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Key Points:
- In stratified Arctic Ocean waters, sampling depth can introduce large errors into air-sea CO_2 flux estimates at individual stations
- Data from an underway system generally overestimated the summer atmospheric CO_2 drawdown in the Canadian Arctic Archipelago

Supporting Information:
- Supporting Information S1
- Table S1
- Table S2
- Table S3

Correspondence to:
L. A. Miller,
lisa.miller@dfo-mpo.gc.ca

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Air-Sea CO_2 Flux Estimates in Stratified Arctic Coastal Waters: How Wrong Can We Be?

Lisa A. Miller[1], Tonya M. Burgers[2], William J. Burt[3], Mats A. Granskog[4], and Tim N. Papakyriakou[2]

[1]Centre for Ocean Climate Chemistry, Institute of Ocean Sciences, Fisheries and Oceans Canada, Sidney, British Columbia, Canada, [2]Centre for Earth Observation Science, Department of Environment and Geography, University of Manitoba, Winnipeg, Manitoba, Canada, [3]Department of Earth, Ocean and Atmospheric Sciences, University of British Columbia, Vancouver, British Columbia, Canada, [4]Norwegian Polar Institute, Fram Centre, Tromsø, Norway

Abstract Summer near-surface seawater sampling in the Canadian Arctic revealed potential for significant errors (nearly 0.1 μmol·(m^{-2} s^{-1})) in CO_2 fluxes calculated from measured air-sea CO_2 gradients. River runoff and sea ice melt strongly stratify these waters, often resulting in surface mixed layers only a few meters thick and isolated from waters sampled by shipboard underway systems. Samples collected with the underway system, rosette, and small boats exposed substantial near-surface gradients in CO_2 partial pressure (pCO_2) over the top 7 m at many stations. Distributions of temperature, salinity, and fluorescence indicated that the sources of the CO_2 system gradients varied between stations, precluding simple corrections to align subsurface data with shallower conditions. Overall, the strong summertime sink of atmospheric CO_2 implied by the underway data was not supported by shallower data.

Plain Language Summary Large quantities of sea ice melt and river runoff in the Arctic Ocean form thin layers of fresh water at the surface that are isolated from deeper water. However, standard methods of sampling surface waters from ships draw water from 2 to 7 m below the surface, which can cause errors in air-sea CO_2 fluxes calculated from measured seawater CO_2 concentrations. We have quantified the potential error for waters of the coastal Arctic Ocean by measuring CO_2 concentrations in samples collected near the surface using different methods from both large ships and small boats. We found that large errors could result from shipboard sampling at some stations. In particular, measuring the CO_2 concentration from automated instruments that draw water from below the ship's hull systematically overestimated atmospheric CO_2 absorption by the ocean.

1. Arctic Ocean Stratification and Estimating Air-Sea CO_2 Fluxes From Bulk Parameterizations

Extreme, widespread stratification, similar to what is observed on smaller scales in temperate and tropical estuaries and coastal waters, is one of the most striking characteristics of the summer surface Arctic Ocean. Both sea ice melt and river runoff result in shallow, low-salinity surface mixed layers in both coastal and deepwater regions of the Arctic (e.g., Burt et al., 2016; Yamamoto-Kawai et al., 2009). These relatively fresh surface layers are often no more than a few meters thick and can persist for extended periods of time, because of the strong stratification at the interface with the more saline waters below, as well as the generally moderate winds during the melt season (e.g., Polyakov et al., 1999).

As a whole, the Arctic Ocean currently appears to serve as a net atmospheric CO_2 sink (e.g., Evans et al., 2015; Land et al., 2013; Yasunaka et al., 2018). However, that net sink is likely sensitive to the seasonal progression of ice coverage (e.g., Else, Galley, et al., 2012; Evans et al., 2015) and presumably river runoff, which appears to be increasing (e.g., Dai et al., 2009; Déry et al., 2016). The sink is also punctuated by instances of strong outgassing, most notably in coastal and river-influenced waters where heterotrophic respiration of terrestrial organic matter and sedimentary methane can release large quantities of CO_2 (e.g., Anderson et al., 2011; Else et al., 2008; Graves et al., 2015). In addition, as sea ice breaks up and retreats from the coasts, upwelling may increasingly bring high CO_2 waters to the surface, where they can outgas (Else, Papakyriakou, et al., 2012; Mathis et al., 2012; Williams & Carmack, 2015), and as summertime surface waters grow warmer, summer outgassing is likely increasing (Else et al., 2013; Else, Papakyriakou, et al., 2012; Geilfus et al., 2018; Land et al., 2013).

Shallow, fresh surface mixed layers in the Arctic Ocean have a number of implications for the net CO_2 sink (as noted by Murata et al., 2008). Whereas many Arctic river waters tend to be supersaturated in CO_2 (i.e., poorly buffered with relatively high CO_2 contents; Tank et al., 2012; Telang et al., 1991), sea ice melt is initially undersaturated (e.g., Geilfus et al., 2015), and therefore, surface Arctic Ocean freshwater lenses can either release or absorb atmospheric CO_2. In addition, because of their limited depth and small total volumes, surface fresh layers can equilibrate rapidly with the atmosphere, and instantaneous fluxes are not sustained over extended periods (Cai et al., 2010; Else et al., 2013). On the other hand, as summer progresses, wind mixing eventually erodes the stratification (while also increasing air-sea flux rates), and particularly as autumn advances, with increasing storminess, mixed layers cool and deepen, changing the surface expression of CO_2 partial pressure (pCO_2) (e.g., Else, Papakyriakou, et al., 2012; Miller et al., 2002; Shadwick et al., 2011). Thus, to assess and understand the processes currently controlling the net air-sea CO_2 source-sink balance in the Arctic Ocean, and how that balance is changing with climate, we need to be confident that our flux estimates are accurate.

Direct, ship-based measurements of air-sea CO_2 fluxes (i.e., by eddy covariance) require specialized equipment and considerable expertise (e.g., Blomquist et al., 2014), even more so in polar regions, where cold temperatures and riming introduce further complications (e.g., Butterworth & Miller, 2016). Therefore, most of our understanding of air-sea CO_2 exchange and its variation depends on calculated fluxes, commonly based on parameterizations of the gas transfer velocity, k (e.g., Fairall et al., 2003; Wanninkhof, 2014), and the measured air-sea gradient in CO_2 partial pressure (ΔpCO_2)

$$F_{CO2} = ks\Delta pCO_2, \tag{1}$$

where F_{CO2} is the CO_2 flux and s is the CO_2 solubility in seawater, as a function of both temperature and salinity (Weiss, 1974). Atmospheric pCO_2 is directly measured in situ, using nondispersive infrared spectrometers deployed on buoys or ships, or values from monitoring stations in the global CO_2 monitoring network can be used (e.g., Dlugokencky et al., 2017), based on a reasonable assumption that the atmosphere is generally well mixed.

In contrast to the lower atmosphere, the upper ocean is poorly mixed, and direct surface seawater measurements are required to generate estimates of the air-sea pCO_2 gradient. The vast majority of the surface pCO_2 measurements available are from automated, shipboard, underway systems, which analyze pCO_2 in continuous water supplies drawn through the ship's hull, well below the water line (e.g., Bakker et al., 2016). Other typical approaches to collecting surface water pCO_2 data are discrete station sampling by rosette, which retrieves water from no shallower than 1 m or from drifting or moored surface buoys (e.g., Bakker et al., 2001; Sutton et al., 2014). In temperate, well-mixed, open ocean waters, all these approaches may give similar estimates of pCO_2 under most conditions, but significant near-surface vertical variability in pCO_2 has been observed across a range of oceanic environments (Calleja et al., 2013; Murata et al., 2008), particularly in river-influenced coastal waters (Gong et al., 2007). Also, under very calm conditions, true surface pCO_2, in the sea-surface microlayer directly in contact with the atmosphere, may be different from even the values measured directly below the surface, because of slow diffusion, reactions occurring in the microlayer, or near-surface temperature gradients (Garbe et al., 2014; Wanninkhof & Knox, 1996; Ward et al., 2004). However, under those circumstances, the fluxes are limited by low winds (i.e., low turbulence, which reduces k in equation (1)), and the influence on net fluxes over long time periods or large areas is likely small.

Under the conditions of extreme stratification often observed in the Arctic Ocean (as well as in many coastal waters in other areas), pCO_2 in the surface layer actively exchanging with the atmosphere can be very different from what would be sampled by either a continuous seawater supply or a rosette in the agitated waters adjacent to a ship, even in the presence of moderate winds. Here we have attempted to estimate the magnitude of the sampling depth-associated errors in calculated air-sea CO_2 fluxes in Arctic coastal waters by analyzing the CO_2 system at various typical "surface" depths during three expeditions in Hudson Bay, Baffin Bay, and the waters of the Canadian Arctic Archipelago (Figure 1). Our data set does not help address the impacts of the thermal (or haline) skin effect on flux estimates (e.g., Woolf et al., 2016) but rather examines the uncertainties associated with pCO_2 values determined at various depths within the bulk waters. Part of this data set has also been presented by Burt et al. (2016), who found that substantial vertical variations in salinity in the surface waters of southwestern Hudson Bay also have implications for interpretations of water mass distributions and CO_2 system geochemistry throughout the bay.

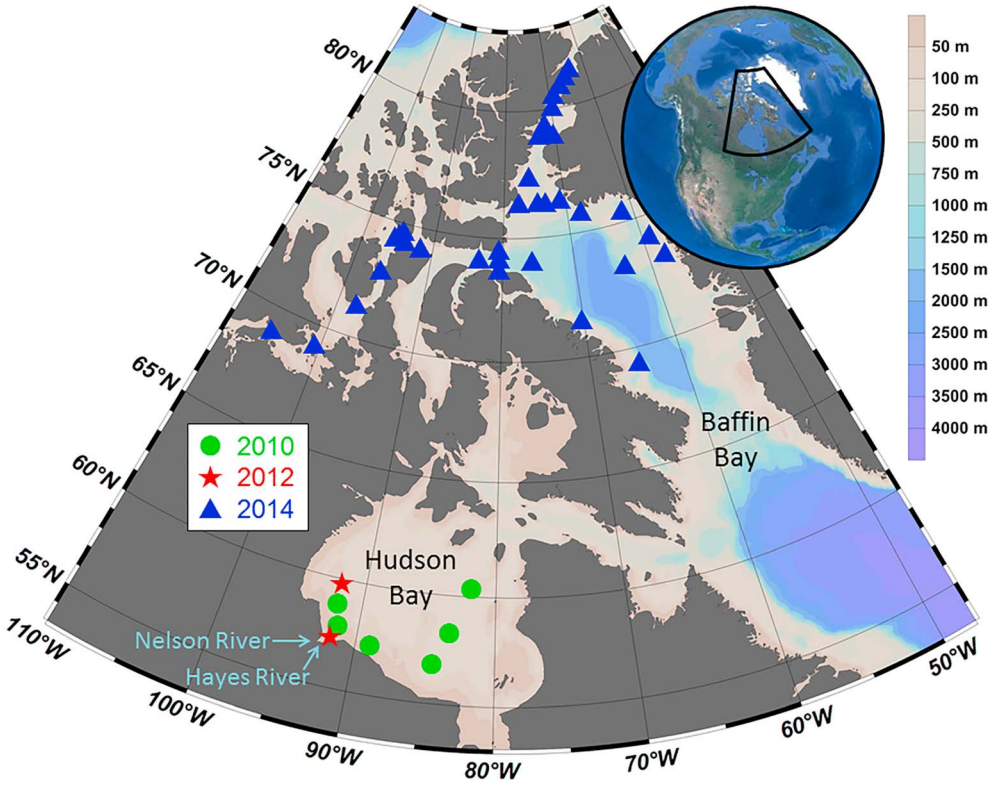

Figure 1. Surface sampling locations in Hudson Bay, Baffin Bay, and the waters of the Canadian Arctic Archipelago. See Table S1 for specific station locations and dates.

2. Methods

The details of our sampling and analytical methods, as well as our calculations, are described in the supporting information. Here we give only a brief description of our overall sampling strategy and the general methods we used.

2.1. Sampling and Chemical Analyses

We collected surface seawater samples in the eastern Canadian Arctic covering a spectrum of freshwater sources, from predominantly river waters to sea ice melt, using the *CCGS Amundsen* in 2010 and 2014 and the *CCGS Pierre Radisson* in 2012 (Figure 1 and Table S1). In late July 2010 and late August 2012, we sampled river-dominated waters off the mouths of the Nelson and Hays Rivers in the southwestern corner of Hudson Bay. In July and August 2014, we sampled stations in northern Baffin Bay and the waters of the eastern Canadian Arctic Archipelago, where we expected sea ice melt to be the dominant freshwater source. For general descriptions of the oceanography of these areas, see Macdonald and Kuzyk (2011), Ingram et al. (2002), McLaughlin et al. (2006), and references therein.

We sampled from shipboard rosettes during all three cruises, but continuous underway pCO_2 measurements were only available in 2014 (Table S1). During each expedition, we also sampled surface waters from small boats away from the ship, on an opportunistic basis. The longest time elapsed during our sampling at any one station was just over 4 hr, but most stations were completed within 2 hr. The average horizontal distance between the small boat and the ship during sampling was 2.4 km (Figure S1).

The underway pCO_2 system (General Oceanics model 8050; Pierrot et al., 2009) onboard the *Amundsen* pulls its seawater supply from approximately 7-m depth. In 2010 and 2014, the rosette was deployed midship (Amundsen Science Data Collection, 2010, 2014), whereas from the *Radisson* in 2012, it was deployed off the bow. Rigid-hull inflatable boats were used to collect samples in waters assumed not to be influenced by mixing from the ship. We collected discrete samples using Niskin bottles deployed off the side; in 2010,

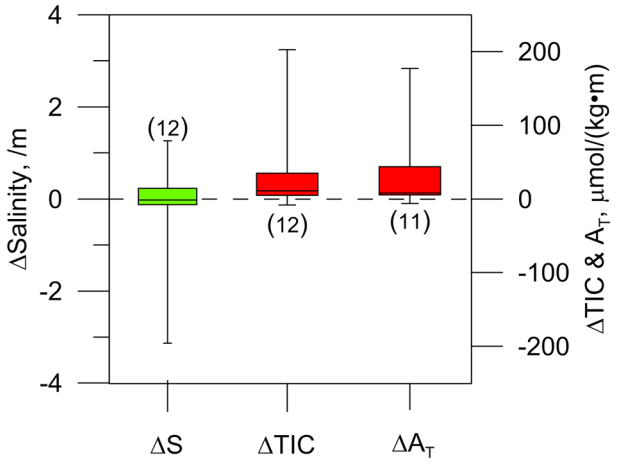

Figure 2. Vertical gradients in salinity, TIC, and A_T (differences at sampling depths, divided by the depth range) between samples collected from small boats versus the shallowest rosette bottle during all three expeditions. Boxes show medians and 25th and 75th quartiles, whiskers indicate maxima and minima, and numbers of values are indicated in parentheses. Positive values indicate decreasing values going upward, toward the surface. TIC = total inorganic carbon; A_T = total alkalinity.

we only sampled from 1-m depth, whereas during the 2012 and 2014 expeditions we sampled multiple depths (Tables S1 and S2). In 2014, we also directly measured pCO_2 from the small boats at multiple depths using a portable custom-built CO_2 monitoring system (Else et al., 2008). We deployed Idronaut 304 CTDs from the small boats in both 2012 and 2014.

Samples for analyses of total inorganic carbon (TIC) and total alkalinity (A_T) were collected using standard protocols (Dickson et al., 2007). Both TIC (coulometric) and A_T (potentiometric titrations with nonlinear least squares end point determination) were analyzed using standard methods (Dickson et al., 2007) at the Institute of Ocean Sciences. Discrete salinity samples collected at every depth were analyzed either onboard or at the Institute of Ocean Sciences (Guildline Autosal 8400B). All of the bottle data, as well as the directly measured pCO_2 data, used in this paper are presented in Table S2. The rosette and underway data from the 2014 cruise are available through the National Centers for Environmental Information Ocean Archive (NCEI Accession 0167322).

2.2. pCO_2 and Flux Calculations

Across our data set, pCO_2 was determined in three different ways: from small boats with the portable CO_2 system, calculated from TIC and A_T analyzed in discrete water samples collected from the ship's rosette and hand casts from the small boats, and with the GO 8050 underway system. The values calculated from TIC and A_T in the discrete water samples were generated using the CO2Sys program (Excel version 2.1; Pierrot et al., 2006), with the CO_2 acid dissociation constants of Lueker et al. (2000). Note that because of the opportunistic nature of our sampling from the small boats, and associated logistical challenges and data gaps, we were only able to confidently calculate pCO_2 fluxes from a limited number of those samples.

Air-sea CO_2 fluxes were calculated using the Wanninkhof (2014) parameterization for the gas transfer velocity with wind speeds measured onboard. During the 2010 and 2014 cruises, we directly measured local atmospheric pCO_2 (LI-COR LI-7000) in air from an intake located on the bow meteorological tower. For 2012, atmospheric pCO_2 data from Alert Station (Ellesmere Island) were downloaded from the World Data Centre for Greenhouse Gases.

3. Results

3.1. Near-Surface Chemical Gradients

We often observed large vertical gradients in TIC, A_T, and pCO_2 in the surface waters we sampled (Figures 2 and 3), and the variations in pCO_2 with depth were often larger than the uncertainties due to the choice of CO_2 system stability constants used to calculate seawater pCO_2 in Arctic waters (approximately 6 μatm; Woosley et al., 2017). Shallower waters sampled from small boats were generally depleted in TIC and A_T, relative to what was observed from the ship, but we rarely saw similar gradients in salinity (Figure 2), indicating that the small boats and the ship were often sampling different water masses. Although the surface waters were generally undersaturated in CO_2, relative to the atmosphere, air-sea exchange cannot fully explain the lower concentrations in the small boat samples, because both TIC and A_T were depleted. We can only speculate about possible sources of the different surface waters, but in general, sea ice melt contains less TIC and A_T than most Arctic river waters of the same salinity (e.g., Rysgaard et al., 2011; Tank et al., 2012). Thus, we may have been sampling surface waters with greater sea ice melt influence overlying waters with more riverine influence.

Depth-resolved sampling from the small boats showed that whereas the changes in pCO_2 with depth at most of the stations were less than 5 μatm (Figure 3, bars with green diagonal stripes), 30% of the stations displayed larger gradients. In some cases, the measurements at 1 and 2 m were similar to each other but different from the shallower measurements at 0.5 m (Table S2), indicating a very thin, stratified layer overlaying a

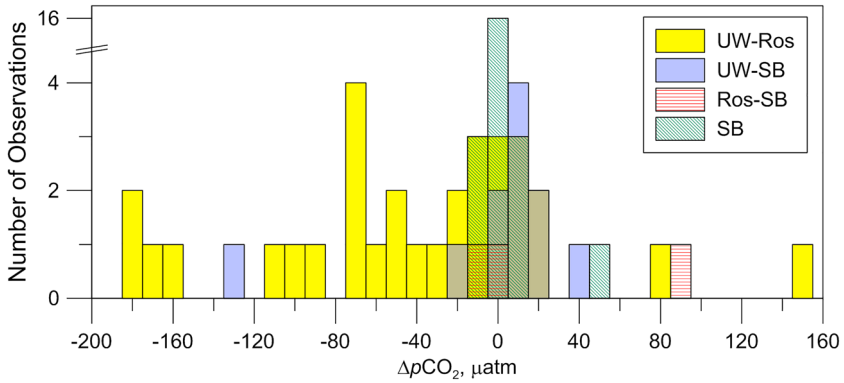

Figure 3. Histograms of observed near-surface vertical pCO_2 differences. UW: underway measurements from 7 m. Ros: shallowest rosette bottles at 1–3 m. SB: small boat samples from 0–5 m. Positive values indicate higher pCO_2 in deeper samples. With the exception of the UW-Ros pairs, all comparisons are between pCO_2 values determined using the same method, either calculated from TIC and A_T in discrete samples or directly measured using the portable or underway systems. Green diagonal-striped bars labeled "SB" represent depth-resolved sampling from the small boats.

thicker, more well mixed layer. The values from the underway system and the small boats also generally agreed rather well (note that all of those data pairs are from the 2014 cruise). At the three stations where we were able to directly compare samples collected from the small boat and the shallowest rosette bottle (Figure 3, bars with red horizontal stripes), two agreed well, but one gave a very large offset of more than 90 μatm.

In general, the underway system gave pCO_2 values that were substantially lower than the shallowest rosette samples (with offsets greater than 30 μatm at more than half of the stations). During our expeditions, the waters we sampled were generally undersaturated with respect to the atmosphere, and thus, data from the underway system consistently indicated a larger atmospheric CO_2 drawdown than the rosette. On average, the differences are not statistically different from zero, but at individual stations, the differences can be quite large. The temperature differences between the underway system and the shallower samples were often contrary to the pCO_2 gradients (Table S3), indicating that pCO_2 was not simply controlled by surface heating and cooling. Subsurface primary production (e.g., Martin et al., 2010) is a likely explanation for many of the low pCO_2 values we observed from the underway system, and the rosette-mounted fluorometer signal often indicated that chlorophyll fluorescence increased with depth in the surface waters (Figure S2).

Table 1
Impact of Sampling Depth on Calculated Fluxes

	Underway-rosette	Underway-small boat[a]	Rosette-small boat[a]	Small boat[a]
n	30	5	3	6
Absolute error[b], $\mu mol \cdot (m^{-2}\ s^{-1})$				
Average	0.0146	0.0037	0.0082	0.0031
Median	0.0083	0.0011	0.0039	0.0004
Standard deviation	0.0178	0.0050	0.0086	0.0065
Minimum	0.0000	0.0001	0.0026	0.0001
Maximum	0.0839	0.0119	0.0181	0.0164
Relative error[c] *(%)*				
Average	147	12	73	34
Median	51	12	27	8
Standard deviation	325	12	101	68
Minimum	0	2	5	0
Maximum	1,796	32	189	172

Note. Fluxes calculated as described in section 2.2 (Table S3).
[a]Comparisons only between samples for which pCO_2 was determined the same way: either measured directly or calculated from TIC and A_T in discrete samples. [b]Absolute values of differences between paired samples at each station (i.e., the values here do not indicate the direction of the error). [c]Assuming that the shallowest sample is the most accurate.

3.2. Impacts on Calculated Fluxes

A difference in pCO_2 does not necessarily imply a significant difference in the calculated air-sea CO_2 flux, particularly at relatively low wind speeds typical of the summertime Canadian Arctic Archipelago. Even if a pCO_2 gradient forms in the near-surface waters, any increase in the wind would act to mix the waters and break down that gradient, and the near-surface pCO_2 gradients we observed were generally larger at lower wind speeds, with a few notable exceptions (Figure S3).

After taking into consideration the fact that wind speeds tended to be lower at the stations with the largest near-surface pCO_2 gradients, the differences in the calculated fluxes can still be quite large (Tables 1 and S3). These errors are nearly as large as the uncertainties associated with parameterizations of the gas transfer velocity (typically a factor of 2 or 100%; Garbe et al., 2014). It is important to note that the median errors in Table 1 are always smaller than the average errors, reemphasizing the observation from Figure 3 that most of the errors in pCO_2 are clustered toward 0 μatm, with some high values skewing the average. The relative

errors in the fluxes were sometimes quite large (lower half of Table 1), but the highest values were generally associated with low absolute fluxes.

4. Implications

Our results demonstrate that surface stratification can introduce substantial uncertainty into studies of the surface CO_2 system in coastal Arctic waters. Notably, averaging over the entire 2014 data set, the underway system on the ship, which drew water from 7-m depth, implied that the waters of the eastern archipelago are a consistent atmospheric CO_2 sink (averaging 4 mmol m^{-2} $d^{-}1$) during the summer. In contrast, samples from the shallowest rosette bottles (at 1–3 m) indicated a drawdown nearly half as large (Table S3, 2014 data). Extrapolating over a 90-day ice melt period and beyond the area of an individual cruise, as when data are incorporated into regional or Earth system models, would compound this error; for example, an error such as what we observed, extrapolated over the entire Arctic basin, would constitute 15% of the total annual drawdown estimated for the high Arctic Ocean (Yasunaka et al., 2018). Further, strong gradients in TIC and A_T between samples collected by the surface rosette and from small boats (Figure 2) indicate that even the shallowest rosette samples often do not accurately represent undisturbed surface waters. The fact that the overall average errors for our entire data set were not statistically different from zero (Table 1) seems to imply that broader and more extensive sampling will generate more robust regional flux estimates. However, our data set does not have sufficient resolution in time or space to robustly resolve how averaging influences the error in the estimated air-sea CO_2 flux under varying conditions (i.e., wind speed, sea state, stratification, and biogeochemical processes).

River waters and sea ice melt both cause stratification, but their impacts on air-sea CO_2 exchange can differ due to variations in the ratio of dissolved inorganic carbon to alkalinity, especially in rivers draining different geological provinces (e.g., Azetsu-Scott et al., 2014). Not only are Arctic river waters often supersaturated in CO_2, whereas sea ice melt is generally undersaturated, but also mixing between river waters and ice melt adds further complication, particularly since the influence of river waters can spread under sea ice over large distances and persist for long periods of time, until ice melt (Burgers et al., 2017; Ingram & Prinsenberg, 1998; Mungall et al., 2017). Regardless, highly stratified, shallow mixed layers equilibrate with the atmosphere more quickly than thicker mixed layers do, and the direction of the exchange with such stratified surface waters is probably less important than the fact that the flux is not sustainable for long. It is also important to remember that once the winds increase sufficiently to break down that stratification, in autumn or even during storm events in summer, the error in surface pCO_2 estimates likely diminishes dramatically.

The differences we observed in the CO_2 system between sampling depths varied from station to station, and the specific factors responsible also varied, including riverine versus sea ice melt freshwater sources, surface warming and cooling, vertical variations in primary productivity, and surface equilibration with the atmosphere. These factors interacted in different ways at different stations, making it difficult to develop a systematic correction to bring the depth-resolved data into agreement. In areas with relatively simple stratification sources (i.e., a single river or just surface warming), it may be possible to develop a robust correction factor, but in areas such as Arctic coastal waters, where the stratification is caused by a complex and variable mixture of factors, shipboard pCO_2 data should include higher error estimates to account for potential vertical pCO_2 gradients. The errors we have derived here could serve as a first estimate, but we advise that whenever possible, expeditions in potentially stratified waters collect some surface waters away from the ship, or at least samples from the surface rosette bottle, for comparison against the underway system.

Undeniably, sampling from small boats, as we did in this study, is impractical for comprehensive mapping or effective monitoring of surface pCO_2. Nonetheless, it is clear that in order to accurately determine air-sea CO_2 exchanges and the net CO_2 source sink balance in ice-covered oceans, it is necessary to take measurements as close to the surface as possible and away from large ships. Whereas buoys (e.g., Sutton et al., 2014) and autonomous surface vehicles (e.g., Cross et al., 2015; Krug et al., 2018) are the best way to sample "undisturbed" surface waters, such platforms cannot (yet) be utilized for long-term pCO_2 measurements in the presence of sea ice, including in the marginal ice zone and during the freeze-up and melt seasons (conditions where air-sea fluxes are likely to be largest). Therefore, our results serve as a call for technical innovations that will allow CO_2 system monitoring in true surface waters from polar ocean observatories

year-round. Because bottom-anchored moorings deployed in the Arctic generally terminate at least 10–20 m below the surface, to avoid snagging by sea ice keels, one possible solution could involve mechanisms to bring surface waters down to sensors on such moorings (e.g., expendable tubing constructions). However, it would be preferable to develop technology to deploy CO_2 system sensors on robust buoys able to survive the full annual cycle of sea ice formation and melt (e.g., Knepp et al., 2010). In particular, sensors deployed in surface waters on ice buoys can become encased within the ice as it thickens, and no existing CO_2 system sensor (for pCO_2 or pH) is likely to survive such treatment, because of both mechanical damage to the probe and the temperature decrease.

Finally, strong surface stratification (and associated deep Chl maxima; Cullen, 2015) is not limited to polar waters. Riverine freshwater is a feature of most coastal waters in the world, and the impacts of major rivers on oceanic surface waters can extend hundreds of kilometers out to sea (e.g., Kim et al., 2009; Muller-Karger et al., 1988). Shipboard surface pCO_2 measurements in these areas might also incur substantial errors, even without the additional complication of sea ice melt (i.e., Gong et al., 2007).

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