increase (to 434 $\mu$atm) near the coast (note that this transect went much closer to the coast than the June transect). The location of the transition from undersaturation to supersaturation occurred over the same depths that *Vallières et al.* [2008] identified as the transition from marine-dominated to river-dominated surface water. *Vallières et al.* [2008] showed that supersaturated Mackenzie River waters are the result of net heterotrophy fueled by riverine dissolved (DOC) and particulate organic carbon (POC). In the marine zone, they found POC concentration to be much lower, DOC to be less labile, and higher primary productivity, resulting in a net autotrophic system with undersaturated $pCO_{2sw}$. The Mackenzie River and adjoining shelf thus behave like many high-latitude shelves [*Chen and Borges*, 2009], but much differently than the western East Siberian and Laptev Seas where net heterotrophy dominates over broad expanses of the shelves [*Anderson et al.*, 2009].

### 4.3. Banks Shelf

#### 4.3.1. Fall (November 2007)

[38] Unlike the Mackenzie Shelf, the Banks Island Shelf showed marked undersaturation (mean of 260 $\mu$atm) in the fall of 2007 (Figure 2a). Using the 2008 observations as an analogue for the conditions prior to fall, this region had similar summer $pCO_{2sw}$ to Amundsen Gulf (Figure 2c). Assuming that the surface mixed layer cooled by a similar amount and experienced similar gas transfer, an additional reduction in $pCO_{2sw}$ of $\sim$40 $\mu$atm occurred compared to Amundsen Gulf. Figure 7 shows that ice is typically funneled from the north along the west coast of Banks Island. Although we lack $pCO_{2sw}$ measurements north of our study area, observations from the Canada Basin (the source area for water advected along Banks Island) reveal that surface waters are typically undersaturated in summer, in the range of 150–350 $\mu$atm [*Bates et al.*, 2011]. Thus, the additional reduction in $pCO_{2sw}$ relative to Amundsen Gulf may be due to horizontal advection. Another possibility is higher biological productivity. The nearby Sachs Harbour meteorological station recorded sustained northerly (i.e., upwelling favorable) winds on four occasions in September 2007, and CIS charts showed that the mobile ice was seaward of the shelf break, which are both conditions conducive to effective shelf break upwelling [*Carmack and Chapman*, 2003]. This upwelling may have supplied a source of nutrients not available to Amundsen Gulf, producing a stronger or more sustained fall bloom.

#### 4.3.2. Spring (May 2008)

[39] Spring ice conditions on the Banks Island Shelf followed a similar to pattern to Amundsen Gulf, with significant open water occurring by mid-May. The spring transects (Figure 2b) were conducted 25–29 May. With the exception of low $pCO_{2sw}$ measurements of $\sim$275 $\mu$atm on the western and northern edges of the transects, the mean $pCO_{2sw}$ was 301 $\mu$atm, similar to observations in Amundsen Gulf (Figures 2b and 3). This suggests that spring on the Banks Island Shelf progressed similarly to Amundsen Gulf, probably with modest uptake by ice algae followed by a spring open water bloom.

[40] The low $pCO_{2sw}$ on the western and northern margins of the transects ($pCO_{2sw}$ values ranging from 275 to 290 $\mu$atm, Figure 2b) correspond to the positions of the sea ice edges at the time of sampling. A key characteristic of Arctic marine ecosystems is the "ice edge bloom," the rapid onset of photosynthesis promoted as light limitation is reduced by melting (or drifting) sea ice [*Sakshaug*, 2004]. The low $pCO_{2sw}$ measurements may be a fingerprint of such ice edge blooms. The lower $pCO_{2sw}$ observed during the northernmost transects also suggests that southerly flow of ice and surface water (Figure 7b) may have helped reduce $pCO_{2sw}$ through horizontal advection.

#### 4.3.3. Summer (July 2008)

[41] We observed a mean $pCO_{2sw}$ of 386 $\pm$ 12 $\mu$atm during the summer 2008 transect on the Banks Island Shelf (Figure 2c), an increase of 85 $\mu$atm from spring. Relative to the spring transects, SST increased from $-1.0$ to 7.0°C and S decreased from 30.46 to 29.71, which we calculate to have caused changes in $pCO_{2sw}$ of +119 and $-17$ $\mu$atm, respectively. Using the wind velocities from the Sachs Harbour weather station and assuming linear increases of $pCO_{2sw}$ and SST, we calculate a change in $pCO_{2sw}$ due to air-sea exchange of +20 $\mu$atm. This leaves a difference of $-37$ $\mu$atm between the calculated and observed changes in $pCO_{2sw}$ that can be attributed to biological uptake. These perturbations to $pCO_{2sw}$ are similar to those in Amundsen Gulf over the same time period (Table 2), reinforcing the idea that the two regions follow similar patterns in the spring and summer. Surface currents remained southerly during this period (Figure 7c), but we observed no gradients in $pCO_{2sw}$ or SST along the northward transect that would suggest an important role for horizontal advection. This may be partly due to the fact that the ice pack (and the associated low $pCO_{2sw}$ water [*Bates et al.*, 2011]) had retreated quite far north by this point in time (Figure 2c).

[42] Extensive open water on the Banks Island Shelf and in Amundsen Gulf occurred about 3–4 weeks earlier than on the Mackenzie Shelf, which may explain why $pCO_{2sw}$ in these regions was in equilibrium with the atmosphere by early July while the Mackenzie Shelf remained undersaturated (Figure 2c). In Amundsen Gulf, *Tremblay et al.* [2008] observed nutrient limitation in surface waters shortly after the ice cleared, whereas on the Mackenzie Shelf, *Carmack et al.* [2004] did not observe nutrient limitation until much later in the summer. If the Banks Island Shelf behaves similarly to Amundsen Gulf, it may become nutrient limited quickly, allowing the surface waters to equilibrate with the atmosphere over the summer months.

## 5. Significance: Testing the Seasonal Rectification Hypothesis

[43] A schematic of the seasonal cycle of $pCO_{2sw}$ and air-sea gas exchange for polynya regions, as proposed by *Yager et al.* [1995] from their work on the NEW polynya, is shown in Figure 9. Schematics for the three regions examined in this study are shown in Figure 10. Differences between our observations and the seasonal rectification hypothesis (i.e., the *Yager et al.* [1995] model) are the result of processes that either did not occur in the NEW polynya (the NEW polynya apparently no longer forms, see note by *Barber and Massom* [2007]) or were not observed there. In the following discussion, we highlight these differences with the goal of improving our understanding of annual $pCO_{2sw}$ cycles in Arctic environments. Broadly, Amundsen Gulf and the Banks Island Shelf followed similar cycles in 2007–2008 (Figures 10a and 10b) with persistent undersaturation, while the Mackenzie Shelf followed a different pattern of high fall/winter supersaturation followed by strong spring undersaturation (Figure 10c). Therefore, we have found it logical to split the discussion between these two groups.

[44] It is worth noting that in contrast to *Yager et al.* [1995], we include the possibility of gas exchange through the ice-covered season. In most years the ice in Amundsen Gulf remains mobile, producing an icescape composed of drifting floes and flaw leads. The fractional area of open water can thus at times be quite high; between November 2007 and January 2008 we estimated the lead fraction to vary from $\sim$0.1 to 10% [*Else et al.*, 2011]. Open water may be even more important on the Banks Island and Mackenzie

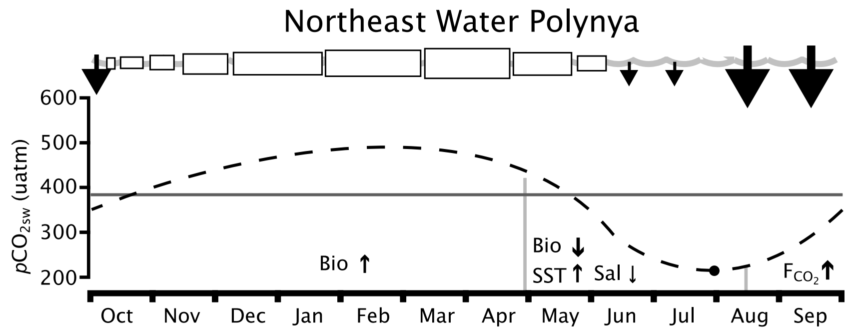


**Figure 9.** Schematic summarizing the seasonal cycles of $pCO_{2sw}$ and potential for air-sea exchange in the NEW polynya, as suggested by *Yager et al.* [1995]. The solid circle represents observed $pCO_{2sw}$, and the dashed line is a rough extrapolation that we propose based on the discussion by *Yager et al.* [1995]. The boxes at the top denote the time series of sea ice concentration in the region. Black arrows at the top indicate the potential for air-sea exchange, with down arrows indicating potential invasion, up arrows indicating potential evasion, and the relative size of the arrows denoting the expected magnitude based on the air-sea $pCO_2$ gradient and wind velocities. The annotations below the $pCO_{2sw}$ curve indicate the processes believed to be important in controlling $pCO_{2sw}$ during the various seasons. The processes are abbreviated as: Bio, biology; SST, sea surface temperature; Sal, salinity; $F_{CO_2}$, air-sea gas exchange. Upward arrows indicate a process that increases $pCO_{2sw}$, downward arrows indicate a process that decreases $pCO_{2sw}$, and the size of the arrows indicates the relative importance of each process.

Shelves, where motion of the Beaufort Sea ice away from the coast can create extensive winter shore-lead polynyas. Given recent water column [*Anderson et al.*, 2004], laboratory [*Loose et al.*, 2009], and micrometeorology [*Else et al.*, 2011] studies showing enhanced gas exchange through such icescapes, we feel it is important to consider that significant air-sea $CO_2$ flux may occur even in the winter.

### 5.1. Amundsen Gulf and the Banks Island Shelf

[45] *Yager et al.* [1995] predicted that as long as wind velocities are sufficient, fall gas exchange will bring $pCO_{2sw}$ to equilibrium with the atmosphere. Despite very strong winds, we found Amundsen Gulf and the Banks Island Shelf to be significantly undersaturated at freezeup in 2007. Our analyses and past investigations [*Arrigo and van Dijken*, 2004; *Brugel et al.*, 2009] indicate that fall phytoplankton blooms and surface water cooling may be responsible for this undersaturation. The potential for fall blooms was not discussed by *Yager et al.* [1995], but should perhaps be revisited for the NEW region.

[46] The seasonal rectification hypothesis also states that for polynya regions to act as net $CO_2$ sinks, a sea ice cover is necessary to prevent outgassing during the winter. Our results show that Amundsen Gulf remained undersaturated throughout the winter, and it is likely that the Banks Island Shelf behaved similarly. $pCO_{2sw}$ did increase under the ice cover, but it did so slowly, such that saturation was not reached until early March when algae production began to reduce $pCO_{2sw}$. This winter cycle is similar to many mid- and high-latitude shelves where the continental shelf pump prevents the recycling of organic matter in the surface layer [see, e.g., *Tsunogai et al.*, 1999; *Anderson et al.*, 2010]. The persistent undersaturation may also be driven by the relatively low DIC to TA ratio typically observed in the polar mixed layer [*Bates et al.*, 2009], which should buffer respiration-driven $pCO_{2sw}$ increases. Amundsen Gulf and the Banks Island Shelf thus did not require a winter ice cover to act as net sinks of $CO_2$ in 2007–2008.

[47] We also observed significant deviation from the *Yager et al.* [1995] model in Amundsen Gulf and the Banks Island Shelf in the spring. The spring $pCO_{2sw}$ in both regions (~275–300 $\mu$atm) was considerably higher than observed in the NEW polynya (mean 218 $\mu$atm). This is consistent with the observations of *Tremblay et al.* [2008] that spring phytoplankton blooms are less intense in the southeastern Beaufort Sea, due mostly to the limited nutrient supply caused by strong surface water stratification. We were, however, able to confirm the hypothesis that under-ice algae blooms play a significant role in lowering $pCO_{2sw}$ prior to break up (as was shown by *Shadwick et al.* [2011]). This was important to the *Yager et al.* [1995] model in order to prevent a release of built-up $CO_2$ when the polynya first forms.

[48] Finally, the surface water of both regions experienced a rise toward near-atmospheric $pCO_{2sw}$ levels in the summer that is not included in the seasonal rectification hypothesis. Significant warming of the sea surface (to 7–8°C) was primarily responsible for this $pCO_{2sw}$ increase (Table 2). In contrast, the maximum surface temperature recorded during the NEW polynya study was 3°C [*Wallace et al.*, 1995]. The lower temperatures in the NEW polynya may reflect the horizontal advection of cold water from the adjoining ice covered areas, as is the case in the North Water polynya [*Melling et al.*, 2001]. The apparent lack of significant horizontal advection in Amundsen Gulf and the Banks Island Shelf during our study, combined with strongly stratified surface waters and a lower-latitude location probably all contributed to the high summer SST. The combination of a limited phytoplankton bloom and summer warming make the potential for open water season $CO_2$ uptake less dramatic in our observations than in the *Yager et al.* [1995] model.

### 5.2. Mackenzie Shelf

[49] The Mackenzie Shelf (Figure 10c) more closely followed the proposed $pCO_{2sw}$ pattern for the NEW region (Figure 9), but the timing of the fall $pCO_{2sw}$ supersaturation was very different. In contrast to a gradual increase in

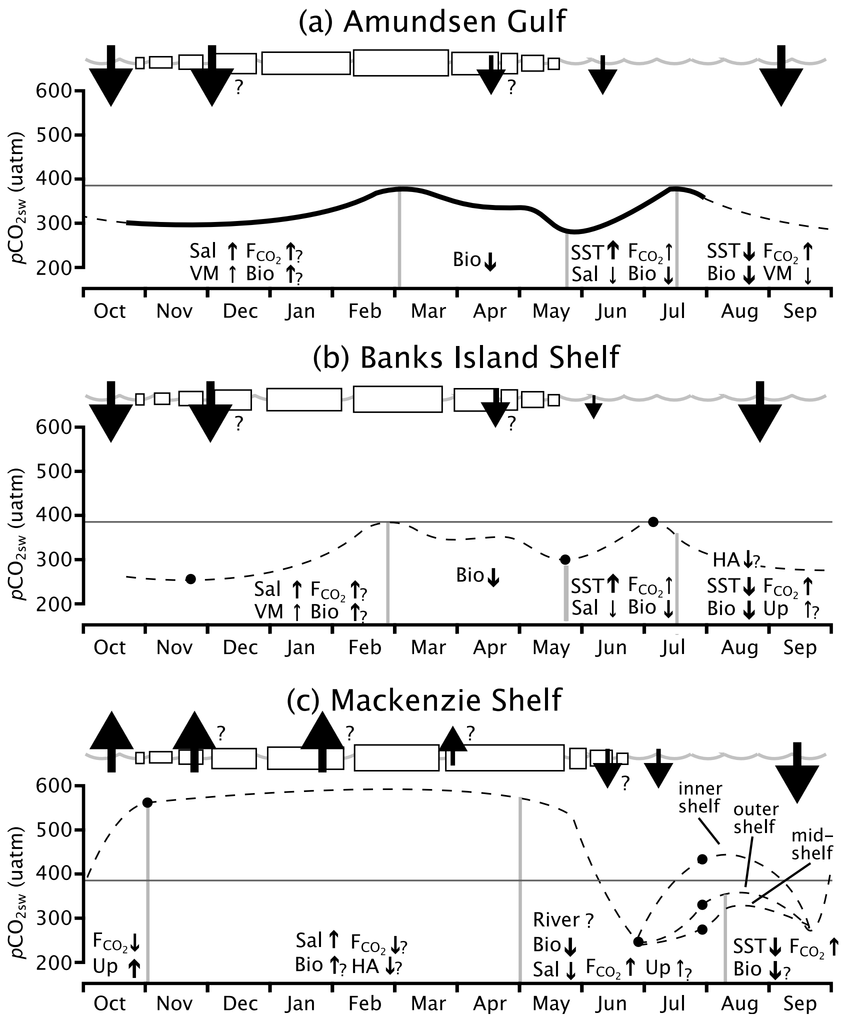


**Figure 10.** Schematic summarizing the seasonal cycles of $pCO_{2sw}$ and potential for air-sea exchange in the three southeastern Beaufort Sea study regions, with annotations as per Figure 9. (a) The solid line and (b and c) the solid dots indicate observations, while the dashed lines are extrapolations based on the processes known to be occurring. Additional annotations for the processes are: HA, horizontal advection; Up, upwelling; VM, vertical mixing; River, riverine input. Question marks denote significant uncertainty in the magnitude of the corresponding arrows.

$pCO_{2sw}$ over the winter driven by respiration in the surface water, we found a rapid increase to high supersaturation due to shelf break upwelling. Our results show that this upwelling is limited to certain coastal regions and weather conditions in the southeastern Beaufort Sea. Since many polynyas exist on continental shelves and along coastlines, fall upwelling is potentially significant across the Arctic, particularly in polynyas that that are partially maintained by the warm water associated with such upwelling. In these upwelling regions, the ability (or inability) of the sea ice cover to prevent outgassing is very important if the region is to act as a net annual $CO_2$ sink.

[50] This region was also more similar to Figure 9 in its spring/summer biological reduction of $pCO_{2sw}$ than the Banks Island Shelf or Amundsen Gulf. Although not as strong as in the NEW or NOW polynyas, we did observe high spring undersaturations, particularly in regions where nutrients were supplied by episodic upwelling [*Tremblay et al.*, 2011]. This undersaturation was maintained through the summer on the midshelf, although we did observe higher $pCO_{2sw}$ where the influence of river discharge was greatest. Again, this is consistent with current understandings of continental shelves affected by river inflow; outgassing can be significant along a narrow coastal band, but undersaturation is typically prevalent across a much larger area of the offshore shelf [*Chen and Borges*, 2009]. Given that river-influenced shelves are very common in the Arctic, we expect this to be an important consideration for many seasonally ice-free regions.

## 6. Summary and Conclusions

[51] This study is perhaps the most comprehensive observation of $pCO_{2sw}$ in an Arctic marine environment. The complex nature of our study area allowed us to examine an annual cycle of $pCO_{2sw}$ and the processes controlling it in three distinct environments: the Amundsen Gulf, a spring-opening polynya region that typically experiences ice

motion and fracturing throughout the winter; the Banks Island Shelf, a flaw-lead polynya region that opens in the spring similar to Amundsen Gulf and can also experience extensive open water during the winter; and the Mackenzie Shelf, which is heavily influenced by riverine inputs and where the ice opens slightly later in the spring.

[52] Our results show that in 2007–2008, none of these systems precisely followed the simple model of annual $pCO_{2sw}$ suggested for the NEW polynya region by *Yager et al.* [1995]. Amundsen Gulf and the Banks Island Shelf showed undersaturation at freezeup due to fall phytoplankton blooms, and gradual increases in under-ice $pCO_{2sw}$ that never exceeded atmospheric levels. Biological uptake of $CO_2$ and reduction of $pCO_{2sw}$ began in early spring in these regions, but was never as intense as observed in more northerly polynyas. Summer warming increased $pCO_{2sw}$ and surface layer stratification restricted photosynthetic $CO_2$ uptake, limiting the potential open water sink of $CO_2$. On the Mackenzie Shelf, fall upwelling of $CO_2$-charged upper halocline waters created rapid supersaturation prior to ice formation. We were unable to measure winter $pCO_{2sw}$ in this region, but the spring undersaturation was more intense than in Amundsen Gulf or on the Banks Island Shelf. Spring and summer $pCO_{2sw}$ distributions on the Mackenzie Shelf were complicated by the Mackenzie River plume and bathymetrically induced upwelling.

[53] Given these results, we propose that the following processes need to be considered when assessing the annual $pCO_{2sw}$ cycle of polynya regions.

[54] 1. Fall phytoplankton blooms may be initiated by nutrient replenishment from strong wind mixing or episodic upwelling, producing undersaturated $pCO_{2sw}$ at freezeup.

[55] 2. Fall upwelling can create high $pCO_{2sw}$ prior to freezeup, if it occurs late enough in the season that light limitation prohibits photosynthetic $CO_2$ drawdown despite the availability of nutrients. Vertical mixing at any time in the year will likely bring high $pCO_2$ water into the surface, and may be particularly important during brine rejection-driven mixing associated with sea ice formation, and stormy open water seasons.

[56] 3. Winter under-ice respiration in surface water needs to be better constrained to understand the potential magnitude of winter $pCO_{2sw}$ increase.

[57] 4. The continental shelf pump may play an important role in suppressing winter $pCO_{2sw}$ increase by preventing the recycling of organic matter in the surface mixed layer.

[58] 5. Winter air-sea gas exchange needs to be included in the annual air-sea $CO_2$ flux and seasonal $pCO_{2sw}$ evolution for polynyas regions whose ice cover is not continuous through the winter.

[59] 6. Spring/summer nutrient supply needs to be considered when determining the magnitude of biological $pCO_{2sw}$ reduction.

[60] 7. Summer warming of the surface layer may counteract some of the biological $pCO_{2sw}$ reduction, reducing the open water uptake potential.

[61] 8. River input may play a complicating role in seasonal $pCO_{2sw}$ patterns in coastal regions where runoff is significant. Remineralization of riverine DOC/POC will cause elevated $pCO_{2sw}$, which is normally constrained close to shore [e.g., *Chen and Borges*, 2009; this study], but can extend well onto the shelves in some Arctic regions [e.g., *Anderson et al.*, 2009].

[62] 9. Horizontal advection can modify $pCO_{2sw}$ if significant surface currents and strong horizontal gradients of $pCO_{2sw}$ exist. This may play an important role in keeping $pCO_{2sw}$ low when water is transported into a polynya region from surrounding ice covered areas.

[63] By better accounting for these processes, we can improve our ability to predict air-sea $CO_2$ exchange budgets for the Arctic, particularly in polynya regions and other regions with variable ice conditions. In identifying these processes, we also hope to instruct future efforts to model the potential impacts of climate change on air-sea $CO_2$ exchange in polynyas. Fall shelf break upwelling is likely to become more important as the perennial ice retreats further beyond the shelf break [*Carmack and Chapman*, 2003] and remains there later into the fall [*Tremblay et al.*, 2011]. Later fall freezeup, increased winter ice motion [*Hakkinen et al.*, 2008] and earlier spring breakup will promote air-sea gas exchange. The biological system is expected to experience significant changes, with longer growing seasons [*Arrigo et al.*, 2008] but possibly reduced nutrient supply due to increasing surface stratification [*Tremblay et al.*, 2008]. The effectiveness of the continental shelf pump may be affected by changes in the biological system as well; for example, *Forest et al.* [2010] found lower vertical carbon export in Amundsen Gulf associated with longer open water seasons. Increases in SST [*Steele et al.*, 2008] may limit the potential for summer $CO_2$ uptake by increasing $pCO_{2sw}$. Perhaps most significantly, the transition of broad reaches of the Arctic Ocean to seasonal ice as the summer sea ice extent declines [*Stroeve et al.*, 2007; *Perovich and Richter-Menge*, 2009] means that a progressively larger area of the Arctic will undergo ice cycles similar to our study region. Ultimately, the new understandings presented in this paper will help predict how the Arctic's current role as a sink for atmospheric $CO_2$ [*Bates and Mathis*, 2009] will change in the future.

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