

Response to Reviewer 2

Reviewer comments in black.

Author responses in blue.

New manuscript text in red.

Reviewer 2 Comments

The interactions among air, water, and ice have long been recognized as critical for accurately estimating gas fluxes in polar oceans. However, measuring CO₂ fluxes in natural sea-ice-covered regions remains extremely challenging, particularly due to the logistical difficulties of conducting long-term eddy covariance (EC) observations in such environments. This study presents 17-month EC measurements of air-sea CO₂ fluxes in a coastal, ice-covered setting, which is a significant contribution to the field. The dataset clearly captures the temporal variability of CO₂ fluxes across multiple timescales. Notably, the identification of CO₂ outgassing associated with ice formation is a novel and important finding that could have substantial implications for refining estimates of the polar ocean carbon sink.

The manuscript is well written, the results are clearly presented, and the conclusions are scientifically sound. I believe the paper is suitable for publication after addressing the following minor comments.

PS, the comments from the other reviewer is referred.

We would like to thank Dr. Dong for his comments. We have incorporated his suggestions to further develop the description of our Kice analysis and add an F_{CO₂} uncertainty analysis. We also appreciate the minor comments pointing out things we missed and the suggestions to improve the readability of the manuscript.

Minor comments,

Lines 45–50: I suggest including the recent study by Prytherch and Yelland (2021), which is a dedicated investigation of the influence of sea ice on CO₂ exchange:
<https://doi.org/10.1029/2020GB006633> . While it is cited in line 89, it appears to be missing from the bibliography.

Removed:

However, both of these examples derived their estimates based on very few actual measurements of CO₂ exchange in these challenging environments.

Added:

More recently, Prytherch and Yelland (2021) used eddy covariance measurements near a central Arctic Ocean lead to develop a lead-specific gas transfer velocity parameterization during the

summer to fall transition period. Additionally, summertime ship-based Arctic eddy covariance measurements by Dong et al. (2021) showed that surface stratification of fresher, cooler melt water resulted in lower surface $p\text{CO}_{2w}$ compared to 6-m deep $p\text{CO}_{2w}$, with resulting implications for estimating carbon budgets of polar oceans. While these efforts identify specific processes, more measurements are required to quantify additional gas exchange processes over the annual cycle, as well as validate previous findings.

Added the following to the bibliography:

Prytherch, J., and Yelland, M. J.: Wind, Convection and Fetch Dependence of Gas Transfer Velocity in an Arctic Sea-Ice Lead Determined From Eddy Covariance CO_2 Flux Measurements, *Global Biogeochem. Cycles*, 35, <https://doi.org/10.1029/2020GB006633>, 2021.

Line 125: It appears that a LI-COR 7500 sensor is installed on the tower, but LICOR7200 does not appear. I see in you 2018 paper, the LI-COR 7500 was used to measure water vapor and CO_2 was measured by LICOR7200? Could you clarify here?

If you're referring to Figure 2 in Butterworth and Else (2018), yes, the LI-7500 appears more prominently in the photograph. But the LI-7200 is also in that figure in Panel A, just a few feet down from the anemometer mounted inside the frame of the tower. Both were operational throughout the measurement campaign presented in the current manuscript. The reason for using the 7500 for H_L was so that tube attenuation would not alter the measurement (as H_2O is sticky when in contact with tube walls). The 7200 was for CO_2 flux because we needed to dry the airstream prior to measuring the CO_2 mixing ratio in order to avoid contamination of the flux measurement due to the overlapping absorption with water vapor.

Line 180: It would be helpful to provide more explanation of the Kice term, specifically, how it was derived or constrained.

We modified the paragraph on Kice to include more information.

Changed from the original:

In the laboratory tank sea ice study of Kotovitch et al. (2016) measurements of F_{CO_2} , $p\text{CO}_{2\text{air}}$, and $p\text{CO}_{2\text{ice}}$ were used to determine K_{ice} – a parameter that encapsulates both the gas transfer velocity and solubility of CO_2 in ice. Here, we estimate $p\text{CO}_{2\text{ice}}$ during periods of full ice cover by setting our measured F_{CO_2} equal to the equation

$$F_{\text{CO}_2} = K_{\text{ice}} [p\text{CO}_{2\text{ice}} - p\text{CO}_{2\text{air}}], \quad (2)$$

where K_{ice} was the gas transfer velocity for ice growth and decay (2.5 and $0.4 \text{ mol m}^{-2} \text{ d}^{-1} \text{ atm}^{-1}$ respectively) found by Kotovitch et al. (2016).

To:

In the laboratory study of Kotovitch et al. (2016), F_{CO_2} was measured in a tank over periods of forming, thickening, and melting sea ice. Supporting measurements of pCO_{2air} and pCO_{2ice} enabled the derivation of a gas transfer coefficient (K_{ice}) using the following bulk formula:

$$F_{CO_2} = K_{ice} [pCO_{2ice} - pCO_{2air}]. \quad (2)$$

The K_{ice} parameter encapsulated both the gas transfer velocity and solubility of CO_2 in ice. This was done to avoid estimating solubility using seawater-based functions of temperature and salinity outside the range for values for which they were designed. K_{ice} during periods of ice growth was $2.5 \text{ mol m}^{-2} \text{ d}^{-1} \text{ atm}^{-1}$, while for periods of ice decay it was $0.4 \text{ mol m}^{-2} \text{ d}^{-1} \text{ atm}^{-1}$ (Kotovitch et al. 2016).

Because we did not collect in situ pCO_{2ice} measurements we could not use Eq. (2) to calculate K_{ice} for independent verification. Instead, we estimated pCO_{2ice} during periods of full ice cover using Eq. (2) with measured F_{CO_2} and pCO_{2air} and the K_{ice} values for ice growth and decay found by Kotovitch et al. (2016). Comparisons of estimated pCO_{2ice} to previous in situ measurements were used to determine if the laboratory-derived K_{ice} values were applicable in field conditions.

Figure 3: Could you include information about wind direction? It seems that some flux data may be missing due to winds coming from the direction of the island?

We added 2 new panels (third row) to show wind direction, as well as the range (shaded area) in which flux measurements are discarded due to winds from aft.

Figure 4: The high-frequency time series is 6-hour averaged. Readers may be interested in the extent to which the observed variability is influenced by EC uncertainty. Could you provide at least a simple estimate of the uncertainty magnitude, include that value in the figure caption, and briefly discuss it in the main text?

Added the following text:

As the product of measurements from different instruments, the accuracy of the F_{CO_2} measurement is challenging to quantify without an independent validation, which was not performed. The LI-7200 has a measurement accuracy of $\pm 1\%$ with an RMS noise of 0.11 ppm at 10 Hz, while the vertical wind speed of the CSAT3 is accurate within $\pm 0.04 \text{ m s}^{-1}$ with an RMS noise of 0.0005 m s^{-1} . While the noise can occasionally be larger than the true environmental fluctuations, it has been found to minimally influence the calculated F_{CO_2} because the noise from the separate instruments is uncorrelated and therefore filtered out by the flux calculation (Miller et al., 2010).

An investigation of F_{CO_2} measurement uncertainties from ships indicated a detection limit for a dried, closed-path eddy covariance system of roughly $|\Delta pCO_2| > 35 \text{ } \mu\text{atm}$ for the mean wind speed observed in this study (Blomquist et al., 2014). The ΔpCO_2 in the region often exceeds this value (Duke et al., 2021; Sims et al., 2023). Additionally, we expect some reduction in the

detection limit (i.e., increased sensitivity) for this study compared to ship-based studies, because the measurements were from a stationary tower. Therefore, the observations avoid some common sources of uncertainty experienced from moving platforms, such as the needed for a complex wind vector motion correction and tilt effects that degrade the performance of the LI-7200 (Miller et al., 2010; Vandemark et al., 2023).

While we cannot perform a direct assessment of F_{CO_2} uncertainty, we can estimate the order of magnitude of the uncertainty by assessing the variation in F_{CO_2} measurements during periods expected to have stable fluxes. Here we do that by calculating the standard deviation for 6-hour intervals during periods of full ice cover, when diurnal variations in F_{CO_2} were expected to be minimal. The standard deviation across these winter periods had a mean of $\pm 1.02 \text{ mmol m}^{-2} \text{ d}^{-1}$ and a median of $\pm 0.75 \text{ mmol m}^{-2} \text{ d}^{-1}$. Spring and summer seasons were excluded from the estimate because standard deviation measured during those periods was expected to be a combination of measurement uncertainty and actual diurnal F_{CO_2} trends.

Added the following text to the Fig. 4 caption:

Uncertainty in the F_{CO_2} measurement was quantified by calculating the standard deviation from each 6-hour average (comprised of eighteen 20-minute flux intervals) during periods of full ice cover, when diurnal F_{CO_2} variations were minimal. The standard deviations across these winter periods had a mean of $\pm 1.02 \text{ mmol m}^{-2} \text{ d}^{-1}$ and a median of $\pm 0.75 \text{ mmol m}^{-2} \text{ d}^{-1}$.

Added the following reference to the bibliography:

Vandemark, D., Emond, M., Miller, S. D., Shellito, S., Bogoev, I., and Covert, J. M.: A CO_2 and H_2O Gas Analyzer with Reduced Error due to Platform Motion. *J Atmos Ocean Technol*, 40, 845–854. doi: 10.1175/JTECH-D-22-0131.1, 2023

Figure 5: I agree with the other reviewer that the possibility of pCO_{2ice} being negative should be explained. I suspect the derived values may be sensitive to the estimation of K_{ice} . While some discussion is included later in the manuscript, it would be helpful to provide an earlier explanation, perhaps around line 185.

Added the following in the Spring Discussion section:

However, it is worth noting that pCO_{2ice} (Fig. 5c) occasionally dropped below zero, which is a physically impossible value. Such instances may indicate that the K_{ice} value used to calculate pCO_{2ice} was too small. Because K_{ice} combines both gas transfer velocity and solubility, inaccuracies in either term could be responsible. However, it is also possible that the negative values of pCO_{2ice} are simply due to the random error inherent in eddy covariance systems. Because random error can cause both positive and negative deviations in measured flux, these data points were retained to avoid biasing the average.

Additional information about the estimation of K_{ice} was provided in Section 2.3.2. Those changes are shown above in response to the comment about Line 180 above.

Line 275: You mention that camera images were collected, but none are shown in the paper, which is a shame. Would it be possible to include several representative images from different stages of the observation period? These could be placed alongside Table 1 or included in the supplementary material.

Figure 2 was already included. It shows exactly what you are requesting.

Line 333: For your reference, we have conducted a related study using eddy covariance and $p\text{CO}_2\text{w}$ measurements in an ice melt region, which indicates substantial CO_2 uptake: Dong et al. (2021), Geophysical Research Letters, <https://doi.org/10.1029/2021GL095266>.

Thank you for pointing us to this manuscript. It is relevant to our Introduction. We have added the following text:

Additionally, summertime ship-based Arctic eddy covariance measurements by Dong et al. (2021) showed that surface stratification of fresher, cooler melt water resulted in lower surface $p\text{CO}_{2\text{w}}$ compared to 6-m deep $p\text{CO}_{2\text{w}}$, with resulting implications for estimating carbon budgets of polar oceans.

Added the following to the bibliography:

Dong, Y., Yang, M., Bakker, D. C. E., Liss, P. S., Kitidis, V., Brown, I., Chierici, M., Fransson, A., and Bell, T. G.: Near-Surface Stratification Due to Ice Melt Biases Arctic Air-Sea CO_2 Flux Estimates, *Geophys. Res. Lett.*, 48, <https://doi.org/10.1029/2021GL095266>, 2021.

Line 370: The first sentence in this paragraph reads awkwardly to me. Please consider rephrasing for improved clarity and flow.

Rephrased from the original:

Figure 8 shows the seasonal temperature dependence of F_{CO_2} on water temperature.

To:

Figure 8 shows the F_{CO_2} dependence on water temperature as it varies across seasons.

Line 533: The square brackets around the reference should be removed to maintain consistency with the formatting style.

Most style guides recommend using square brackets within parentheses when nesting parenthetical information. There was no reference to the subject in the Copernicus Style Guide. Therefore, we would prefer to leave them as they are, to differentiate the levels of information being presented within the parentheses.

Line 569: The abbreviation “EC” appears here without prior definition.

Changed “EC” to “eddy covariance”

Conclusions: The comparison with Sims et al. (2023) is valuable, but might be more impactful if introduced earlier in the discussion section. As currently presented, it reads more like a discussion point than a concluding remark.

Moved Sims et al. (2023) discussion from Conclusions to Process Summary section, and added additional text. It now reads:

“The direction of fluxes that we measured across the annual cycle were in general agreement with $\Delta p\text{CO}_2$ gradients measured by Sims et al. (2023) within a ~100 km radius of the flux station. Sims et al. (2023) did note substantial spatial variability, which makes it difficult to confidently extrapolate the net annual flux over a larger area. However, an estimate of k calculated using tower F_{CO_2} and ship-based $p\text{CO}_{2\text{w}}$ measurements of Sims et al. (2023) during temporally-aligned courses past the island showed good agreement with existing open-water k parameterizations, providing evidence the capability of the tower-based F_{CO_2} for estimating $p\text{CO}_{2\text{w}}$ (Butterworth and Else, 2018).”

Final suggestion: It may strengthen the conclusions if you emphasize that concurrent measurements of $p\text{CO}_{2\text{w}}$ would provide more robust support for some of the interpretations presented in this study.

Added:

Future research from this site may be able to highlight the magnitude of individual processes with greater precision. Due to its relevance to the F_{CO_2} cycle, direct measurements of $p\text{CO}_{2\text{w}}$ were collected at the site during subsequent years. These were made possible by the installation of a mobile power station/research lab (with sleeping quarters), installed on the island in 2018. These measurements will be incorporated into future research investigating CO_2 gas transfer velocity continuously through the annual cycle.

-Yuanxu Dong

Added to the Acknowledgements:

We would also like to thank Yuanxu Dong and one anonymous reviewer for their constructive reviews.