River inflow dominates methane emissions in an Arctic coastal system

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Key Points:

- Methane concentrations in an Arctic estuary show strong seasonality; elevated concentrations are associated with early freshet river inflow
- Observations with a novel robotic kayak demonstrate that methane and carbon dioxide in the estuary are rapidly ventilated following ice melt
- River discharge is estimated to account for >95% of annual methane emissions from the estuary

Abstract

Measurements of greenhouse gases in Arctic waters are strongly biased toward low-ice summer conditions, with few observations during periods of seasonal ice retreat. We present a year-round time series of dissolved methane (CH_4) and nitrous oxide (N_2O), along with targeted observations during ice melt of CH_4 and carbon dioxide (CO_2) in a river and estuary adjacent to Cambridge Bay, Nunavut, Canada. CH_4 displayed dramatic seasonality, in contrast to limited seasonal changes in N_2O. During the river freshet, CH_4 concentrations in the river and ice-covered estuary were up to 240,000% saturation and 19,000% saturation, respectively, but quickly dropped by >100-fold following ice melt. Observations with a robotic kayak revealed that river-derived CH_4 and CO_2 were transported to the estuary and rapidly ventilated to the atmosphere once ice cover retreated. We estimate that river discharge accounts for >95% of annual CH_4 sea-to-air emissions from the estuary.

Plain Language Summary

The primary cause of recent global climate change is increasing concentrations of heat-trapping greenhouse gases in the atmosphere. Ongoing rapid Arctic climate change is affecting the annual cycle of sea ice formation and retreat, however most published studies of greenhouse gases in Arctic waters have been conducted during ice-free, summertime conditions. In order to characterize seasonal variability in greenhouse gas distributions, we collected year-round measurements of the greenhouse gases methane (CH_4) and nitrous oxide (N_2O) in a coastal Arctic system near Cambridge Bay, Nunavut, Canada. We found that during the ice melt season, river water contains methane concentrations up to 2000 times higher than the wintertime methane concentrations in the coastal ocean. We utilized a novel robotic kayak to conduct high-resolution mapping of greenhouse gas distributions during ice melt. From these data, we demonstrate that the river water containing elevated levels of methane and carbon dioxide (CO_2) flowed into the coastal ocean, and when ice cover melted, these greenhouse gases were rapidly emitted into the atmosphere. We estimate that in this system more than 95% of all annual methane emissions from the coastal ocean are driven by river inflow.

1 Introduction

Methane (CH_4) emissions from Arctic waters and sediments may accelerate in the future as part of positive feedback from ongoing climate change (Biastoch et al., 2011; James et al., 2016; Shakhova et al., 2010). Landscapes that were once permanently frozen are now seasonally thawing, and the ice-free season is lengthening in freshwater and marine systems (Magnuson, 2000; Stroeve et al., 2012; Zona et al., 2016). Thawing can result in the mobilization of labile organic matter and emissions of greenhouse gases such as carbon dioxide (CO_2), methane (CH_4), and nitrous oxide (N_2O) (Karlsson et al., 2013; Kvenvolden et al., 1993; Lamarche-Gagnon et al., 2019; Voigt et al., 2017; Zona et al., 2016). Studies of terrestrial and freshwater Arctic systems have demonstrated strong temporal variability in greenhouse gas emissions in these environments (Denfeld et al., 2018; Karlsson et al., 2013; Lamarche-Gagnon et al., 2019; Phelps et al., 1998; Voigt et al., 2017; Zona et al., 2016), yet published measurements in Arctic marine and estuarine waters are strongly biased toward summertime, low-ice conditions (Fenwick et al., 2017; Shakhova et al., 2010).

Ice acts as a barrier to gas exchange, sustaining strong disequilibria in gas concentrations between the atmosphere and ice-covered waters (Butterworth & Miller, 2016; Denfeld et al., 2018; Karlsson et al., 2013; Wand et al., 2006). Rapid re-equilibration of the mixed layer can occur following ice melt. Quantifying the impacts of sea ice loss on Arctic greenhouse gas emissions requires seasonally-resolved measurements; yet few measurements of dissolved CH_4 or other greenhouse gases are available in ice-covered or recently ice-liberated Arctic Ocean waters and connected estuaries. Here we present new observations that address this critical observational gap, demonstrating that the vast majority of annual CH_4 release in an Arctic estuary occurs during the ice melt period.

2 Observations, Results, and Discussion

2.1 Field observations

To quantify the annual sea-air emissions of greenhouse gases in a coastal Arctic system, we collected measurements in a well-sheltered bay with two inlets (west arm and east arm, Figure 1a) adjacent to the town of Cambridge Bay (Iqaluktuuttiaq), Nunavut, Canada. Surface waters are seasonally ice covered, and the dominant freshwater source is Freshwater Creek, which discharges water into the east arm of Cambridge Bay from Greiner Lake and the associated watershed. Terrestrial snowmelt in this region typically begins in late May (Tedesco et al., 2009), and as a result, Freshwater Creek begins to flow before significant sea ice melt has occurred. This freshwater discharge causes the rapid melt of sea ice along the east arm, creating open water in June (Figure 1b), with the rest of the bay typically becoming ice-free 2–3 weeks later, in late June to early July. During 2017 and 2018, we collected a time-series of dissolved CH_4 and nitrous oxide (N_2O) measurements in the estuary and river (Figures 1 and S1). Additionally, in 2018, we used a remotely operated robotic kayak, the ChemYak (Kimball et al., 2014; Nicholson et al., 2018), to characterize fine-scale spatiotemporal changes in dissolved CH_4 and carbon dioxide (CO_2) in the estuary during peak river inflow (Figures 2–3), and collected water samples from Greiner Lake. Methodological details for bottle samples and the ChemYak are provided in the Supporting Information.

During winter and spring (January–May) in 2017 and 2018, CH_4 concentrations throughout the estuary water column (station B1 in Fig. 1b) were closely distributed around the atmospheric equilibrium of 4 nM (range 3–10 nM). In early June, river discharge from the spring thaw began to enter the estuary, and elevated CH_4 concentrations up to 860 nM (19,000% saturation) were measured in near-surface waters of Cambridge Bay (2 m below the surface of the ice). A water mass analysis using salinity and water isotope data from station B1 confirmed that the elevated CH_4 concentrations were associated with river runoff rather than ice melt (Figure S2 and Text S1). Ice-free summer surface waters sampled in July 2017 and 2018 had much lower CH_4 concentrations, ranging from 4–65 nM.

From 28 June to 2 July 2018, we used the ChemYak for high-resolution spatial mapping and vertical profiling of CH_4, CO_2, salinity, and temperature distributions in a ~1 km^2 open water area between the river mouth and the ice edge during the dynamic melt period (Figures 2, 3 and S3–S6). These ChemYak measurements confirmed elevated greenhouse gas concentrations in river-derived estuary water. The river-derived water occurred throughout the study area as a

shallow, fresh surface mixed layer (<2 m depth), separated from deeper waters by a sharp pycnocline (Figure 2 f-g). During the ChemYak measurement period, CH_4 concentrations in the surface water decreased as the water flowed from the river toward the coastal ocean, suggesting a rapid ventilation within the estuary. For example, the CH_4 concentration in Freshwater Creek decreased from 560±10 nM on 27 June to 290±20 nM by 3 July, whereas CH_4 at station B1 was 130±10 nM on 3 July (Figure 4b). In the ChemYak sampling area (between Freshwater Creek and station B1), on 28 June, CH_4 and CO_2 concentrations in the upper 1 m of the water column were up to 470 nM and 1470 µatm, respectively (mean 410±20 nM and 1340±40 µatm). Concentrations in the upper 1 m decreased over the campaign to 150±70 nM CH_4 and 600±150 µatm CO_2 by 2 July (Figures 3 and S6).

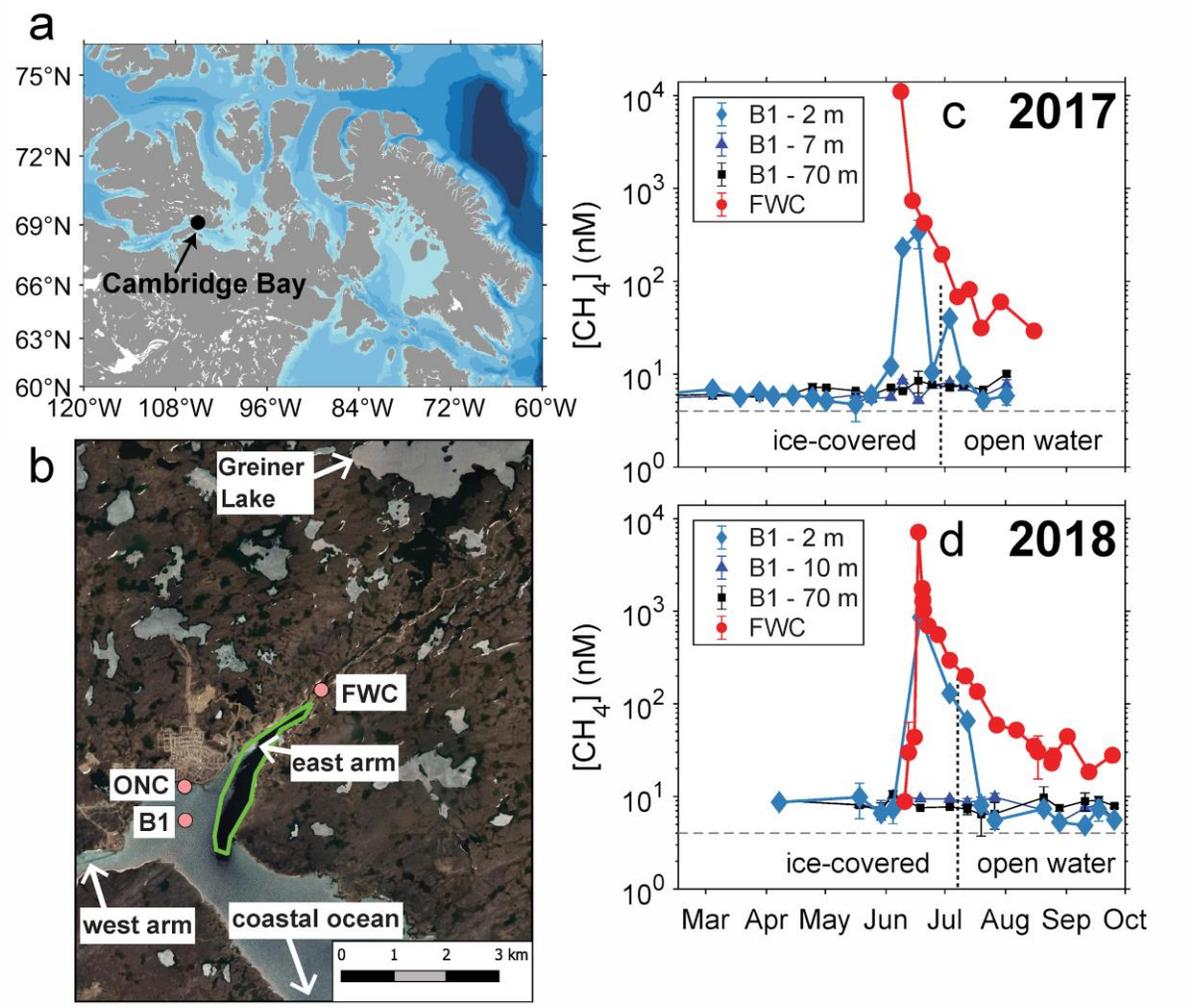

Figure 1. Map of study site and time-series data. **a** Map of eastern Canadian Arctic showing the location of Cambridge Bay. **b** Satellite image of study area on 21 June 2017 (obtained by Google, DigitalGlobe). Pink circles indicate the locations of the main sampling stations FWC (Freshwater Creek) and B1, as well as ONC (Ocean Networks Canada observatory with ice profiler). The approximate region where the ChemYak was deployed is shown with a green outline. Time-series of CH_4 concentrations in Cambridge Bay estuary and Freshwater Creek in **c** 2017 and **d** 2018. Surface samples in Cambridge Bay were collected at 2 m depth below the ice surface, or 0.75 m below the open water surface. The dashed horizontal line represents atmospheric equilibrium and the dashed vertical line indicates when sampling station B1 became ice-free. Error bars reflect the standard deviation of duplicate measurements.

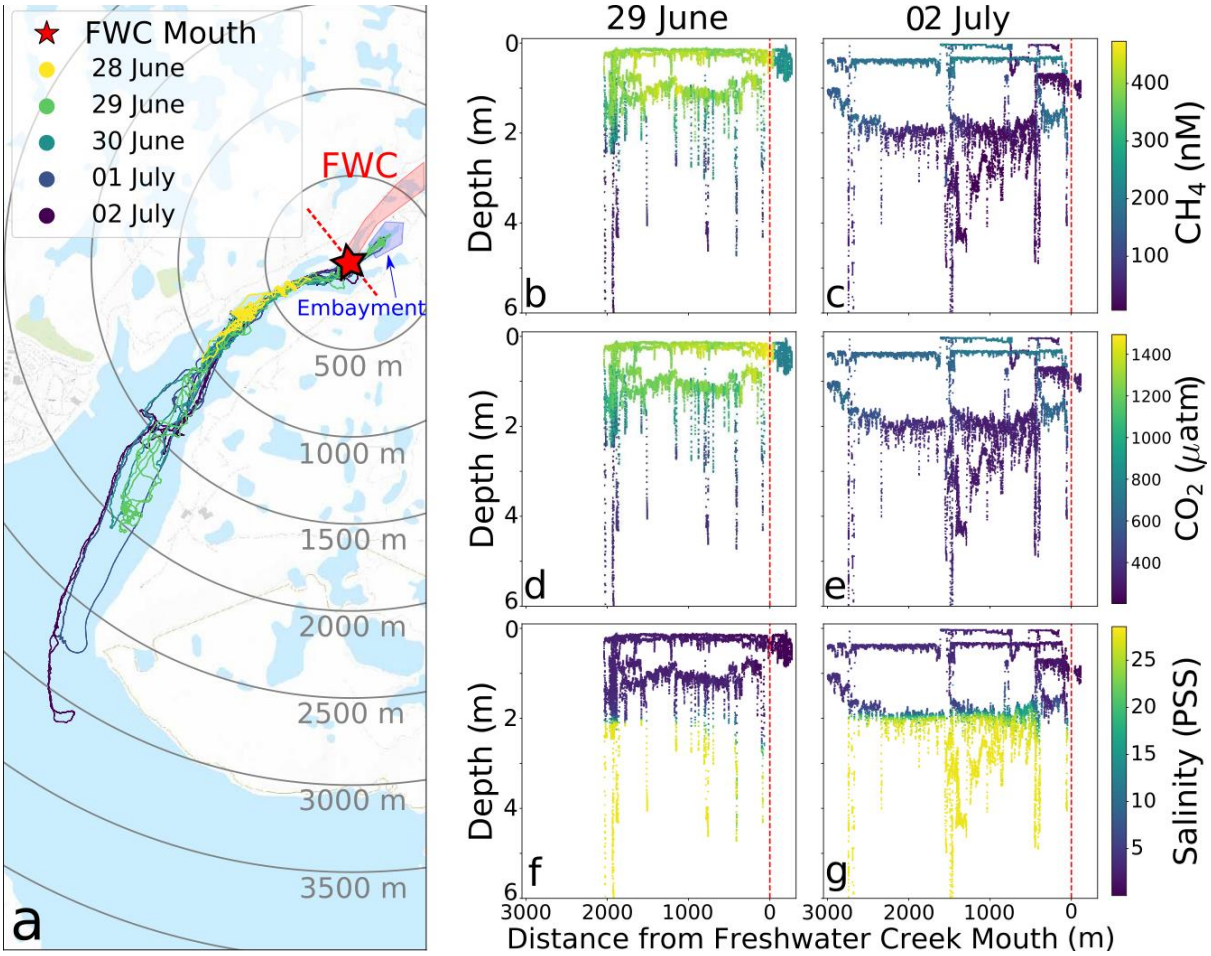

Figure 2. Spatial observations made by the ChemYak vehicle. **a** The study site with ChemYak trajectories from each day overlaid. The mouth of Freshwater Creek (69.1257 ^{o}N, 105.0042 ^{o}W) is marked with a star, and concentric rings at increments of 500 m centered at the mouth are provided for scale. Northeast of the red dashed line lies Freshwater Creek (red arrow and box) and a small embayment (blue label and box) which receives input from a much smaller river. **b-g** Observations made by the ChemYak for two representative days, 29 June and 2 July, are plotted by depth versus distance from the Freshwater Creek mouth. Negative distances (to the right of the axis) represent points northeast of the mouth (a small embayment) and positive distance (to the left of the axis) represent points southwest of the mouth (downstream). As indicated by the salinity plots (**f-g**), the mixed layer depth is <2 m throughout the study area, and the fresh surface layer was generally higher in both CH_4 and CO_2 concentration than layers deeper than 2 m. The gas concentrations decreased over the multi-day measurement campaign. Equivalent plots and temperature data for the other measurement days are shown in Figure S5.

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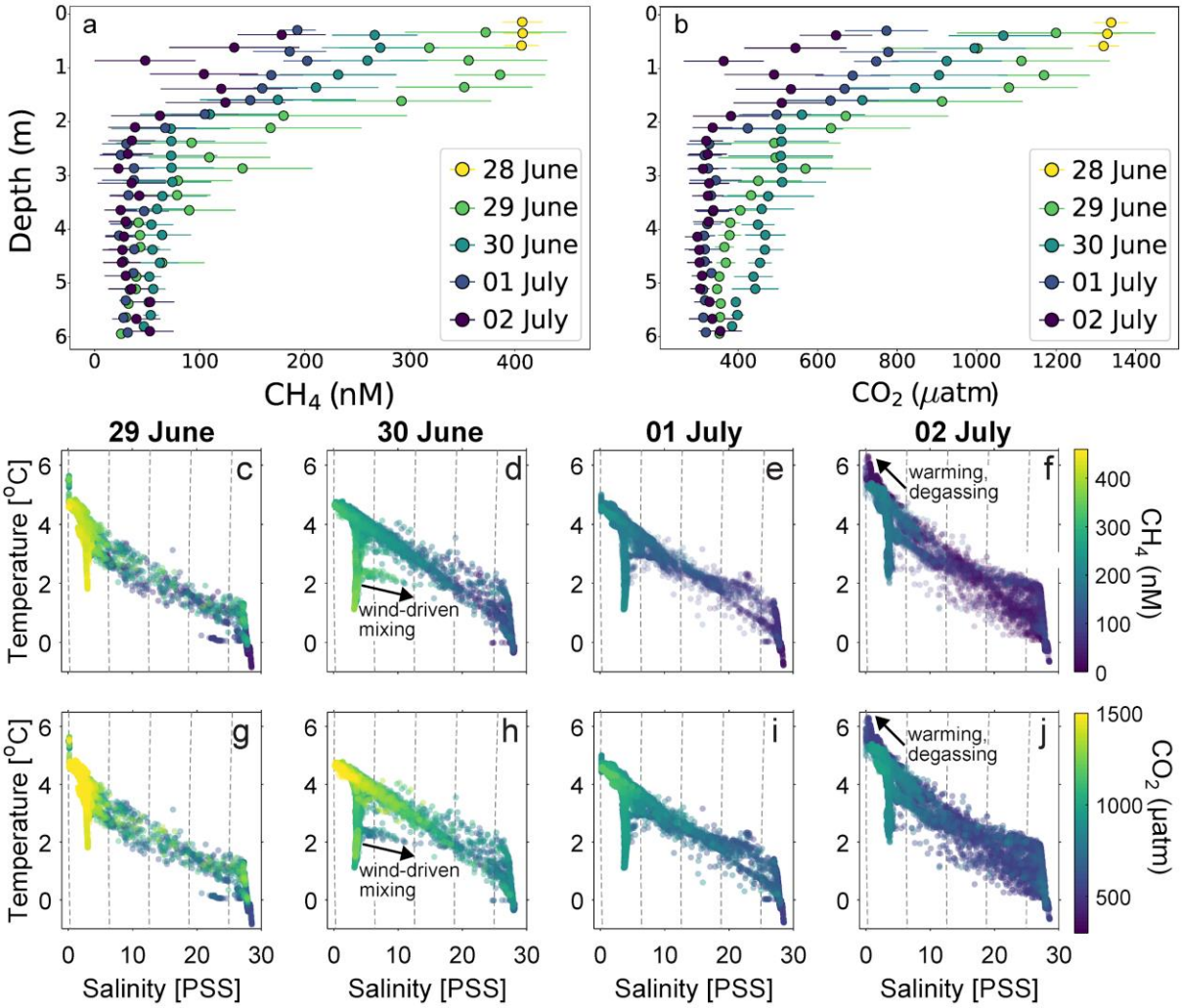

Figure 3. Spatial and temporal trends observed by the ChemYak. **a-b** Each day of the measurement campaign is marked with a unique color, and samples collected are binned into 0.25 m increments from the surface to 6 m. Both CH_4 (**a**) and CO_2 (**b**) exhibit decreasing trends for each subsequent day, and there is strong stratification between the surface layer and water below 2 m. Error bars represent the standard deviation of measurements for each depth bin. **c-j** Temperature-salinity plots showing changes in CH_4 (**c-f**) and CO_2 (**g-j**) concentrations and water mass distributions over the time-series.

In the estuary, at depths below the mixed layer (>2 m depth), CH_4 and CO_2 concentrations decreased from 29 June to 2 July. Elevated wind speeds (up to 10 m s^{-1}) appear to have enhanced mixing across the sharp pycnocline on 30 June (Figures 3d, 3h, S5, and S6). On 30 June, the depth of the pycnocline shoaled and CH_4 and CO_2 concentrations below the mixed layer increased near the ice edge and the river mouth. Over the following days, lower wind speeds (3.7±1.1 m s^{-1}), coupled with decreasing river inflow concentrations and restratification of the water column, led to decreased gas concentrations throughout the water column by 2 July. Changes in the observed temperature-salinity properties of the water suggest that mixing reduced the vertical salinity gradient over the measurement period. The mixed layer near the river mouth showed significant warming between 28 June and 2 July (Figures 3c-j, S5, and S6).

To evaluate the importance of atmospheric ventilation to the CH_4 budget in the estuary, we performed sea-air flux calculations (Wanninkhof, 2014) using observed wind speeds . In the absence of lateral transport and river discharge, CH_4 and CO_2 concentrations in the estuary over our sampling period would be expected to decrease to ~70 nM and ~570 µatm, respectively. In actuality, we observed a mean surface CH_4 concentration of ~150 nM at the end of the sampling period, suggesting that the continued inflow of high-CH_4 river water into the ChemYak sampling region contributed to maintaining elevated CH_4 concentrations following ice melt (Figure 4a). Based on the observed river discharge of ~40 m^3 s^{-1}, we estimate that the residence time of water in the ChemYak measurement region was ~0.6 d.

In addition to measuring the estuary downstream of the Freshwater Creek mouth, the ChemYak was also used to collect observations in a small embayment at the outlet of a much smaller river on 29 June, 1 July, and 2 July (Figures 2, 3, S4, and S5). This embayment generally exhibited higher temperatures and lower CH_4 and CO_2 concentrations relative to adjacent waters. For example, on 29 June, the mean CH_4 concentration in the upper 2 m was 242±41 nM in the embayment, in contrast to 417±31 nM within 100 m downstream of the river mouth. For CO_2, the mean concentration was 790±140 µatm in the embayment and 1400±110 µatm downstream of the river mouth. In late June to early July 2018, we collected bottle samples at the head of the embayment in this smaller river and found that CH_4 concentrations in Freshwater Creek were two times higher than in the smaller river. The CH_4 and CO_2 levels in the embayment may therefore reflect lower inflowing CH_4 and CO_2 from the smaller river, and/or a longer residence time for river-derived surface water to exchange with the atmosphere in the embayment.

Overall, we conclude that the declining CH_4 and CO_2 concentrations throughout the water column between 28 June and 2 July, and along the spatial gradient from Freshwater Creek to station B1, primarily reflect a combination of decreasing gas concentrations in the river water (Figure 1c), loss due to gas exchange within the ice-liberated area, and lateral/vertical mixing. Below, we present a more complex physical model for the estuarine mixed layer CH_4 budget, and discuss potential impacts of microbial processes on the CH_4 budget. The observed differences between the smaller river and embayment compared to Freshwater Creek and the rest of the estuary demonstrate the need to conduct studies in a diverse range of Arctic coastal systems to better understand the complex hydrological controls on the magnitude and location of greenhouse gas emissions.

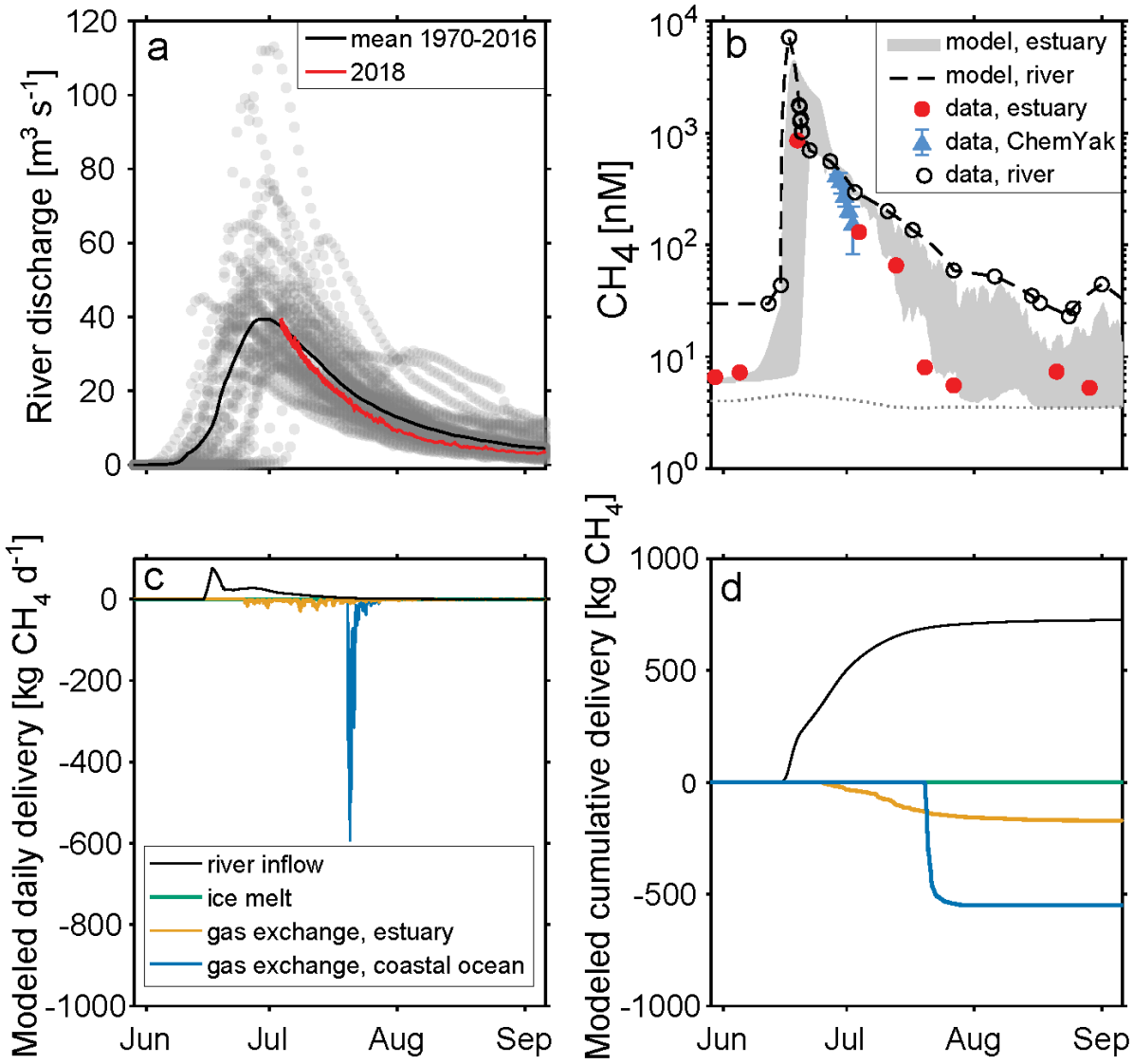

Figure 4. Observations and model-derived output of CH_4 delivery to the estuary mixed layer. **a** Historical river discharge data from Freshwater Creek. **b** Modeled and measured CH_4 concentration in the river (Freshwater Creek) and the Cambridge Bay estuary mixed layer (Model Regions 1 and 2), based on data and the model. The range of modeled values across the estuary is shown with grey shading and the range of values measured with the ChemYak is shown with blue symbols (error bars represent the standard deviation of daily measurements). The red symbols represent bottle measurements at station B1, and the black outlined symbols represent measurements at Freshwater Creek. The grey dotted line shows the equilibrium concentration in the estuary. **c-d** Modeled daily (**c**) and cumulative (**d**) CH_4 delivery to the estuary, from river inflow, ice melt, and gas exchange (positive delivery represents an input to the mixed layer). The CH_4 delivery caused by ice melt is negligible relative to the other terms.

2.2 Mixed layer model

To quantify the fate of river-derived CH_4 over the entire river inflow season, we developed a mixed layer model for the Cambridge Bay estuary (Figures 4 and S7). The model was constrained with measured CH_4 concentrations in Freshwater Creek (bottle samples), river discharge and wind speed measurements, and ice thickness records from the Ocean Networks Canada (ONC) cabled observatory (Figure S8 and Text S1). The results of this analysis suggest that the annual CH_4 cycle in the estuary is driven by river inflow, with sea ice melt contributing a comparatively negligible amount of CH_4 to the mixed layer (Figure 4d). This conclusion is consistent with a water mass property (salinity/water isotope) analysis showing an insignificant impact of sea ice melt on the CH_4 budget (Figure S2 and Text S1). The model was able to simulate the observed changes in estuarine CH_4 concentrations (measured at station B1 and with the ChemYak) without including an additional sink for microbial oxidation of CH_4 within the bay.

Using the model, we estimate that ~800 kg CH_4 was released from Freshwater Creek into the estuary in 2018 (volume-weighted mean concentration in river water of 360 nM), with 20% (160 kg) ventilated to the atmosphere from the estuary following ice cover retreat (Figure 4d). The remaining 80% of the river-derived CH_4 was laterally transported across the estuary beneath sea ice to the coastal ocean, where it was likely ventilated to the atmosphere following ice melt in mid-late July. Indeed, a model run with a larger spatial footprint (including 60 km^2 of coastal ocean surrounding the Cambridge Bay estuary) yielded a cumulative annual sea-air emission of 640 kg CH_4 from the coastal ocean derived from river discharge, which occurs rapidly following ice melt (Figure 4d). To estimate the CH_4 emissions from the estuary in the absence of river inflow, we prescribe a fixed CH_4 concentration of 6 nM (~150% saturation), the typical surface concentration before and after the river inflow period. Under this scenario, with no river discharge, we derived annual estuarine CH_4 emissions of 7.4 kg, 22 times lower than the emissions derived from the full model including riverine CH_4 inputs. Given that our model predicts that 80% of the riverine CH_4 is ventilated beyond the estuary in the adjacent coastal ocean, small river systems such as Freshwater Creek may be of primary importance to annual methane budgets through much of the coastal Arctic Ocean. Accurate calculation of such short-lived, high magnitude CH_4 emissions following ice melt, requires a more extensive under-ice sampling program, including melt-season measurements in multiple river-influenced Arctic estuaries and coastal systems.

2.3 Comparison to other systems

The CH_4 concentrations we measured in Freshwater Creek (ranging from 10–11000 nM, volume-weighted mean 360 nM) are similar to other river systems in the Arctic and worldwide. For example, mean CH_4 concentrations observed in the Yukon River, Lena Delta, and Leverett Glacier runoff range from 70–750 nM (Bussmann, 2013; Lamarche-Gagnon et al., 2019; Striegl et al., 2012). Furthermore, a data compilation of over 900 rivers and streams worldwide reported a mean CH_4 concentration of 1400 ± 5200 nM and median of 250 nM (Stanley et al., 2016). The peak CH_4 concentrations observed in Cambridge Bay estuary (up to 900 nM during the freshet, prior to ice melt) are similar to maximum values measured in other Arctic coastal waters (Bussmann et al., 2017; Shakhova et al., 2010).

In contrast to CH_4, N_2O concentrations throughout 2017-2018 measured at station B1 and Freshwater Creek displayed limited seasonal variability (Figure S1). During open water conditions in Cambridge Bay, N_2O was typically undersaturated or close to equilibrium in near-surface waters. Anoxic conditions in the sediments and water column that promote CH_4 accumulation may simultaneously drive N_2O consumption via denitrification (Naqvi et al., 2010). These conditions contrast with the lower- and mid-latitudes where rivers and estuaries are typically considered significant N_2O sources (Seitzinger & Kroeze, 1998; Seitzinger S.P. et al., 2000).

2.4 Future work

This research motivates two directions for future work in Cambridge Bay: characterization of natural sinks of CH_4 (e.g., microbial oxidation) and identification of CH_4 sources. The extent of microbial CH_4 oxidation in river-derived water transported from Freshwater Creek to the coastal ocean is currently unknown. The early-season river discharge containing >1000 nM CH_4 may remain under the ice for ~1 month before being exposed to the atmosphere, during which time microbial oxidation could potentially decrease concentrations. Recent studies of CH_4 oxidation rates in Arctic estuarine and marine waters have found rates $\leq$2 nM CH_4 d^{-1} (Bussmann et al., 2017; Gentz et al., 2014; Mau et al., 2013; Uhlig & Loose, 2017). Oxidation rates $\leq$2 nM CH_4 d^{-1} would have a small impact on under-ice CH_4 levels in Cambridge Bay estuary (considering that we measured up to 860 nM CH_4 under ice in the estuary). However, some studies in ice-covered lakes have reported significantly higher oxidation rates (Bastviken et al., 2002; Ricão Canelhas et al., 2016). Additionally, our model reproduces the seasonally observed progression of CH_4 levels in the estuary without invoking CH_4 oxidation. To further investigate the extent and dynamics of under-ice CH_4 plumes, robotic underwater vehicles and moored sensors could be developed and deployed to enable high resolution under-ice measurements. Tracer-based incubation experiments could be performed to measure oxidation rates (Uhlig & Loose, 2017).

Another area of future research is determining CH_4 sources and characterizing the relative emissions of CH_4 and CO_2 from the lake versus the river and coastal ocean. Our preliminary measurements in Greiner Lake suggest that anoxic zones in the lake are a significant source of CH_4. However, the formation mechanism is not clear. For example, CH_4 could be generated in situ each winter within anoxic sediments and/or overlying anoxic waters, or, alternatively, could be liberated from existing pools in methane seeps or thawing permafrost. More extensive measurements of CH_4 concentration and isotopic composition in the watershed surrounding Freshwater Creek would assist in determining the source of the CH_4. Additionally, radiocarbon measurements would demonstrate whether ancient CH_4 sources such as thawing permafrost are significant (Sparrow et al., 2018).

This study demonstrates the importance of fully resolving seasonal processes in inter-connected marine and freshwater environments to accurately quantify CH_4 emissions from Arctic systems. The results motivate future coastal Arctic field campaigns at other sites with measurement technologies capable of high spatial and temporal resolution mapping immediately before and during ice melt. Such studies will provide critical information to characterize current and future Arctic greenhouse gas emission, improving quantitative estimates of changes in CH_4 and CO_2 emissions across the rapidly changing Arctic environment.

3 Conclusions and implications

Our results, derived from a year-round times series of CH_4 measurements and dense spatio-temporal observations from a remotely-operated robotic kayak, show that CH_4 discharge via Freshwater Creek drives intense CH_4 emissions immediately following ice melt in the Cambridge Bay estuary and surrounding waters. River discharge also acts as a significant seasonal source of CO_2 to the estuary, whereas N_2O shows limited seasonality. Samples collected exclusively during low-ice summer conditions would likely miss the primary driver of the annual CH_4 budget, and underestimate the sea-air fluxes. Similar seasonal variability in CH_4 emissions likely occurs in other river-influenced, seasonally ice-covered Arctic estuaries, which receive ~10% of global river discharge (Dai & Trenberth, 2002). Our results suggest that the ongoing and projected future increases in Arctic river discharge (Macdonald et al., 2015) could drive increased CH_4 and CO_2 emissions from Arctic estuaries. The low and stable CH_4 concentrations observed below the mixed layer in the estuary indicate that sedimentary CH_4 sources within the estuary are negligible relative to river-derived inputs, in contrast to published studies in some other Arctic coastal and shelf systems where significant sedimentary sources are observed (Gentz et al., 2014; Shakhova et al., 2010).

Acknowledgments, Samples, and Data

All data generated by the authors that were used in this article have been submitted to PANGAEA, where publication is pending, and a PANGAEA DOI will be included in the final published manuscript. Code for the biogeochemical model used to estimate CH_4 transport is available on GitHub (https://github.com/caramanning/cambridge-bay-model). We acknowledge the use of imagery from the NASA Worldview application (https:/worldview.earthdata.nasa.gov), part of the NASA Earth Observing System Data and Information System (EOSDIS), and data from Ocean Networks Canada, and Environment Canada. We thank everyone involved in the fieldwork including C. Amegainik, Y. Bernard, A. Cranch, F. Emingak, S. Marriott, and A. Pedersen. Laboratory analysis and experiments were performed by A. Cranch, R. McCulloch, A. Morrison, and Z. Zheng. We thank J. Brinckerhoff, the Arctic Research Foundation, and the staff of the Canadian High Arctic Research Station for support with field logistics. Funding for the work was provided by MEOPAR NCE funding to B. Else, a WHOI Interdisciplinary Award to A. Michel., D. Nicholson. and S. Wankel, and Canadian NSERC grants to P. Tortell. and B. Else. Authors received fellowships, scholarships and travel grants including an NSERC postdoctoral fellowship to C. Manning., an NDSEG fellowship to V. Preston., NSERC PGS-D and Izaak Walton Killam Pre-Doctoral scholarships to S. Jones, Northern Scientific Training Program funds (Polar Knowledge Canada) to S. Jones. and P. Duke.. We also thank Polar Knowledge Canada (POLAR) and Nunavut Arctic College for laboratory space and field logistics support.

References

Biastoch, A., Treude, T., Rüpke, L. H., Riebesell, U., Roth, C., Burwicz, E. B., et al. (2011). Rising Arctic Ocean temperatures cause gas hydrate destabilization and ocean acidification. *Geophysical Research Letters*,

38(8). https://doi.org/10.1029/2011GL047222

Bliss, L. C. (1981). North American and Scandinavian tundras and polar deserts. In L. C. Bliss, O. W. Heal, & J. J. Moore (Eds.), *Tundra ecosystems: a comparative analysis* (pp. 8–24). Cambridge, UK: Cambridge University Press.

Bussmann, I. (2013). Distribution of methane in the Lena Delta and Buor-Khaya Bay, Russia. *Biogeosciences*, *10*(7), 4641–4652. https://doi.org/10.5194/bg-10-4641-2013

Bussmann, I., Hackbusch, S., Schaal, P., & Wichels, A. (2017). Methane distribution and oxidation around the Lena Delta in summer 2013. *Biogeosciences*, *14*(21), 4985–5002. https://doi.org/10.5194/bg-14-4985-2017

Butterworth, B. J., & Miller, S. D. (2016). Air-sea exchange of carbon dioxide in the Southern Ocean and Antarctic marginal ice zone. *Geophysical Research Letters*, *43*(13), 7223–7230. https://doi.org/10.1002/2016GL069581

Cai, W.-J., Hu, X., Huang, W.-J., Jiang, L.-Q., Wang, Y., Peng, T.-H., & Zhang, X. (2010). Alkalinity distribution in the western North Atlantic Ocean margins. *Journal of Geophysical Research: Oceans*, *115*(C8). https://doi.org/10.1029/2009JC005482

Capelle, D. W., Dacey, J. W., & Tortell, P. D. (2015). An automated, high through-put method for accurate and precise measurements of dissolved nitrous-oxide and methane concentrations in natural waters: Automated PT-GCMS for N_2O and CH_4. *Limnology and Oceanography: Methods*, *13*(7), 345–355. https://doi.org/10.1002/lom3.10029

Dai, A., & Trenberth, K. E. (2002). Estimates of Freshwater Discharge from Continents: Latitudinal and Seasonal Variations. *Journal of Hydrometeorology*, *3*(6), 660–687. https://doi.org/10.1175/1525-7541(2002)003<0660:EOFDFC>2.0.CO;2

Denfeld, B. A., Baulch, H. M., Giorgio, P. A. del, Hampton, S. E., & Karlsson, J. (2018). A synthesis of carbon dioxide and methane dynamics during the ice-covered period of northern lakes. *Limnology and Oceanography Letters*, *3*(3), 117–131. https://doi.org/10.1002/lol2.10079

Dickson, A. G. (1990). Thermodynamics of the dissociation of boric acid in synthetic seawater from 273.15 to 318.15 K. *Deep Sea Research Part A. Oceanographic Research Papers*, *37*(5), 755–766. https://doi.org/10.1016/0198-0149(90)90004-F

Environment and Climate Change Canada Historical Hydrometric Data website, River discharge data for station 10TF001, Freshwater Creek near Cambridge Bay https://wateroffice.ec.gc.ca/mainmenu/historical_data_index_e.html. Water Survey of Canada, Environment and Climate Change Canada. Downloaded on January 10, 2019.

Environment and Climate Change Canada Historical Database (2019) Hourly weather data for Cambridge Bay, Nunavut from Jan 1, 2018 to Jan 1, 2019. Station Climate ID: 2400602, WMO ID: 71288 TC ID: XCM http://climate.weather.gc.ca . Downloaded on February 25, 2019.

Fenwick, L., Capelle, D., Damm, E., Zimmermann, S., Williams, W. J., Vagle, S., & Tortell, P. D. (2017). Methane and nitrous oxide distributions across the North American Arctic Ocean during summer, 2015. *Journal of Geophysical Research: Oceans*, 1–23. https://doi.org/10.1002/2016JC012493

Gentz, T., Damm, E., Schneider von Deimling, J., Mau, S., McGinnis, D. F., & Schlüter, M. (2014). A water column study of methane around gas flares located at the West Spitsbergen continental margin. *Continental Shelf Research*, *72*, 107–118. https://doi.org/10.1016/j.csr.2013.07.013

Gran, G. (1952). Determination of the equivalence point in potentiometric titrations. Part II. *Analyst*, *77*(920), 661–671. https://doi.org/10.1039/AN9527700661

James, R. H., Bousquet, P., Bussmann, I., Haeckel, M., Kipfer, R., Leifer, I., et al. (2016). Effects of climate change on methane emissions from seafloor sediments in the Arctic Ocean: A review. *Limnology and Oceanography*, *61*(S1), S283–S299. https://doi.org/10.1002/lno.10307

Karlsson, J., Giesler, R., Persson, J., & Lundin, E. (2013). High emission of carbon dioxide and methane during ice thaw in high latitude lakes. *Geophysical Research Letters*, *40*(6), 1123–1127. https://doi.org/10.1002/grl.50152

Kimball, P., Bailey, J., Das, S., Geyer, R., Harrison, T., Kunz, C., et al. (2014). The WHOI Jetyak: An autonomous surface vehicle for oceanographic research in shallow or dangerous waters. *2014 IEEE/OES Autonomous Underwater Vehicles (AUV)*, 1–7. https://doi.org/10.1109/AUV.2014.7054430

Kvenvolden, K. A., Lilley, M. D., Lorenson, T. D., Barnes, P. W., & McLaughlin, E. (1993). The Beaufort Sea continental shelf as a seasonal source of atmospheric methane. *Geophysical Research Letters*, *20*(22), 2459–2462. https://doi.org/10.1029/93GL02727

Lamarche-Gagnon, G., Wadham, J. L., Sherwood Lollar, B., Arndt, S., Fietzek, P., Beaton, A. D., et al. (2019).

Greenland melt drives continuous export of methane from the ice-sheet bed. *Nature*, *565*(7737), 73–77. https://doi.org/10.1038/s41586-018-0800-0

Lee, K., Kim, T.-W., Byrne, R. H., Millero, F. J., Feely, R. A., & Liu, Y.-M. (2010). The universal ratio of boron to chlorinity for the North Pacific and North Atlantic oceans. *Geochimica et Cosmochimica Acta*, *74*(6), 1801–1811. https://doi.org/10.1016/j.gca.2009.12.027

Macdonald, R. W., Kuzyk, Z. A., & Johannessen, S. C. (2015). It is not just about the ice: a geochemical perspective on the changing Arctic Ocean. *Journal of Environmental Studies and Sciences*, *5*(3), 288–301. https://doi.org/10.1007/s13412-015-0302-4

Macdonald, R. W., Paton, D. W., Carmack, E. C., & Omstedt, A. (1995). The freshwater budget and under-ice spreading of Mackenzie River water in the Canadian Beaufort Sea based on salinity and 18O/16O measurements in water and ice. *Journal of Geophysical Research: Oceans*, *100*(C1), 895–919. https://doi.org/10.1029/94JC02700

Magnuson, J. J. (2000). Historical Trends in Lake and River Ice Cover in the Northern Hemisphere. *Science*, *289*(5485), 1743–1746. https://doi.org/10.1126/science.289.5485.1743

Millero, F. J. (2010). Carbonate constants for estuarine waters. *Marine and Freshwater Research*, *61*(2), 139–142. https://doi.org/10.1071/MF09254

Naqvi, S. W. A., Bange, H. W., Farías, L., Monteiro, P. M. S., Scranton, M. I., & Zhang, J. (2010). Marine hypoxia/anoxia as a source of CH_4 and N_2O. *Biogeosciences*, *7*(7), 2159–2190. https://doi.org/10.5194/bg-7-2159-2010

Nicholson, D. P., Michel, A. P. M., Wankel, S. D., Manganini, K., Sugrue, R. A., Sandwith, Z. O., & Monk, S. A. (2018). Rapid Mapping of Dissolved Methane and Carbon Dioxide in Coastal Ecosystems Using the ChemYak Autonomous Surface Vehicle. *Environmental Science & Technology*. https://doi.org/10.1021/acs.est.8b04190

Ocean Networks Canada Data Archive (2019) Corrected ice draft data from Cambridge Bay, Nunavut, from Jan 1, 2018 to Jan 1, 2019. http://www.oceannetworks.ca, Ocean Networks Canada, University of Victoria, Canada. Downloaded on May 25, 2019.

Phelps, A. R., Peterson, K. M., & Jeffries, M. O. (1998). Methane efflux from high-latitude lakes during spring ice melt. *Journal of Geophysical Research: Atmospheres*, *103*(D22), 29029–29036.

https://doi.org/10.1029/98JD00044

Pierrot, D., Lewis, E., & Wallace, D. W. R. (2006). *MS Excel Program Developed for CO2 System Calculations* (Technical Report). Oak Ridge, Tenn: Carbon Dioxide Inf. Anal. Cent., Oak Ridge Natl. Lab., US DOE.

Seitzinger, S. P., & Kroeze, C. (1998). Global Distribution of Nitrous Oxide Production and N Inputs in Freshwater and Coastal Marine Ecosystems, *12*(1), 93–113.

Seitzinger S.P., Kroeze C., & Styles R.V. (2000). Global distribution of N2O emissions from aquatic systems: natural emissions and anthropogenic effects. *Chemosphere: Global Change Science*, *2*, 267–279. https://doi.org/10.1016/S1465-9972(00)00015-5

Shakhova, N., Semiletov, I., Salyuk, A., Yusupov, V., Kosmach, D., & Gustafsson, Ö. (2010). Extensive Methane Venting to the Atmosphere from Sediments of the East Siberian Arctic Shelf. *Science*, *327*(5970), 1246–1250. https://doi.org/10.1126/science.1182221

Sparrow, K. J., Kessler, J. D., Southon, J. R., Garcia-Tigreros, F., Schreiner, K. M., Ruppel, C. D., et al. (2018). Limited contribution of ancient methane to surface waters of the U.S. Beaufort Sea shelf. *Science Advances*, *4*(1), eaao4842. https://doi.org/10.1126/sciadv.aao4842

Stanley, E. H., Casson, N. J., Christel, S. T., Crawford, J. T., Loken, L. C., & Oliver, S. K. (2016). The ecology of methane in streams and rivers: Patterns, controls, and global significance. *Ecological Monographs*, *86*(2), 146–171. https://doi.org/10.1890/15-1027.1

Striegl, R. G., Dornblaser, M. M., McDonald, C. P., Rover, J. R., & Stets, E. G. (2012). Carbon dioxide and methane emissions from the Yukon River system. *Global Biogeochemical Cycles*, *26*(4). https://doi.org/10.1029/2012GB004306

Stroeve, J. C., Serreze, M. C., Holland, M. M., Kay, J. E., Malanik, J., & Barrett, A. P. (2012). The Arctic's rapidly shrinking sea ice cover: a research synthesis. *Climatic Change*, *110*(3–4), 1005–1027. https://doi.org/10.1007/s10584-011-0101-1

Uhlig, C., & Loose, B. (2017). Using stable isotopes and gas concentrations for independent constraints on microbial methane oxidation at Arctic Ocean temperatures. *Limnology and Oceanography: Methods*, *15*(8), 737–751. https://doi.org/10.1002/lom3.10199

Voigt, C., Marushchak, M. E., Lamprecht, R. E., Jackowicz-Korczyński, M., Lindgren, A., Mastepanov, M., et al. (2017). Increased nitrous oxide emissions from Arctic peatlands after permafrost thaw. *Proceedings of the*

National Academy of Sciences, *114*(24), 6238–6243. https://doi.org/10.1073/pnas.1702902114

Walter, K. M., Zimov, S. A., Chanton, J. P., Verbyla, D., & Chapin, F. S. (2006). Methane bubbling from Siberian thaw lakes as a positive feedback to climate warming. *Nature*, *443*(7107), 71–75. https://doi.org/10.1038/nature05040

Wand, U., Samarkin, V. A., Nitzsche, H.-M., & Hubberten, H.-W. (2006). Biogeochemistry of methane in the permanently ice-covered Lake Untersee, central Dronning Maud Land, East Antarctica. *Limnology and Oceanography*, *51*(2), 1180–1194. https://doi.org/10.4319/lo.2006.51.2.1180

Wanninkhof, R. (2014). Relationship between wind speed and gas exchange over the ocean revisited. *Limnology and Oceanography: Methods*, *12*(6), 351–362. https://doi.org/10.4319/lom.2014.12.351

Weiss, R. F., & Price, B. A. (1980). Nitrous oxide solubility in water and seawater. *Marine Chemistry*, *8*(4), 347–359. https://doi.org/10.1016/0304-4203(80)90024-9

Wiesenburg, D. A., & Guinasso, N. L. (1979). Equilibrium solubilities of methane, carbon monoxide, and hydrogen in water and sea water. *Journal of Chemical & Engineering Data*, *24*(4), 356–360. https://doi.org/10.1021/je60083a006

Wilson, S. T., Bange, H. W., Arévalo-Martínez, D. L., Barnes, J., Borges, A. V., Brown, I., et al. (2018). An intercomparison of oceanic methane and nitrous oxide measurements. *Biogeosciences*, *15*(19), 5891–5907. https://doi.org/10.5194/bg-15-5891-2018

Yamamoto, S., Alcauskas, J. B., & Crozier, T. E. (1976). Solubility of methane in distilled water and seawater. *Journal of Chemical & Engineering Data*, *21*(1), 78–80. https://doi.org/10.1021/je60068a029

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: Oceans*, *114*(4), 2003–2007. https://doi.org/10.1029/2008JC005000

Zhou, J., Delille, B., Eicken, H., Vancoppenolle, M., Brabant, F., Carnat, G., et al. (2013). Physical and biogeochemical properties in landfast sea ice (Barrow, Alaska): Insights on brine and gas dynamics across seasons. *Journal of Geophysical Research: Oceans*, *118*(6), 3172–3189. https://doi.org/10.1002/jgrc.20232

Zona, D., Gioli, B., Commane, R., Lindaas, J., Wofsy, S. C., Miller, C. E., et al. (2016). Cold season emissions dominate the Arctic tundra methane budget. *Proceedings of the National Academy of Sciences of the United States of America*, *113*(1), 40–45. https://doi.org/10.1073/pnas.1516017113