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Key Points:

- In stratified Arctic Ocean waters, sampling depth can introduce large errors into air-sea CO₂ flux estimates at individual stations
- Data from an underway system generally overestimated the summer atmospheric CO₂ drawdown in the Canadian Arctic Archipelago

Supporting Information:

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

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Air-Sea CO₂ Flux Estimates in Stratified Arctic Coastal Waters: How Wrong Can We Be?

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Abstract Summer near-surface seawater sampling in the Canadian Arctic revealed potential for significant errors (nearly 0.1 μmol·(m⁻² s⁻¹)) in CO₂ fluxes calculated from measured air-sea CO₂ 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 CO₂ partial pressure (*p*CO₂) over the top 7 m at many stations. Distributions of temperature, salinity, and fluorescence indicated that the sources of the CO₂ system gradients varied between stations, precluding simple corrections to align subsurface data with shallower conditions. Overall, the strong summertime sink of atmospheric CO₂ 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 CO₂ fluxes calculated from measured seawater CO₂ concentrations. We have quantified the potential error for waters of the coastal Arctic Ocean by measuring CO₂ 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 CO₂ concentration from automated instruments that draw water from below the ship's hull systematically overestimated atmospheric CO₂ absorption by the ocean.

1. Arctic Ocean Stratification and Estimating Air-Sea CO₂ 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 CO₂ 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 CO₂ (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 CO₂ 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).

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Shallow, fresh surface mixed layers in the Arctic Ocean have a number of implications for the net CO₂ sink (as noted by Murata et al., 2008). Whereas many Arctic river waters tend to be supersaturated in CO₂ (i.e., poorly buffered with relatively high CO₂ 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 CO₂. 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 CO₂ partial pressure ($p\text{CO}_2$) (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 CO₂ 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 CO₂ 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 CO₂ 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 CO₂ partial pressure ($\Delta p\text{CO}_2$)

$$F_{\text{CO}_2} = ks\Delta p\text{CO}_2, \quad (1)$$

where F_{CO_2} is the CO₂ flux and s is the CO₂ solubility in seawater, as a function of both temperature and salinity (Weiss, 1974). Atmospheric $p\text{CO}_2$ is directly measured in situ, using nondispersive infrared spectrometers deployed on buoys or ships, or values from monitoring stations in the global CO₂ 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 $p\text{CO}_2$ gradient. The vast majority of the surface $p\text{CO}_2$ measurements available are from automated, shipboard, underway systems, which analyze $p\text{CO}_2$ 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 $p\text{CO}_2$ 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 $p\text{CO}_2$ under most conditions, but significant near-surface vertical variability in $p\text{CO}_2$ 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 $p\text{CO}_2$, 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), $p\text{CO}_2$ 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 CO₂ fluxes in Arctic coastal waters by analyzing the CO₂ 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 $p\text{CO}_2$ 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 CO₂ system geochemistry throughout the bay.

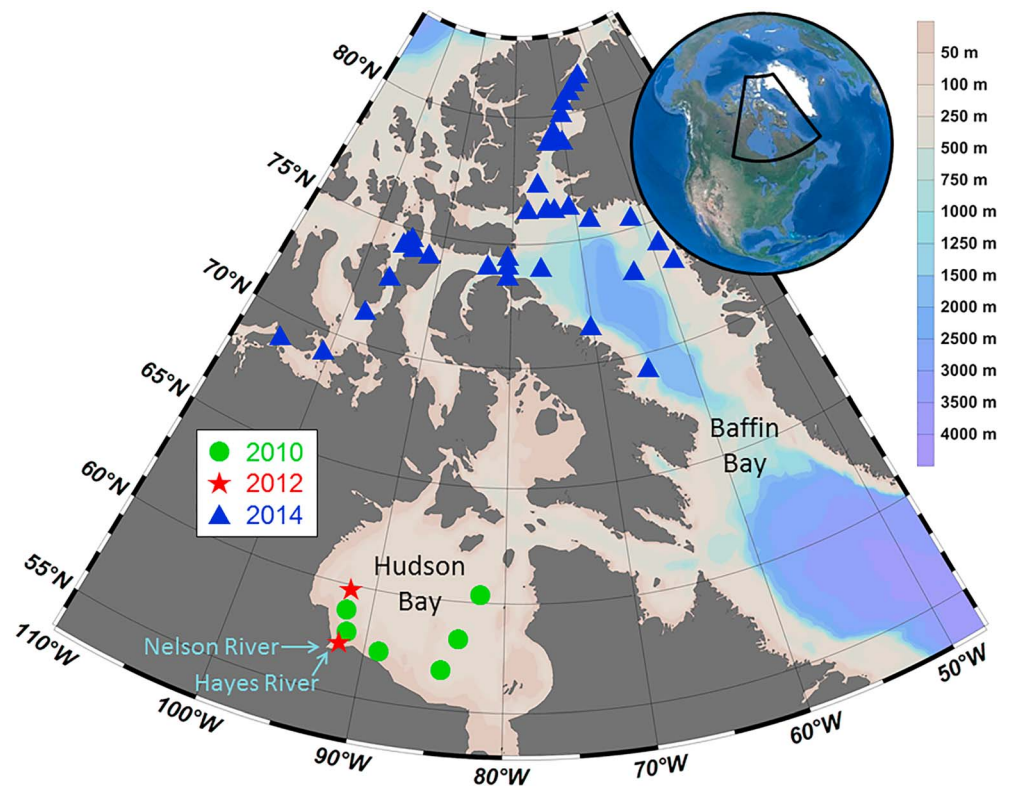


Figure 1. Surface sampling locations in Hudson Bay, Baffin Bay, and the waters of the Canadian Arctic Archipelago. See Table S1 for specific station locations and dates.

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 $p\text{CO}_2$ 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 $p\text{CO}_2$ 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,

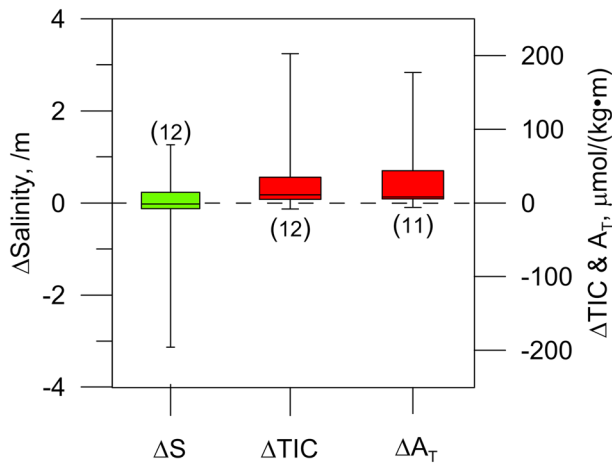


Figure 2. Vertical gradients in salinity, TIC, and A_T (differences at sampling depths, divided by the depth range) between samples collected from small boats versus the shallowest rosette bottle during all three expeditions. Boxes show medians and 25th and 75th quartiles, whiskers indicate maxima and 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 $p\text{CO}_2$ 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 Autosol 8400B). All of the bottle data, as well as the directly measured $p\text{CO}_2$ 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. $p\text{CO}_2$ and Flux Calculations

Across our data set, $p\text{CO}_2$ 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 $p\text{CO}_2$ 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 $p\text{CO}_2$ (LI-COR LI-7000) in air from an intake located on the bow meteorological tower. For 2012, atmospheric $p\text{CO}_2$ 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 $p\text{CO}_2$ in the surface waters we sampled (Figures 2 and 3), and the variations in $p\text{CO}_2$ with depth were often larger than the uncertainties due to the choice of CO_2 system stability constants used to calculate seawater $p\text{CO}_2$ in Arctic waters (approximately $6 \mu\text{atm}$; 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 $p\text{CO}_2$ with depth at most of the stations were less than $5 \mu\text{atm}$ (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 overlying a

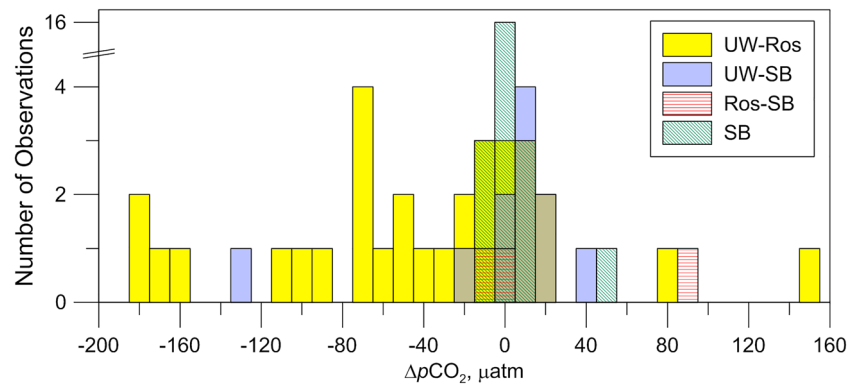


Figure 3. Histograms of observed near-surface vertical $p\text{CO}_2$ differences. UW: underway measurements from 7 m. Ros: shallowest rosette bottles at 1–3 m. SB: small boat samples from 0–5 m. Positive values indicate higher $p\text{CO}_2$ in deeper samples. With the exception of the UW-Ros pairs, all comparisons are between $p\text{CO}_2$ 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 $p\text{CO}_2$ 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 $p\text{CO}_2$ gradients (Table S3), indicating that $p\text{CO}_2$ 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 $p\text{CO}_2$ 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).

3.2. Impacts on Calculated Fluxes

A difference in $p\text{CO}_2$ 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 $p\text{CO}_2$ 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 $p\text{CO}_2$ 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 $p\text{CO}_2$ 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 $p\text{CO}_2$ are clustered toward 0 μatm , with some high values skewing the average. The relative

Table 1
Impact of Sampling Depth on Calculated Fluxes

	Underway-rosette	Underway-small boat ^a	Rosette-small boat ^a	Small boat ^a
<i>n</i>	30	5	3	6
<i>Absolute error^b, $\mu\text{mol}\cdot(\text{m}^{-2}\text{s}^{-1})$</i>				
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
<i>Relative error^c (%)</i>				
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).
^aComparisons only between samples for which $p\text{CO}_2$ was determined the same way: either measured directly or calculated from TIC and A_T in discrete samples. ^bAbsolute values of differences between paired samples at each station (i.e., the values here do not indicate the direction of the error). ^cAssuming that the shallowest sample is the most accurate.

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 CO₂ 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 CO₂ 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 CO₂ 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 CO₂ 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 CO₂, 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 pCO₂ estimates likely diminishes dramatically.

The differences we observed in the CO₂ 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 pCO₂ data should include higher error estimates to account for potential vertical pCO₂ 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 pCO₂. Nonetheless, it is clear that in order to accurately determine air-sea CO₂ exchanges and the net CO₂ 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 pCO₂ 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 CO₂ 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 CO₂ 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 CO₂ system sensor (for pCO₂ 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 pCO₂ 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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References

- Amundsen Science Data Collection (2010, 2014). CTD data collected by the CCGS Amundsen in the Canadian Arctic. Processed data. Version 1. ArcticNet Inc., Québec, Canada. Archived at www.polardata.ca, Canadian Cryospheric Information Network (CCIN), Waterloo, Canada. <https://doi.org/10.5884/12713>
- Anderson, L. G., Björk, G., Jutterström, S., Pipko, I., Shakhova, N., Semiletov, I., & Wählström, I. (2011). East Siberian Sea, an Arctic region of very high biogeochemical activity. *Biogeosciences*, 8, 1745–1754. <https://doi.org/10.5194/bg-8-1745-2011>
- Azetsu-Scott, K., Starr, M., Mei, Z.-P., & Granskog, M. (2014). Low calcium carbonate saturation state in an Arctic inland sea having large and varying fluvial inputs: The Hudson Bay system. *Journal of Geophysical Research: Oceans*, 119, 6210–6220. <https://doi.org/10.1002/2014JC009948>
- Bakker, D. C. E., Etcheto, J., Boutin, J., & Merlivat, L. (2001). Variability of surface water fCO₂ during seasonal upwelling in the equatorial Atlantic Ocean as observed by a drifting buoy. *Journal of Geophysical Research*, 106(C5), 9241–9253.
- Bakker, D. C. E., Pfeil, B., Landa, C. S., Metzl, N., O'Brien, K. M., Olsen, A., et al. (2016). A multi-decade record of high-quality fCO₂ data in version 3 of the Surface Ocean CO₂ Atlas (SOCAT). *Earth System Science Data*, 8(2), 383–413. <https://doi.org/10.5194/essd-8-383-2016>
- Blomquist, B. W., Huebert, B. J., Fairall, C. W., Bariteau, L., Edson, J. B., Hare, J. E., & McGillis, W. R. (2014). Advances in air-sea CO₂ flux measurement by eddy correlation. *Boundary-Layer Meteorology*, 152(3), 245–276. <https://doi.org/10.1007/s10546-014-9926-2>
- Burgers, T. M., Miller, L. A., Thomas, H., Else, B. G. T., Gosselin, M., & Papakyriakou, T. (2017). Surface water pCO₂ variations and sea-air CO₂ fluxes during summer in the eastern Canadian Arctic. *Journal of Geophysical Research: Oceans*, 122, 9663–9678. <https://doi.org/10.1002/2017JC013250>
- Burt, W. J., Thomas, H., Miller, L. A., Granskog, M. A., Papakyriakou, T. N., & Pengelly, L. (2016). Inorganic carbon cycling and biogeochemical processes in an Arctic inland sea (Hudson Bay). *Biogeosciences*, 13, 4659–4671. <https://doi.org/10.5194/bg-13-4659-2016>
- Butterworth, B. J., & Miller, S. D. (2016). Automated underway eddy covariance system for air-sea momentum, heat, and CO₂ fluxes in the Southern Ocean. *Journal of Atmospheric and Oceanic Technology*, 33(4), 635–652. <https://doi.org/10.1175/JTECH-D-15-0156.1>
- Cai, W.-J., Chen, L., Chen, B., Gao, Z., Lee, S. H., Chen, J., et al. (2010). Decrease in the CO₂ uptake capacity in an ice-free Arctic Ocean basin. *Science*, 329(5991), 556–559. <https://doi.org/10.1126/science.1189338>
- Calleja, M. L., Duarte, C. M., Álvarez, M., Vaquer-Sunyer, R., Agustí, S., & Herndl, G. J. (2013). Prevalence of strong vertical CO₂ and O₂ variability in the top meters of the ocean. *Global Biogeochemical Cycles*, 27, 941–949. <https://doi.org/10.1002/gbc.20081>
- Carignan, R. (1998). Automated determination of carbon dioxide, oxygen, and nitrogen partial pressures in surface waters. *Limnology and Oceanography*, 43(5), 969–975.
- Cross, J. N., Mordy, C. W., Tabisola, H. M., Meinig, C., Cokelet, E. D., & Stabeno, P. J. (2015). Innovative technology development for Arctic Exploration. In *Oceans 2015 - MTS/IEEE Washington* (pp. 1–8). Washington, DC: IEEE. <https://doi.org/10.23919/OCEANS.2015.7404632>
- Cullen, J. J. (2015). Subsurface chlorophyll maximum layers: Enduring enigma or mystery solved? *Annual Review of Marine Science*, 7(1), 207–239. <https://doi.org/10.1146/annurev-marine-010213-135111>
- Dai, A., Qian, T., Trenberth, K. E., & Milliman, J. D. (2009). Changes in continental freshwater discharge from 1948 to 2004. *Journal of Climate*, 22(10), 2773–2792. <https://doi.org/10.1175/2008JCLI2592.1>
- Déry, S. J., Stadnyk, T. A., MacDonald, M. K., & Gauli-Sharma, B. (2016). Recent trends and variability in river discharge across northern Canada. *Hydrology and Earth System Sciences*, 20(12), 4801–4818. <https://doi.org/10.5194/hess-20-4801-2016>
- Dickson, A. G. (1990). Standard potential of the reaction: AgCl(s) + 1/2H₂(g) = Ag(s) + HCl(aq), and the standard acidity constant of the ion HSO₄⁻ in synthetic sea water from 273.15 to 318.15 K. *Journal of Chemical Thermodynamics*, 22, 113–127.
- Dickson, A. G., Sabine, C. L., & Christian, J. R. (Eds.) (2007). *Guide to best practices for ocean CO₂ measurements*, ICES Special Publication 3. Sidney, BC: North Pacific Marine Science Organization.
- Dlugokencky, E. J., Lang, P. M., Mund, J. W., Crotwell, A. M., Crotwell, M. J., & Thoning, K. W. (2017). Atmospheric carbon dioxide dry air mole fractions from the NOAA ESRL carbon cycle cooperative global air sampling network, 1968–2016, version: 2017-07-28, (ftp://afpt.cmdl.noaa.gov/data/trace_gases/co2/flask/surface/)
- Else, B. G. T., Galley, R. J., Lansard, B., Barber, D. G., Brown, K., Miller, L. A., et al. (2013). Further observations of a decreasing atmospheric CO₂ uptake capacity in the Canada Basin (Arctic Ocean) due to sea ice loss. *Geophysical Research Letters*, 40, 1132–1137. <https://doi.org/10.1002/grl.50268>
- Else, B. G. T., Galley, R. J., Papakyriakou, T. N., Miller, L. A., Mucci, A., & Barber, D. (2012). Sea surface pCO₂ cycles and CO₂ fluxes at landfast sea ice edges in Amundsen Gulf, Canada. *Journal of Geophysical Research*, 117, C09010. <https://doi.org/10.1029/2012JC007901>
- Else, B. G. T., Papakyriakou, T. N., Galley, R. J., Mucci, A., Gosselin, M., Miller, L. A., et al. (2012). Annual cycles of pCO_{2sw} in the southeastern Beaufort Sea: New Understandings of air-sea CO₂ exchange in Arctic polynya regions. *Journal of Geophysical Research*, 117, C00G13. <https://doi.org/10.1029/2011JC007346>

- Else, B. G. T., Papakyriakou, T. N., Granskog, M. A., & Yackel, J. J. (2008). Observations of sea surface $f\text{CO}_2$ distributions and estimated air-sea CO_2 fluxes in the Hudson Bay region (Canada) during the open water season. *Journal of Geophysical Research*, *113*, C08026. <https://doi.org/10.1029/2007JC004389>
- Evans, W., Mathis, J. T., Cross, J. N., Bates, N. R., Frey, K. E., Else, B. G. T., et al. (2015). Sea-air CO_2 exchange in the western Arctic coastal ocean. *Global Biogeochemical Cycles*, *29*, 1190–1209. <https://doi.org/10.1002/2015GB005153>
- Fairall, C. W., Bradley, E. F., Hare, J. E., Grachev, A. A., & Edson, J. B. (2003). Bulk parameterization of air-sea fluxes: Updates and verification for the COARE algorithm. *Journal of Climate*, *16*, 571–591.
- Garbe, C. S., Rutgersson, A., Boutin, J., de Leeuw, G., Delille, B., Fairall, C. W., et al. (2014). Transfer across the air-sea interface. In P. S. Liss & M. T. Johnson (Eds.), *Ocean-atmosphere interactions of gases and particles* (pp. 55–112). New York: Springer. https://doi.org/10.1007/978-3-642-25643-1_2
- Geifuss, N.-X., Galley, R. J., Crabeck, O., Papakyriakou, T., Landy, J., Tison, J.-L., & Rysgaard, S. (2015). Inorganic carbon dynamics of melt pond-covered first year sea ice in the Canadian Arctic. *Biogeosciences*, *12*, 2047–2061. <https://doi.org/10.5194/bg-12-2047-2015>
- Geifuss, N.-X., Pind, M. L., Else, B. G. T., Galley, R. J., Miller, L. A., Thomas, H., et al. (2018). Spatial and temporal variability of seawater $p\text{CO}_2$ within the Canadian Arctic Archipelago and Baffin Bay during the summer and autumn 2011. *Continental Shelf Research*, *156*, 1–10. <https://doi.org/10.1016/j.csr.2018.01.006>
- Gong, H., Zhang, Z., Zhang, C., Liu, L., & Xing, L. (2007). Multilayer distribution of carbon dioxide system in surface water of the Yellow Sea in spring. *Chinese Journal of Oceanology and Limnology*, *25*(1), 1–15. <https://doi.org/10.1007/s00343-007-0001-4>
- Graves, C. A., Steinle, L., Rehder, G., Niemann, H., Connelly, D. P., Lowry, D., et al. (2015). Fluxes and fate of dissolved methane released at the seafloor at the landward limit of the gas hydrate stability zone offshore western Svalbard. *Journal of Geophysical Research: Oceans*, *120*, 6185–6201. <https://doi.org/10.1002/2015JC011084>
- Ingram, R. G., Bâcle, J., Barber, D. G., Gratton, Y., & Melling, H. (2002). An overview of physical processes in the North Water. *Deep Sea Research Part II: Topical Studies in Oceanography*, *49*, 4893–4906.
- Ingram, R. G., & Prinsenber, S. (1998). Coastal oceanography of Hudson Bay and surrounding eastern Canadian Arctic waters. In A. R. Robinson & K. H. Brink (Eds.), *The global coastal ocean: Regional studies and syntheses, the Sea* (Vol. 11, pp. 835–861). Toronto: John Wiley & Sons, Inc.
- Johnson, K. M., Wills, K. D., Butler, D. B., Johnson, W. K., & Wong, C. S. (1993). Coulometric total carbon dioxide analysis for marine studies: Maximizing the performance of an automated gas extraction system and coulometric detector. *Marine Chemistry*, *44*, 167–187.
- Kim, H.-C., Yamaguchi, H., Yoo, S., Zhu, J., Okamura, K., Kiyomoto, Y., et al. (2009). Distribution of Changjiang diluted water detected by satellite chlorophyll- a and its interannual variation during 1998–2007. *Journal of Oceanography*, *65*(1), 129–135. <https://doi.org/10.1007/s10872-009-0013-0>
- Knepp, T. N., Bottenheim, J., Carlsen, M., Carlson, D., Donohoue, D., Friederich, G., et al. (2010). Development of an autonomous sea ice tethered buoy for the study of ocean-atmosphere-sea ice-snow pack interactions: The O-buoy. *Atmospheric Measurement Techniques*, *3*(1), 249–261. <https://doi.org/10.5194/amt-3-249-2010>
- Krug, M., Swart, S., & Hermes, J. (2018). Ocean gliders ride the research wave in the Agulhas current. *EOS*, *99*. <https://doi.org/10.1029/2018EO100105>
- Land, P. E., Shutler, J. D., Cowling, R. D., Woolf, D. K., Walker, P., Findlay, H. S., et al. (2013). Climate change impacts on sea-air fluxes of CO_2 in three Arctic seas: A sensitivity study using Earth observation. *Biogeosciences*, *10*(12), 8109–8128. <https://doi.org/10.5194/bg-10-8109-2013>
- Lueker, T. J., Dickson, A. G., & Keeling, C. D. (2000). Ocean $p\text{CO}_2$ calculated from dissolved inorganic carbon, alkalinity, and equations for K_1 and K_2 : Validation based on laboratory measurements of CO_2 in gas and seawater at equilibrium. *Marine Chemistry*, *70*, 105–119.
- Macdonald, R. W., & Kuzik, Z. Z. A. (2011). The Hudson Bay system: A northern inland sea in transition. *Journal of Marine Systems*, *88*, 337–340. <https://doi.org/10.1016/j.jmarsys.2011.06.003>
- Martin, J., Tremblay, J.-É., Gagnon, J., Tremblay, G., Lapoussière, A., Jose, C., et al. (2010). Prevalence, structure and properties of subsurface chlorophyll maxima in Canadian Arctic waters. *Marine Ecology Progress Series*, *412*, 69–84. <https://doi.org/10.3354/meps08666>
- Mathis, J. T., Pickart, R. S., Byrne, R. H., McNeil, C. L., Moore, G. W. K., Juranek, L. W., et al. (2012). Storm-induced upwelling of high $p\text{CO}_2$ waters onto the continental shelf of the western Arctic Ocean and implications for carbonate mineral saturation states. *Geophysical Research Letters*, *39*, L07606. <https://doi.org/10.1029/2012GL01574>
- McLaughlin, F. A., Carmack, E. C., Ingram, R. G., Williams, W. J., & Michel, C. (2006). Oceanography of the northwest passage. In A. R. Robinson & K. H. Brink (Eds.), *The global coastal ocean: Interdisciplinary regional studies and syntheses, the Sea* (Vol. 14B, pp. 1213–1244). Cambridge, MA: Harvard University Press.
- Miller, L. A., Yager, P. L., Erickson, K. A., Amiel, D., Bâcle, J., Cochran, J. K., et al. (2002). Carbon distributions and fluxes in the North Water, 1998 and 1999. *Deep Sea Research Part II: Topical Studies in Oceanography*, *49*(22-23), 5151–5170. [https://doi.org/10.1016/S0967-0645\(02\)00183-2](https://doi.org/10.1016/S0967-0645(02)00183-2)
- Muller-Karger, F. E., McClain, C. R., & Richardson, P. L. (1988). The dispersal of the Amazon's water. *Nature*, *333*, 56–59.
- Mungall, E. L., Abbatt, J. P. D., Wentzell, J. J. B., Lee, A. K. Y., Thomas, J. L., Blaise, M., et al. (2017). Microlayer source of oxygenated volatile organic compounds in the summertime marine Arctic boundary layer. *Proceedings of the National Academy of Sciences of the USA*, *114*(24), 6203–6208. <https://doi.org/10.1073/pnas.1620571114>
- Murata, A., Shimada, K., Nishino, S., & Itoh, M. (2008). Distributions of surface water CO_2 and air-sea flux of CO_2 in coastal regions of the Canadian Beaufort Sea in late summer. *Biogeosciences Discussions*, *5*(6), 5093–5132.
- Pierrot, D., Lewis, E., & Wallace, D. W. R. (2006). *MS excel program developed for CO_2 system calculations*. ORNL/CDIAC-105a. Oak Ridge, Tennessee: Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U.S. Department of Energy. https://doi.org/10.3334/CDIAC/otg.CO2SYS_XLS_CDIAC105a
- Pierrot, D., Neill, C., Sullivan, K., Castle, R., Wanninkhof, R., Lüger, H., et al. (2009). Recommendations for autonomous underway $p\text{CO}_2$ measuring systems and data-reduction routines. *Deep Sea Research, Part II*, *56*(8-10), 512–522. <https://doi.org/10.1016/j.dsr2.2008.12.005>
- Polyakov, I. V., Proshutinsky, A. Y., & Johnson, M. A. (1999). Seasonal cycles in two regimes of Arctic climate. *Journal of Geophysical Research*, *104*(C11), 25,761–25,788. <https://doi.org/10.1029/1999JC900208>
- Rysgaard, S., Bendtsen, J., Delille, B., Dieckmann, G. S., Glud, R. N., Kennedy, H., et al. (2011). Sea ice contribution to the air-sea CO_2 exchange in the Arctic and Southern Oceans. *Tellus B*, *63*(5), 823–830. <https://doi.org/10.1111/j.1600-0889.2011.00571.x>
- Shadwick, E. H., Thomas, H., Chierici, M., Else, B., Fransson, A., Michel, C., et al. (2011). Seasonal variability of the inorganic carbon system in the Amundsen Gulf region of the southeastern Beaufort Sea. *Limnology and Oceanography*, *56*(1), 303–322. <https://doi.org/10.4319/lo.2011.56.1.0303>
- Smith, S. R., Bourassa, M. A., & Sharp, R. J. (1999). Establishing more truth in true winds. *Journal of Atmospheric and Oceanic Technology*, *16*(7), 939–952.

- Stull, R. B. (1988). *An introduction to boundary layer meteorology*. Dordrecht: Kluwer Academic Publishers.
- Sutton, A. J., Sabine, C. L., Maenner-Jones, S., Lawrence-Slavas, N., Meinig, C., Feely, R. A., et al. (2014). A high-frequency atmospheric and seawater $p\text{CO}_2$ data set from 14 open-ocean sites using a moored autonomous system. *Earth System Science Data*, 6(2), 353–366. <https://doi.org/10.5194/essd-6-353-2014>
- Takahashi, T., Olafsson, J., Goddard, J. G., Chipman, D. W., & Sutherland, S. C. (1993). Seasonal variation of CO_2 and nutrients in the high-latitude surface oceans: A comparative study. *Global Biogeochemical Cycles*, 7(4), 843–878.
- Tank, S. E., Raymond, P. A., Striegl, R. G., McClelland, J. W., Holmes, R. M., Fiske, G. J., & Peterson, B. J. (2012). A land-to-ocean perspective on the magnitude, source and implication of DIC flux from major Arctic rivers to the Arctic Ocean. *Global Biogeochemical Cycles*, 26, GB4018. <https://doi.org/10.1029/2011GB004192>
- Telang, S. A., Pocklington, R., Naidu, A. S., Romankevich, E. A., Gitelson, I. I., & Gladyshev, M. I. (1991). Carbon and mineral transport in major North American, Russian Arctic, and Siberian rivers: The St Lawrence, the Mackenzie, the Yukon, the Arctic Alaskan rivers, the Arctic basin rivers in the Soviet Union, and the Yenisei. In E. T. Degens, S. Kempe, & J. E. Richey (Eds.), *Biogeochemistry of major world rivers, SCOPE* (Vol. 42, pp. 75–104). Toronto: John Wiley & Sons.
- Wanninkhof, R. (2014). Relationship between wind speed and gas exchange over the ocean revisited. *Limnology and Oceanography: Methods*, 12, 351–362. <https://doi.org/10.4319/lom.2014.12.351>
- Wanninkhof, R., & Knox, M. (1996). Chemical enhancement of CO_2 exchange in natural waters. *Limnology and Oceanography*, 41(4), 689–697.
- Ward, B., Wanninkhof, R., McGillis, W. R., Jessup, A. T., DeGrandpre, M. D., Hare, J. E., & Edson, J. B. (2004). Biases in the air-sea flux of CO_2 resulting from ocean surface temperature gradients. *Journal of Geophysical Research*, 109, C08S08. <https://doi.org/10.1029/2003JC001800>
- Weiss, R. F. (1974). Carbon dioxide in water and seawater: The solubility of a non-ideal gas. *Marine Chemistry*, 2, 203–215.
- Williams, W. J., & Carmack, E. C. (2015). The 'interior' shelves of the Arctic Ocean: Physical oceanographic setting, climatology and effects of sea-ice retreat on cross-shelf exchange. *Progress in Oceanography*, 139, 24–41. <https://doi.org/10.1016/j.pocean.2015.07.008>
- Woolf, D. K., Land, P. E., Shutler, J. D., Goddijn-Murphy, L. M., & Donlon, C. J. (2016). On the calculation of air-sea fluxes of CO_2 in the presence of temperature and salinity gradients. *Journal of Geophysical Research: Oceans*, 121, 1229–1248. <https://doi.org/10.1002/2015JC011427>
- Woosley, R. J., Millero, F. J., & Takahashi, T. (2017). Internal consistency of the inorganic carbon system in the Arctic Ocean. *Limnology and Oceanography: Methods*, 15(10), 887–896. <https://doi.org/10.1002/lom3.10208>
- Yamamoto-Kawai, M., McLaughlin, F. A., Carmack, E. C., Nishino, S., Shimada, K., & Kurita, N. (2009). Surface freshening of the Canada Basin, 2003–2007: River runoff versus sea ice meltwater. *Journal of Geophysical Research*, 114, C00A05. <https://doi.org/10.1029/2008JC005000>
- Yasunaka, S., Siswanto, E., Olsen, A., Hoppema, M., Watanabe, E., Fransson, A., et al. (2018). Arctic Ocean CO_2 uptake: An improved multiyear estimate of the air-sea CO_2 flux incorporating chlorophyll *a* concentrations. *Biogeosciences*, 15(6), 1643–1661. <https://doi.org/10.5194/bg-15-1643-2018>